# Microwave-Irradiated Copolymerization of Styrene and Butyl Acrylate

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**Summary:** The emulsion copolymerization of butyl acrylate and styrene in microwave irradiated condition was investigated. The microwave irradiated condition afforded the enhanced conversion rate at high feeding contents of butyl acrylate monomer feeding and the relative increase of butyl acrylate composition in copolymer compared with the conventional condition as an water bath heating. The reactivity ratio was calculated from Finemann-Ross plot, and showed difference between two methods that increased reactivity ratio of butyl acrylate was obtained in microwave irradiated condition. The morphology of copolymer was observed by microscopy, then it was founded that the size of spherical polymer particles in microwave irradiated condition showed more regular than that in conventional heating condition.

**Keywords:** butyl acrylate; emulsion polymerization; microwave irradiation; reactivity ratio; styrene

## Introduction

The use of microwave irradiation as an alternative method for the polymerization has received growing interest recently.[1–6] The reported results in application of microwave for polymerization involve bulk polymerization[2] and emulsion polymerization[3] for various monomers from styrene to acrylates, and have shown advantages of conversion rate acceleration, greater yield, morphological control,[4,5] and low energy consumption.[6]

In our approach, the emulsion copolymerization of two monomers with different dipole moment was explored to evaluate the effect of microwave irradiation compared to the conventional heating condition. Although there have been many results about the emulsion polymerization in microwave irradiation condition, the investigation of emulsion co-monomer system is hardly founded. The divided phase into oil droplets in 100 nm range and water medium is supposed to be a good model system to evaluate the dielectric heating effect that makes thermal heat generated by monomer droplet itself depending on its own microwave susceptibility. In this study, the two polymerization conditions of conventional heating and microwave irradiation were applied to polymerization with various mole fractions of co-monomer emulsion. Styrene and butyl acrylate were used as co-monomers due to their large dipole moment difference, which may cause the varied dielectric heating effect on co-monomer droplet as their feeding ratio is changed. To compare the two different conditions for emulsion polymerization, the conversion rate, monomer composition ratio in copolymer, and reactivity ratio were determined in respective conditions.

## Experimental Part

### Materials and Equipment

Styrene and butyl acrylate purchased from Aldrich were washed three times with

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10 wt% aqueous sodium hydroxide solution to eliminate inhibitors and stored at −10 °C before use. Potassium persulfate(KPS, Fluka) as an initiator and sodium lauryl sulfate(SLS, Aldrich) as an emulsifier were used as supplied. Microwave oven (Korea Microwave Instrument Co.) equipped with 2.45 GHz frequency magnetron was used. The microwave oven with 1.5 kW power generator could be operated at variable power levels. The mechanical stirrer, condenser, thermocouple, and nitrogen inlet were connected to the reaction vessel in chamber of microwave oven.

### Copolymerization

The 70 g of mixed monomers (varying the feed ratio of butyl acrylate and styrene) was emulsified with 210 g aqueous solution of SLS (1 wt % based on water) by 250 rpm stirring for 10 min. Prepared emulsion and KPS (0.1 wt % based on monomers) were transferred into a 500 mL reaction vessel for microwave irradiation or into a 500 mL 3-necked round bottom flask for conventional water bath heating. Emulsion polymerizations were carried out at 300 W powered, 2.45 GHz microwave irradiation for individual reaction times under nitrogen atmosphere. For the constant reaction temperature during the microwave irradiation, the cooling fan was controlled to keep the temperature at 70 °C. The samples were withdrawn at appropriate intervals during the reaction and quickly cooled down by immersing into a liquid nitrogen vessel. Typical reaction times for determining the composition ratio were from 5 min to 15 min in microwave irradiation method, and to obtain the copolymer particles, the reaction was carried out for 3 hrs.

Monomer conversion was determined by measuring the reduced amount of monomers using internal standard, 1,2-dichlorobenzene by gas chromatography (Focus GC Thermo Electronics Company). The overall conversion of each reaction was also determined gravimetrically. $^1$H NMR spectroscopy was used to determine the copolymer compositions. Spectra were recorded with a Bruker 300 spectrometer operating at 300 MHz using $CDCl_3$ as a solvent with ca. 5 wt % sample concentration.

## Results and Discussion

The emulsion polymerization of styrene and butyl acrylate in microwave irradiation condition was investigated and compared with the conventional water bath heating method. To exclude the influence of temperature difference between two conditions, the reaction mixture in a microwave oven was controlled to keep the temperature below 70 °C as the same temperature of conventional heating polymerization condition. The monomer conversion plot is shown on Figure 1, where microwave irradiated polymerization at each monomer mole fraction of styrene and butyl acrylate was compared with the conventional heating method.

The microwave irradiation method resulted in conversion rate enhancement at an initial stage in the case of pure butyl acrylate, and the difference of conversion profile between microwave irradiation and conventional heating (water bath heating) was very large. On the other hand, the pure styrene monomer afforded relatively small difference between two conditions. The mixtures of two monomers were also showing similar tendency that the larger difference of conversion rate was obtained as butyl acrylate mole fraction was increased. The conversion rate differences depending on the monomer ratio between two polymerization conditions would be caused simply by the different heat conducting situation. However, considering the pure styrene and 0.75(St)/0.25(BA) mole fraction case were also placed under identical situation of different heat transfer in respective conditions, relatively small difference of conversion rate in styrene rich case indicates that microwave irradiation provided not only uniform heating on medium but also direct dielectric heating

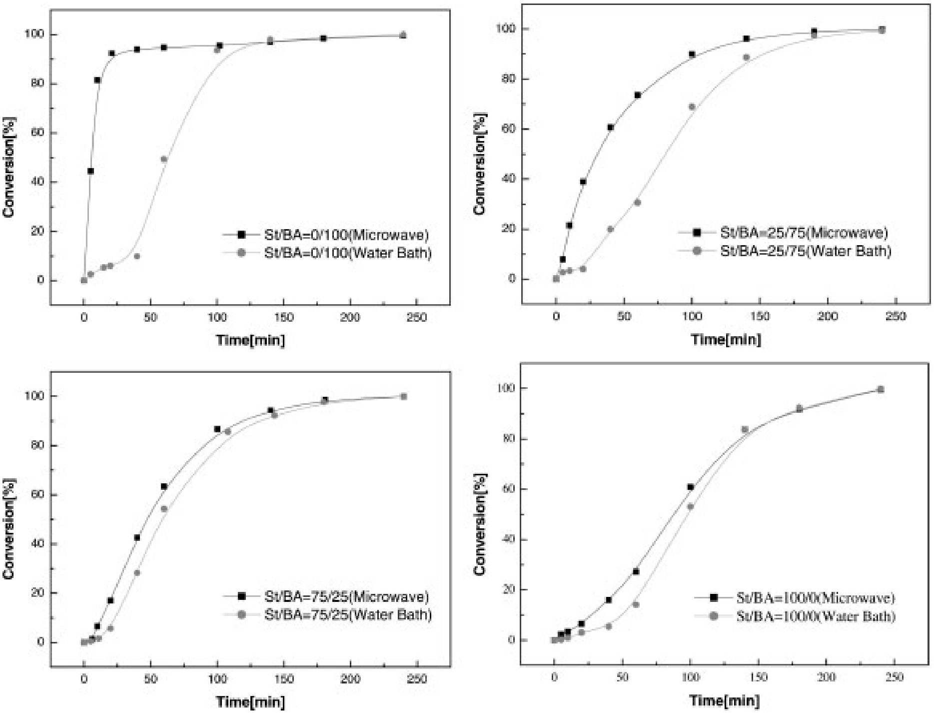

***Figure 1.***
Monomer conversion from microwave irradiation and conventional heating conditions.

effect onto monomer droplets depending on monomer susceptibilities in water-oil emulsion.

In the emulsion copolymerization, the microwave irradiation is expected to give a different thermal effect on monomer droplet as the variation of monomer feeding ratio when more than two monomers with different dipole moment are mixed in copolymerization. The thermal effect with microwave irradiation on various monomer and water was studied. The susceptibilities of each monomer to microwave irradiation were estimated by the temperature elevation in continuous 500 W powered microwave irradiation. The resulting temperature elevation rates were mainly dependent upon their dipole moments (Figure 2). The differences of temperature elevation rate between monomers imply that the oil droplets comprised of styrene and acrylate have different thermal influence from microwave irradiation as their monomer ratio is changed.

The initiator decomposition rate was investigated as another factor to influence monomer conversion rate. The decomposition rates of potasium persulfate(KPS) in polymerization conditions were estimated by the plot of time vs concentration change which was expressed by following equation.[7]

$$\ln \frac{[I]_0}{[I]_t} = k_d t$$

$k_\mathrm{d}$: decomposition rate of KPS, $[I]_0$: concentration of KPS at the beginning of reaction, $[I]_\mathrm{t}$: concentration of KPS at time $t$, $t$: reaction time.

The decomposition rates in respective 300 W and 500 W powered microwave irradiation were almost same, and slightly faster than the rate in the conventional heating condition at the temperature, 70 °C

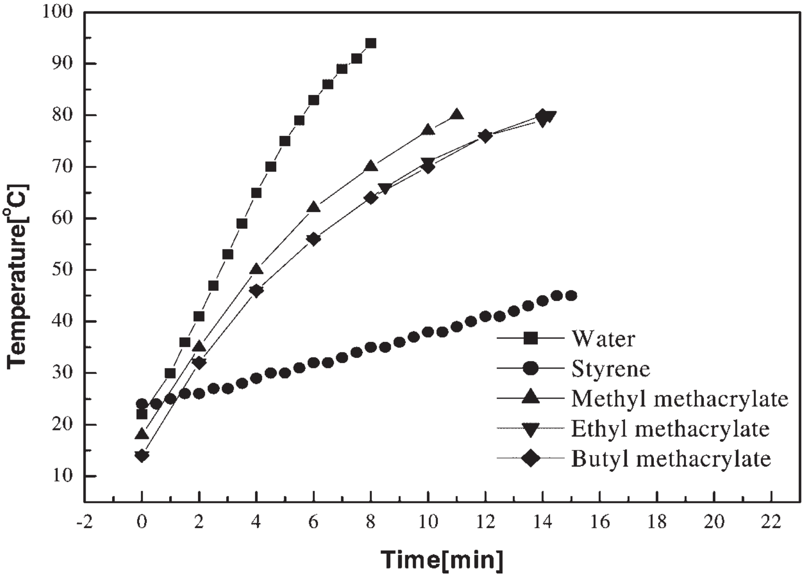

***Figure 2.***
Temperature elevation of monomers by microwave irradiation.

(Figure 3). Since the temperature of reaction medium was 52 °C by 100 W irradiation, the rate decrease at 100 W irradiation seemed to be caused by lowered temperature. Although decomposition rate acceleration effect was reported by J. Bao *et al*,[5] rate increase was only siginficant at temperature lower than 70 °C. At the

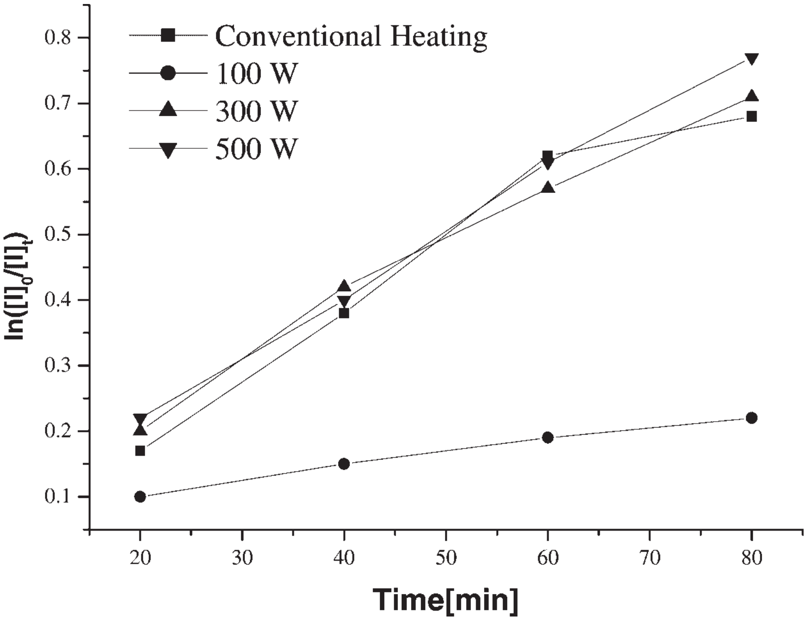

***Figure 3.***
KPS decomposition rate under microwave irradiation.

***Table 1.***
Compositions of butyl acrylate and styrene in the feeds and copolymers[a].

| $f_{BA}$ | $f_{St}$ | Conventional Heating | | Microwave Irradiation | |
|---|---|---|---|---|---|
| | | $F_{BA}$ | $F_{St}$ | $F'_{BA}$ | $F'_{St}$ |
| 0.1 | 0.9 | 0.12 | 0.88 | 0.09 | 0.91 |
| 0.25 | 0.75 | 0.26 | 0.74 | 0.23 | 0.77 |
| 0.3 | 0.7 | 0.30 | 0.70 | – | – |
| 0.5 | 0.5 | 0.40 | 0.60 | 0.45 | 0.55 |
| 0.7 | 0.3 | 0.46 | 0.54 | – | – |
| 0.75 | 0.25 | 0.55 | 0.45 | 0.70 | 0.30 |
| 0.9 | 0.1 | 0.75 | 0.25 | 0.84 | 0.16 |

[a] $f_{BA}$ and $f_{St}$ are mole fractions of butyl acrylate and styrene in the feeds, respectively. $F_{BA}$ and $F_{St}$ are mole fractions of butyl acrylate and styrene in copolymer from the conventional heating polymerization method. $F'_{BA}$ and $F'_{St}$ are mole fractions of butyl acrylate and styrene in copolymer from the microwave irradiated polymerization method.

adjusted temperature, 70 °C in this work, the negligible difference was observed between two methods in decomposition rates.

The feed and incorporated compositions of butyl acrylate and styrene in the copolymers are summarized in Table 1. The both monomer compositions in copolymer were estimated by $^1$H NMR analysis. The protons of $–CO_2–CH_2–$ group in butyl acrylate appeared at $\delta$ 2.9 ~ 3.4 ppm were used for calculation of butyl acrylate ratio in copolymer. And the styrene composition in copolymer was estimated from the peak area of phenyl group protons ranged at $\delta$ 6.4 ~ 7.3 ppm.

The composition of butyl acrylate and styrene in the copolymer was plotted versus monomer feed ratio in Figure 4. The interesting feature of this plot is a large difference between compositions in copolymers obtained from two polymerization methods. The low contents of butyl arcylate in feeds made small differences, but over 0.5 mole fraction butyl acrylate feed in microwave irradiation condition gave the higher incorporating ratio of butyl acrylate, then resulted in 0.15 mole fraction increasing from that by conventional heating method.

The reactivity ratio from each method was calculated based on monomer feed ratios and compositions of copolymer. The monomer reactivity ratios of $r_{St}$ and $r_{BA}$ were evaluated using the Finemann-Ross equation:[7]

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

where:

$$F_2 = 1 - F_1, f_1 = 1 - f_2$$

From the above equation,

$$\frac{f_1(1-2F_1)}{F_1(1-f_1)} = r_2 + r_1\left(\frac{f_1^2(F_1-1)}{F_1(1-f_1)^2}\right)$$

and in this work, $r_1$ is $r_{St}$ and $r_2$ is $r_{BA}$.

The composition ratios for calculation were used at low conversion that ranged from 7.6% to 16.0%. The reactivity ratio $r_{St}$ and $r_{BA}$ from conventional heating method were 0.689 and 0.164, respectively. These values are very similar to those from literature, $r_{St} = 0.698$ and $r_{BA} = 0.164$.[8] As shown in Table 2, the values of monomer reactivity ratios were increased in microwave irradiation method, and $r_{BA}$ value was noticeably increased from 0.164 to 0.638. The calculated $r_{St}$ from microwave irradiation method was also increased, but $r_{BA(\mathrm{microwave})}/r_{BA(\mathrm{conventional})} = 3.89$ exceeded $r_{St(\mathrm{microwave})}/r_{St(\mathrm{conventional})} = 1.48$. The amount of monomer conversion may affect the reactivity ratio, but the low conversions below 16 % in this work could be under the assumption that the drift in the co-monomer composition is supposed to be negligible. The reactivity ratio at higher conversion in the microwave irradiation method was also investigated. The values of $r_{St}$ and $r_{BA}$ at 21 ~ 39% conversion were 1.013 and 1.070, respectively. According to the result reported by Nekoomanesh *et al*, the increase of reactivity ratio was founded at high conversion, but it was mainly an increase in $r_{St}$, not in $r_{BA}$.[9]

The microwave irradiation condition made the effect on the increase the $r_{BA}$ value at both low and high conversions. The main reason to make differences in Finmann- Ross plots from two

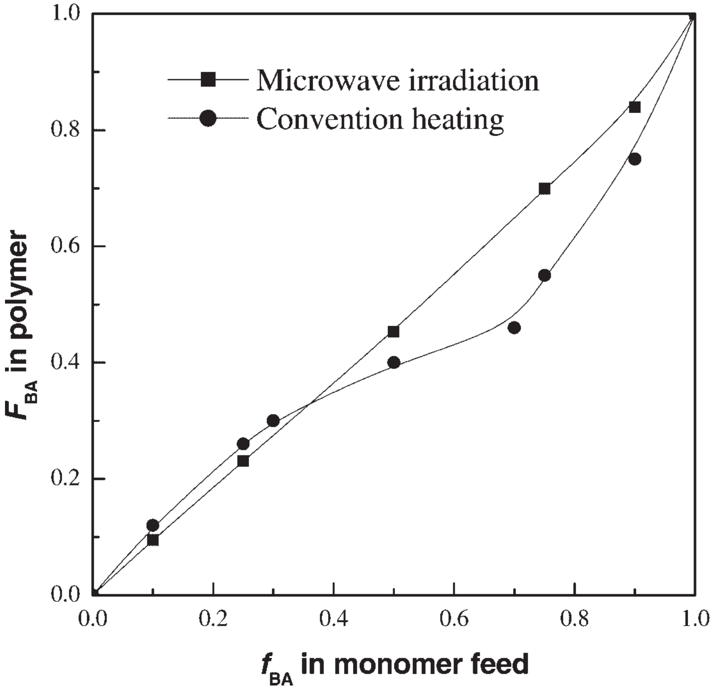

***Figure 4.***
Plot of butyl acrylate composition *vs* monomer feed.

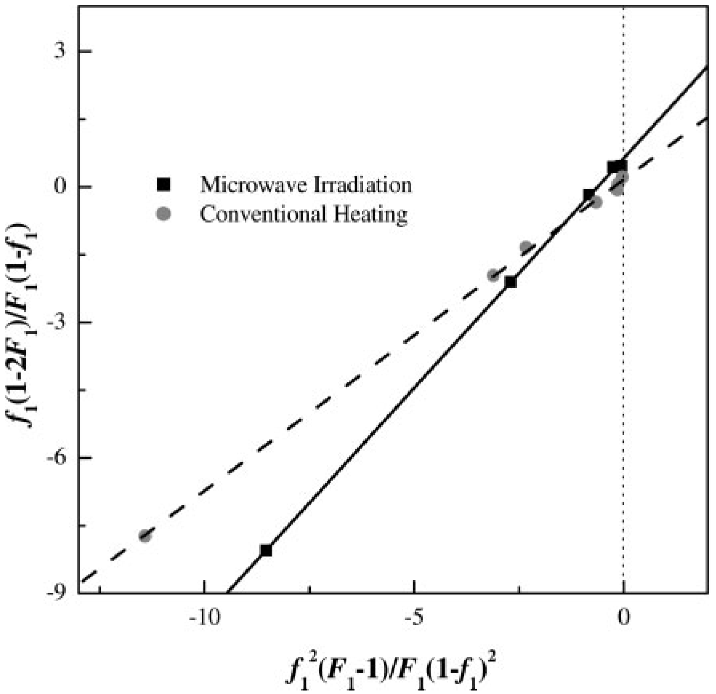

***Figure 5.***
Plots for the determination of reactivity ratio by the Finemann-Ross method.

***Table 2.***
Resulting monomer reactivity ratios.

| Calculated Method | $r_{St}$ | $r_{BA}$ | Reaction Condition |
|---|---|---|---|
| Finemann-Ross | 0.689 | 0.164 | This work/Conventional Heating |
| Finemann-Ross | 1.018 | 0.638 | This work/Microwave Irradiation |
| Finemann-Ross | 0.884 | 0.208 | ref |
| Kelen-Tudos | 0.883 | 0.207 | ref |
| Kelen-Tudos | 0.698 | 0.164 | ref |
| Mao-Huglin | 0.887 | 0.261 | ref |

polymerization methods is the differences of the copolymer composition ratios especially in the range of high butyl acrylate feeding ratio. As shown in Figure 4, large differences of composition ratios between two polymerization methods were obtained where the butyl acrylate feeding ratio was over 0.5 mole fraction. This result was

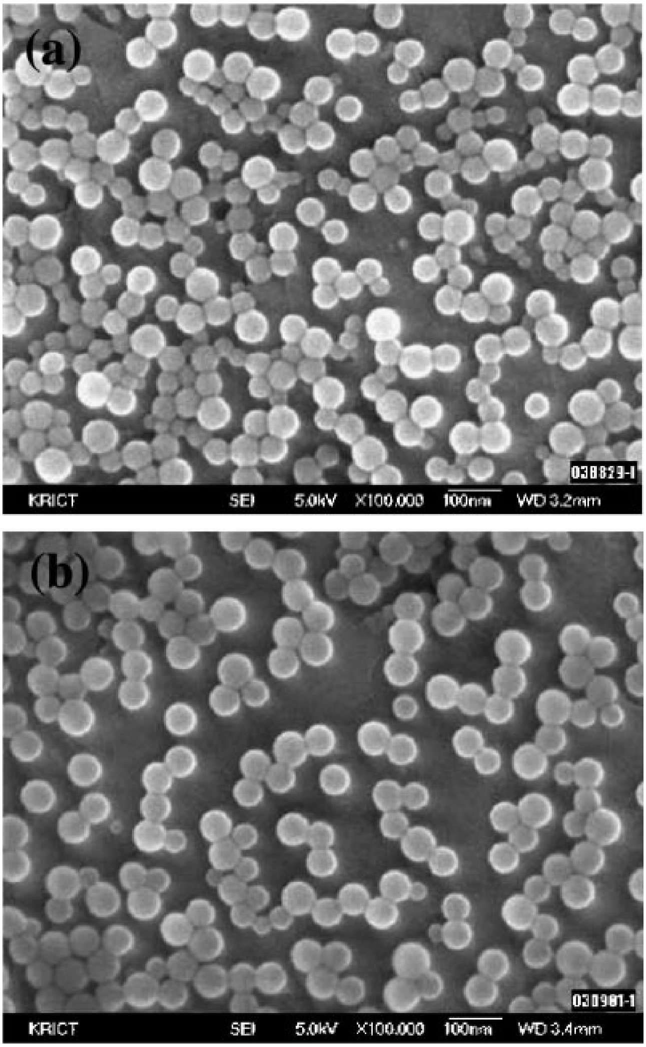

***Figure 6.***
FE-SEM images of the butyl acrylate-styrene copolymer particles.

supposed to be caused by the heating situation of individual monomer droplet in emulsion polymerization condition. In the conventional heating condition, the conducted heat to the monomer droplets was through the medium phase, water. In the microwave irradiation condition, individual monomer droplets could generate heat by themselves additionally to the conducted heat from a medium phase. The heat generation in the monomer droplet in latter case would be influenced by the ratio of monomers which varies susceptibilities to the microwave irradiation. Since the dipole moment 1.72 D for butyl acrylate is higher than 0.36 D for styrene, the higher mole fraction of butyl acrylate in the monomer feed makes the lager dielectric heating effect on monomer droplets. Although the real temperature of monomer droplet in water medium could not be measured and only the averaged temperature of whole medium was measured, the real temperature of monomer droplets in the microwave irradiation condition would be varied from that in conventional heating. And then this temperature difference caused that the change of reactivity of monomers in each condition and also affected the diffusion of each monomer to growing polymer chains.[11] As a result, it is suposed that the increase of apparent reactivity ratio, $r_{BA}$ was observed.

The morphologies of resulting copolymers from both polymerization methods were observed through microscopy, and size distributions were investigated. Figure 6 shows the FE-SEM images of the copolymer particles obtained from 50/50 monomer feed ratio of butyl acrylate and styrene in conventional heating condition (a) and microwave irradiation condition (b). The particle shapes from both conditions were similar, and the sizes of the particles were $D_v = 62$ nm, $D_n = 35$ nm for conventional heating condition and $D_v = 58$ nm, $D_n = 41$ nm for the microwave irradiated condition. The microwave irradiated condition afforded more regular size particles, $D_v/D_n = 1.32$, while conventional heating condition showed $D_v/D_n = 1.77$.

## Conclusion

The effect of microwave irradiation on the emulsion copolymerization of butyl acrylate and styrene was investigated. The conversion rate enhancement was founded at a high ratio of butyl acrylate monomer feeding in microwave irradiation condition. The reactivity ratio calculated by Finemann-Ross method showed the relatively large increase of $r_{BA}$ value, which may be influenced by the direct heating in monomer droplets. The emulsion copolymerization with microwave irradiated condition resulted in more regular size spherical particles than those from conventional heating condition.

*Acknowledgements:* This work is supported by Korean Ministry of Commerce, Industry, and Energy through the Next Generation New Technology Development program.

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