1. Introduction

Self-organization of nano-structures, and the resultant periodic structures have high potential for advances in the field of nanotechnology and materials. Such self-organization can be directed by non-equilibrium thermodynamics, but the process sometimes becomes non-linear, so that control becomes quite difficult. For example, the oscillatory reaction is characterized by spontaneous periodic transitions between the oxidized and reduced forms of the intermediates, and the behaviors of reaction and diffusion are sensitive to local disturbances around the interface such as convection. Consequently, non-linear reactions have been investigated under various external influences such as magnetic, ultrasonic and electromagnetic fields to understand the mechanisms and to discover new insights for industrial application.

Our first study demonstrated the possibility of controlling non-linear reactions by microwave irradiation in a liquid-air system. For example, the oscillatory period of the reaction in a pendant drop was measured in the liquid-air system under microwave irradiation. Microwaves were absorbed throughout the droplet because the penetration depth of microwaves in a liquid was similar to the droplet size. Although molecular rotations of the polar molecules caused by the microwave irradiation directly induce faster reactions around the liquid-air interface, evaporation from the interface under microwave irradiation is unavoidable. Accordingly, the pendant drop method is not suitable for long term measurement of the liquid-air system because of such volume decrease.

Our further study found that the conditions at the interface of the liquid-liquid system are quite important for the oscillatory reaction because subtle concentration instability, which is the trigger of the oscillatory reaction, occurs around the interface. Moreover, the unusual properties caused by the non-equilibrium conditions indicate that even small changes in the surroundings may lead to instability in the system. Accordingly, non-equilibrium conditions for the concentration of chemical species around the interface must be controlled. Microwave irradiation is more attractive for such control processes because it can penetrate through the oil phase and affect the interface directly. Use of the two-phase system is common in industry, but the effects of microwave radiation on the transport phenomena around the liquid-liquid interface are unclear.

The present study investigated the oscillatory reaction in a liquid-liquid system to understand the mecha-
nisms of special effects such as faster reaction rate and molecular diffusion caused by microwave irradiation.

2. Experimental

The Belousov-Zhabotinsky (BZ) reaction was used as the model oscillatory reaction, in which cerium-catalyzed oxidation of malonic acid by bromate occurred in an acidic medium resulting in a clear color change of the solution. First, the solution was prepared for the BZ reaction, and a drop of the solution with a diameter of 2, 4 or 7 mm was placed into oleic acid at the center of a Teflon container using a pipette. The Teflon container size was 26 mm in diameter and 10 mm in height, with a circular groove of 0.5 mm depth at the bottom to prevent self-propelled motion of the droplet due to Marangoni convection. Finally, the container with the solution was positioned inside the tube-guide microwave reactor (designed and built by Micro Denshi Co., Inc.) as shown in Fig. 1.

Normally, the oscillatory period of the BZ reaction is calculated from the potential difference measured by an electrode. However, an electrode cannot be used in a microwave reactor because the metal parts may induce electric sparks. The microwave reactor has many holes (4 mm in diameter) at the top and bottom for the purposes of lighting and camera installations. Therefore, the solution color of the BZ droplet was captured through one of the holes by a camera located over the reactor as a non-contact measurement, allowing analysis of the reaction dynamics during irradiation. Microwave irradiation was begun at 300 s after the oscillatory reaction started and had become stable. Effects of the irradiation power (300-720 W) and the duration time (60-360 s) on the oscillatory period were investigated for different droplet sizes (2, 4 and 7 mm).

Figure 2 shows examples of the color changes of the BZ solution. Chemical waves, which appear as shifts in the border of different colors, are related to the diffusion of chemical species and the reaction rate. For example, the clear border progresses as nonuniformity of concentration if the reaction is much faster than diffusion. Three colors, red (R), green (G), and blue (B), were extracted from the digital movie data as shown in Fig. 3. These data have similar profiles to the potential curve obtained from an electrode for the oscillatory period. In this analysis, the digital data of blue were used as the profiles of the oscillatory reaction because blue was the clearest color.

Temperature is an important factor for the reaction rate. However, the droplet temperature is difficult to measure because it is too small to insert the tip of an optical fiber and the movement caused by Marangoni convection. Moreover, the solid-liquid interface introduced by insertion of the fiber might affect the reaction. On the other hand, the oil temperature increases gradually during irradiation and the rise is around 5-10 °C in the case of higher power and longer irradiation. As heat conduction becomes dominant for smaller droplet size, the effect of temperature rise by microwave absorbance should be kept smaller.

3. Results and Discussion

3.1. Effect of Irradiation Power

Figure 4 shows the intensity of the blue color for the oscillatory reaction for each droplet size at different microwave powers. The intensities at different powers are compared with the same graph, so the values were shifted up and down. The profiles of color intensity for the oscillatory reaction were slightly more disordered and fluctuated during irradiation, as shown in the red square. For example, the oscillatory period of the reaction before irradiation was about 60 s, but became much shorter around 0-20 s during irradiation, indicating that the chemical reaction during irradiation was considerably faster. Heat caused by microwave absorbance is released to the surrounding oil more
easily and quickly from a smaller droplet size. Consequently, the temperature within the droplet of aqueous solution is similar to that of the oil phase. Accordingly, the reaction rate is accelerated due to the larger frequency factor and the lower activation energy as a direct effect of microwave irradiation, and the shorter oscillatory period during irradiation is mainly caused by non-thermal effects of microwave irradiation. However, the temperature of larger droplets can become higher than that of the oil because heat generation induced by microwave absorbance exceeds heat release to the surroundings. Therefore, the reaction progresses faster during irradiation due to both the thermal effect of the temperature rise as well as the direct microwave effect, but the two effects are difficult to distinguish clearly and quantitatively.

Reaction under conditions of lower power and smaller droplet recovered to the original oscillatory period after irradiation as shown in Fig. 4(a), and the behavior was similar to profiles before irradiation. However, reaction trends did not change after irradiation in smaller droplets (2 mm) in the oil phase even at higher power (720 W). The oscillatory reaction was apparently stable within the recording time under higher power irradiation (600 W) in larger droplets (7 mm) as shown in Fig. 4(c). In fact, the frequency is too high to designate peaks, and the trend looks almost flat. However, the oscillatory reaction after lower power irradiation (300 W) became similar to the profile before irradiation. Intermediate behavior for the frequency of the oscillatory reaction was observed under conditions of medium droplets (4 mm) and higher power (600 W and 720 W) in Fig. 4(b) or larger droplets (7 mm) and medium power (480 W) in Fig. 4(c). The oscillatory reaction after irradiation was clearly shorter than before irradiation, but gradually increased with time.

Therefore, the microwave effect after irradiation demonstrates three trends, A, B and C in Fig. 4, which depend on the droplet size and irradiation power. Oscillatory periods were calculated from each peak of the oscillatory profiles and plotted against time, as shown in Fig. 5. The difference between trends A and B became clearer. The oscillatory period quickly recovered after irradiation in trend A, and finally surpassed the original period. In contrast, the oscillatory period was maintained at lower values for longer in trend B, but gradually became larger. Calculation of the period for trend C was almost impossible because the frequency is too high.

Generally, tiny changes at the liquid-liquid interface, such as disturbance of concentration, temperature or convection, can trigger the oscillatory reaction. For example, the reaction is related to the Marangoni effect, which is caused by a subtle gradient of surface tension caused by the temperature or concentration distribution at the interface. Depletion of chemical species after progress of the reaction caused longer oscillatory periods as seen in trend A because the likelihood of steep gradient is reduced at lower concentration. On the other hand, the oscillatory period of trend B was shorter, and chemical species remained at relatively higher concentrations, which can initiate the oscillatory reaction frequently. Therefore, the trigger must occur at the interface as a result of microwave irradiation because the shorter oscillatory period continued in the long term. Our study detected a microwave special effect for interfacial tension during and after irradiation. Accordingly, the non-equilibrium condition continues as a result of microwave irradiation. Microwaves can pass through the oil phase, which has lower dielectric constant, and reach the aqueous phase (BZ solution).
As a result, the interface absorbs excess microwaves. Higher power is advantageous for changing the interfacial condition by the formation of fine bubbles. Extinction and coalescence of bubbles, which are trapped by the two different liquid phases, might become the trigger of disturbance of the interface. Larger droplets with wider interface reached higher temperature with the absorbance of higher power irradiation, so activation of the interface is likely to result from microwave irradiation. Accordingly, the oscillatory period of trend B for larger droplets greatly fluctuated because of the unstable interface although maintaining the shorter period. However, the oscillatory period of trend B became gradually longer as the number of triggers was reduced by extinction of bubbles.

Finally, the oscillatory periods of trends B and C eventually recovered over the long period if the chemical species were not depleted.

### 3.2 Effect of Irradiation Time

Figure 6 shows the profiles of intensity of the oscillatory reaction for different irradiation times and different particle sizes at 300 W, and the data are summarized as the oscillatory period in Fig. 7. The characteristics of the oscillatory reaction could not be changed in smaller and medium droplet sizes even by longer irradiation time. Irradiation at 300 W was not enough to

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**Fig. 5** Oscillatory Period vs. Reaction Time for Various Microwave Irradiation Powers and Different Droplet Sizes

**Fig. 6** Oscillatory Behaviors of the Blue Color of BZ Solution for Various Microwave Irradiation Times and Different Particle Sizes
have any effects at the interface of smaller droplets. On the other hand, the oscillatory period became shorter with larger droplets after irradiation. Accordingly, longer irradiation time is effective to disorder the interface and can change the behavior of non-linear reactions.

3.3. Mechanism of Microwave Effects

Figures 8(a) and 8(b) are plots of the minimum oscillatory period during irradiation obtained in Figs. 5 and 7 for the power and time. The minimum periods become shorter, and trend B appears after irradiation. Due to the higher activation of the interface during irradiation, the effect continues after microwave irradiation is stopped.

Reaction behavior varied with droplet size of the same solution in oil after microwave irradiation. The controlling factor should be the activation of the interface, which is related to the power and the duration time. Overall, activation of the interface by microwave irradiation should be useful for controlling non-linear reactions in liquid-liquid systems. However, the droplet size is important for non-thermal or persisting effects. For example, thermal and non-thermal effects are more difficult to distinguish with larger droplet size during irradiation although persistent effects can be obtained by higher power or longer irradiation time. On the other hand, persistent effects after irradiation in fine droplets like emulsion might be difficult although non-thermal effects like faster reaction rate can be expected during irradiation.

4. Conclusion

An oscillatory reaction was observed in a liquid-liquid system under microwave irradiation, and the oscillatory period during and after irradiation was examined. Microwave irradiation induced both the thermal effect of temperature rise and non-thermal effects like lower activation energy and higher frequency
factors, so higher power and longer irradiation time promoted the oscillatory reaction in larger droplets and changed the reaction profile during irradiation. On the other hand, the droplet size affected the oscillatory reaction after stopping the microwave irradiation. For example, with smaller droplet size (2 mm), the intensity of the solution color during irradiation was slightly disordered by the non-thermal effects because the droplet temperature was similar to that of the surrounding oil phase. After the irradiation, the oscillatory period returned to its original value. Microwave irradiation can pass through the oil phase and reach the aqueous phase, so microwave absorbance at the interface causes activation of the interface, which can trigger the oscillatory reaction. Moreover, with larger droplet sizes (4 mm and 7 mm), subtle disturbance around the interface caused by the absorbance persists after stopping microwave irradiation. Accordingly, the oscillatory period did not recover perfectly. However, the thermal and non-thermal effect of microwave irradiation are difficult to distinguish with larger droplets.

Overall, non-contact treatment with microwave irradiation is useful for promoting the reaction of aqueous solution droplets in an oil phase like an emulsion, in contrast to thermal conduction or conventional heating convection. Accordingly, microwave irradiation has potential to induce non-equilibrium conditions at the liquid-liquid interface because the characteristics of non-linear chemical reaction are changed by microwave irradiation to some extent.

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