Chapter 5

Development of a Novel Straight-Through Microchannel Emulsification

5.1 Introduction

Kawakatsu *et al.* (1997, 1999) proposed microchannel (MC) emulsification for the preparation of monodisperse emulsions with coefficients of variation below 5% using uniform MC arrays microfabricated on a single-crystal silicon microchip. Remarkably developed micromachining techniques over the last ten years realized the microfabrication of an ingenious emulsification device, referred to as a silicon MC plate. MC emulsification does not require any turbulent mixing since a grooved MC with an elongated section can spontaneously form monodisperse droplets (Sugiura *et al.* 2001b). Droplet formation from the MC makes use of fluid dynamics on a micron-scale, which involves the significant effects of interfacial tension, viscosity, and laminar flow. However, small number of channels per silicon chip, which is attributable to their limited layout, leads to low throughput of emulsions.

We have recently proposed a novel emulsification devise, called a silicon straight-through MC plate, which can overcome the low throughput of emulsions in MC emulsification. The straight-through MC plate contains arrays of uniform through-holes, named a straight-through MC. A highly integrated layout of this MC achieves higher throughput of emulsions. A recently developed deep reactive ion etching (RIE) in miromachining techniques allowed the microfabrication of uniform through-holes with a high aspect ratio. In the present chapter, we attempted to fabricate the straight-through MC plates with oblong and circular straight-through MCs using deep RIE and developed a micro-visualization system of straight-through MC emulsification. The effect of the cross-sectional shape of the straight-through MCs was also investigated in the production of monodisperse emulsions.

5.2 Silicon Straight-Trough MC Plate

Device fabrication

Figure 5.1 schematically depicts the fabrication process of a silicon straight-through MC plate. The microfabrication of a silicon straight-through MC plate started from a

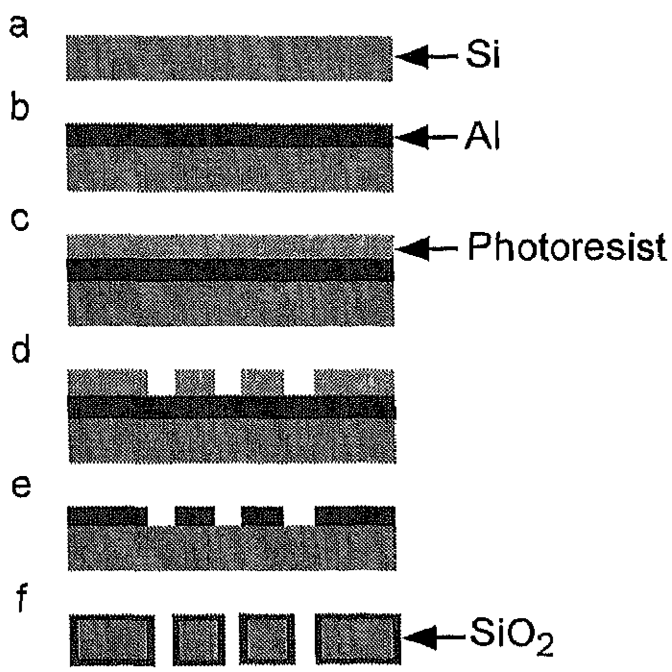

Fig. 5.1 Fabrication process of a straight-through silicon MC plate. (a) Standard silicon wafer (4-in.); (b) alminun vapor deposition; (c) spin-coating of positive photoresist; (d) photolithography and development; (e) aluminun etching and photoresist removal; (f) deep silicon etching with ICP-RIE and thermal oxidation of the substrate.

4-inch silicon wafer with a 200 μm-thickness. A 0.2 μm-thickness aluminum layer was vapor-deposited on the silicon wafer as a protective layer against deep RIE (Fig. 5.1b). A positive photoresist was spun on the substrate, and the designed channel patterns were transferred to the substrate via a mask and ultraviolet (UV) light as a radiation source (Figs. 5.1c and d). After this substrate was developed, the aluminum etching and photoresist removal were carried out (Fig. 5.1e). These photolithography processing and chemical etching give an aluminum mask against deep RIE on the substrate. Deep silicon etching was then performed by a deep RIE (inductively coupled plasma (ICP)-RIE, Plasma Thermo Inc., France) until deep microholes completely penetrated the substrate (Fig. 5.1f). This process plays a critical role in fabricating uniformly sized straight-through MCs. Thermal oxidation was used to grow a hydrophilic silicon oxide layer to prevent wetting by the dispersed oil phase on the substrate, and then the silicon substrate was cut into individual chips. The fabricated silicon straight-through MC plate was shown in Fig. 5.2.

Device design

A schematic model of the straight-through silicon MC plate is presented in Fig. 5.3. The micromachined straight-through MC plate measures 24 mm×24 mm×0.2 mm, with two 1-mm diameter feed-holes for a dispersed phase fabricated at the corners of the plate (Fig. 5.3a). A total of five thousands channels is placed around the center of this plate (Fig. 5.3b). The measured effective channel area was 1.0×10^{-4} m^2. Figure 5.3c shows scanning electron microscopy (SEM) photographs of the micromachined straight-through MCs. In order to prevent droplets growing at adjacent channel tips from contacting each other, each channel is positioned at a 100 μm interval for both cross-sectional shapes of the straight-through MCs. Dimensions of the straight-through MCs used in this chapter was presented in Table 5.1. The circular and oblong straight-through MCs had equivalent diameters of 10.0 and 17.3 μm, respectively. The definition of the channel equivalent diameter is described in Chapter 2.2. These MCs had coefficients of variation below 1%, exhibiting high uniformity required as emulsification devices for preparing monodisperse

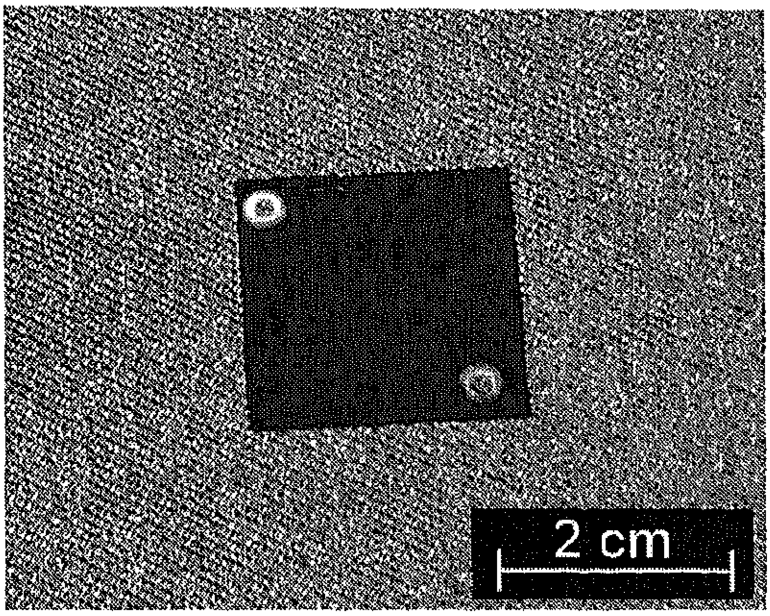

Fig. 5.2 Photograph of silicon straight-through MC plate.

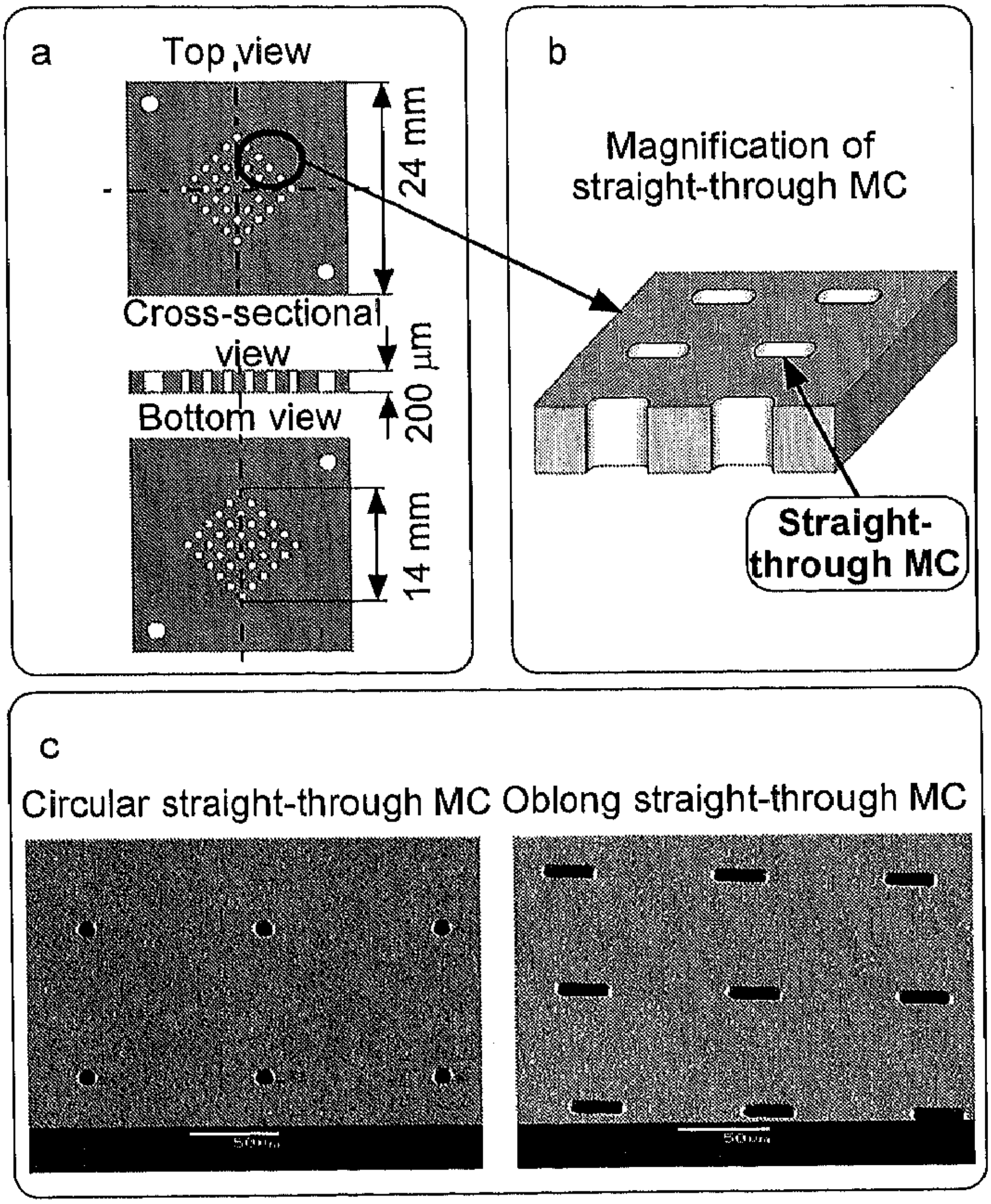

Fig. 5.3 Straight-through MC plate and SEM photographs of straight-through MCs. (a) The top view, cross-sectional view, and bottom view of the straight-through MC plate; (b) magnification of an oblong straight-through MC; (c) SEM photographs of straight-through MCs.

Table 5.1 Dimensions of silicon straight-through MCs used in this chapter.

Channel cross section	Channel equivalent diameter[a] (μm)	Longer channel length L (μm)	Shorter channel length S (μm)	Channel elongation L/S (-)
Circular	10.0	-	-	-
Oblong	17.3	29.7	9.6	3.1

[a]Channel equivalent diameter is defined as four times the cross-sectional area divided by the wetted perimeter of the channel.

emulsions.

5.3 Materials and Methods

Materials

Soybean oil (Wako Pure Chemical Ind., Osaka, Japan) was used as the dispersed phase of the emulsification system, and 0.3 wt.% sodium dodecyl sulfate [SDS; hydrophilic lipophilic balance (HLB), 40] (Wako Pure Chemical Ind., Osaka, Japan) aqueous solution as the continuous phase.

Straight-through MC emulsification system

The straight-through MC emulsification system (Fig. 5.4a) consisted of the straight-through MC module, the straight-through MC plate, a reservoir to feed the dispersed phase, a syringe pump (Model 11, Harvard Apparatus Inc., Massachusetts, USA) to feed the continuous phase, and a microscope video system (Kikuchi *et al.*, 1992). The microscope video system used in this chapter was described in detail in Chapter 4.2. Using the microscope video system, the droplet formation behavior was directly observed on a TV monitor with total magnifications of 500 to 2000.

Straight-through MC emulsification

The straight-through MC plate was presoaked in the continuous phase with ultrasonification for 20 min and was then mounted in the module, which was initially filled with the continuous phase. The straight-through MC plate was tightly held between two rubber spacers in the module. The reservoir for the dispersed phase and the syringe pump for the continuous phase were connected to the inlets of the module, which was initially filled with the continuous phase. The dispersed phase pressurized slowly was fed into the module, contacting the backside of the straight-through MC plate via the flow path for the dispersed phase. When the applied pressure exceeded the breakthrough pressure, the dispersed phase broke through the straight-through MC, initiating droplet formation as

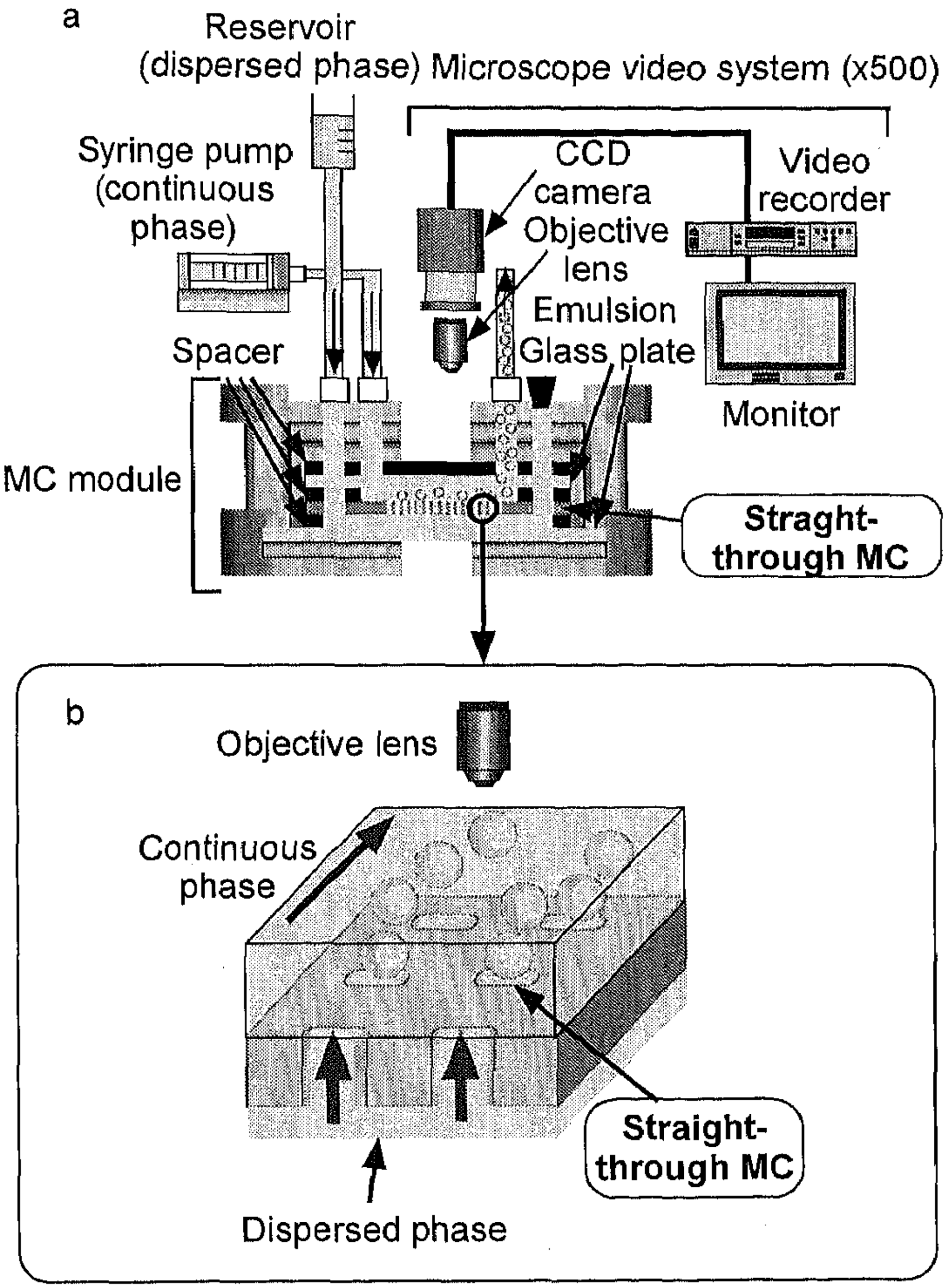

Fig. 5.4 Experimental setup for straight-through MC emulsification. (a) The system for straight-through MC emulsification; (b) flow through straight-through MC in the module.

illustrated in Fig. 5.4b. The oil droplets formed were recovered by the continuous phase flow. The applied pressure of the dispersed phase and the continuous-phase flow velocity are regulated by real-time direct observations during droplet formation.

Measurements and analysis

Video images taken during the experimental runs were analyzed to understand the droplet formation from the straight-through MCs. An image processing software (WinRoof, Mitani Co., Fukui, Japan) was used to measure the droplet diameter of over 200 droplets from pictures taken with the microscope video system. Their average droplet diameter and coefficient of variation were then calculated from the measured droplet diameters. The coefficient of variation, which was used to present the width of the droplet size distribution, was described in detail in Chapter 2.2.

5.4 Results and Discussion

Droplet formation from circular straight-through MC

The droplet formation from a circular straight-through MC with a 10.0 μm equivalent diameter was first investigated. Figure 5.5 depicts microscopic photographs of the emulsification process for the circular straight-through MC. Droplet formation started with a hemispherically shaped droplet after breaking through the channels at a breakthrough pressure of 3.16 kPa. However, the droplets continued growing up to about 100 μm, which is nearly ten times the channel equivalent diameter, before detaching from the channel tip as shown in Fig. 5.5a. A microscopic photograph of the oil droplet formed is provided in Fig. 5.5b. The droplets appeared to be difficult to detach from the circular channel tip. Furthermore, the diameter of the droplets formed in the circular straight-through MC tended to decrease with an increase in the continuous-phase flow velocity and to increase with the applied pressure of the dispersed phase. Oil droplet formation from a polycarbonate membrane with circular pores and a 10 μm pore diameter on average, described in Chapter 4.3, also showed a simular trend to that from the circular a

b

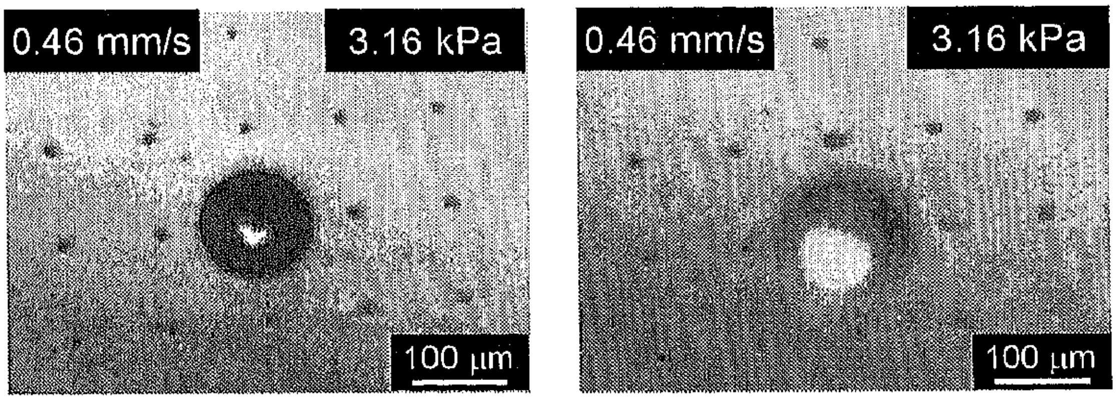

Fig. 5.5 Microscopic photographs of oil droplet formation from the circular straight-through MC. (a) Breaking through the channels and droplet formation using a circular straight-through MC; (b) photograph of an oil droplet formed using circular straight-through MC.

straight-through MC. The resultant droplet size was thus significantly influenced by the operating conditions, indicating that a circular straight-through MC has a difficulty in forming monodisperse emulsion droplets.

Droplet formation from oblong straight-through MC

Figure 5.6 depicts microscopic photographs of the emulsification process for an oblong straight-through MC with a 17.3 μm equivalent diameter. When the applied pressure reached 1.80 kPa, the dispersed phase broke through the channels and droplet formation started (Fig. 5.6a). The oil droplets formed had an average diameter of 32.5 μm and a coefficient of variation of 1.5%, verifying their excellent monodispersity. The resultant droplet diameter was less than one-third those obtained from the circular straight-through MC. The monodispersity of the droplets formed from the oblong straight-through MC can also be confirmed by their microscopic photograph in Fig. 5.6b. Microscopic observations of droplet formation from the oblong straight-through MC clarified that the oblong straight-through MC has a performance in forming monodisperse emulsion droplets.

The effect of the continuous-phase flow velocity on the droplet size and size distribution for the oblong straight-through MC was investigated. The continuous-phase flow velocity was regulated between 0 and 9.2 mm/s. The Reynolds number (Landau and Lifshitz, 1987), *Re* [ ], is used to characterize the tendency of a flowing liquid phase to develop turbulence. The calculated Reynolds numbers in this chapter were below 0.2, indicating a laminar continuous phase flow. The average diameter and coefficient of variation of the droplets formed were independent of the continuous-phase flow velocity in the range examined (Table 5.2). In addition, the oblong straight-through MC yielded monodisperse emulsion droplets even without the continuous phase flow, as shown in Fig. 5.6c. This result suggests that droplets were spontaneously detached from the channel tip without the shear force necessary for droplet formation from a circular capillary (Peng and Williams, 1998) and circular polycarbonate membrane pores (see Chapter 4.3). We

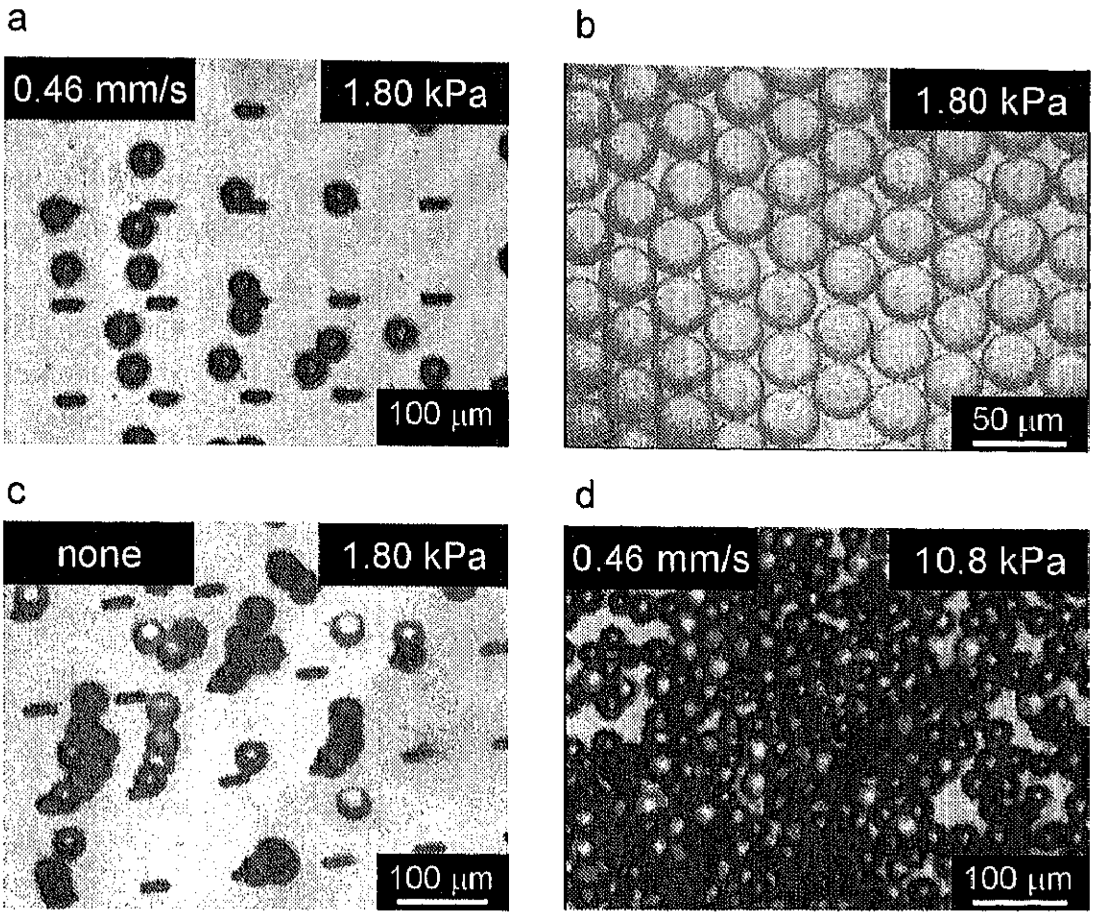

Fig. 5.6 Microscopic photographs of droplet formation from the oblong straight-through MC. (a) Breaking through the channels and droplet formation using an oblong straight-through MC; (b) photograph of monodisperse O/W emulsion droplets formed using an oblong straight-through MC; (c) monodisperse emulsion droplet formation without continuous-phase flow; (d) droplet formation from most of the channels.

Table 5.2 Effect of the continuous-phase flow velocity and the applied pressure of the dispersed phase on the average droplet diameter and the coefficient of variation of the O/W emulsions prepared using the oblong straight-through MC.

Continuous-phase flow velocity (mm/s)	Applied pressure of dispersed phase (kPa)	Average droplet diameter (μm)	Coefficient of variation (%)
0	1.80	32.7	1.4
2.3	1.80	32.9	1.7
4.6	1.80	32.4	1.8
9.2	1.80	32.6	2.1
0.46	1.80	32.5	1.5
0.46	3.60	33.0	1.6
0.46	7.21	32.9	1.7
0.46	10.8	32.8	1.6

therefore found that an oblong straight-through MC is capable of forming stably monodisperse emulsion droplets in a gentle continuous phase flow.

The effect of the applied pressure of the dispersed phase on the droplet size and size distribution for an oblong straight-through MC was also investigated. Less than 10% of the channels worked at around the breakthrough pressure. The ratio of the channels that formed droplets increased as the applied pressure increased over the breakthrough pressure, and more than 95% of the channels formed droplets at a 10.8 kPa applied pressure, as shown in Fig. 5.6d. The average droplet diameter and coefficient of variation of the droplets formed changed little over the examined applied pressures (Table 5.2). This result shows that this elongated cross-sectional shape of a straight-through MC enables stable formation of monodisperse emulsion droplets over a wide range of applied pressures above the breakthrough pressure. The dispersed phase flux increased with the applied pressure, and reached 65 $l/(m^2 h)$, which corresponded to the droplet formation volume rate of 6.5 ml/h per straight-through MC plate. It was observed that channels stably formed uniformly sized droplets at rates between 3 and 11 droplets per second.

The results in this section demonstrate that the cross-sectional shape of the straight-through MC critically influences droplet formation, and that an oblong straight-through MC has a potential to prepare monodisperse emulsions with high throughput.

Effect of cross-sectional shape of straight-through MC

The effect of the cross-sectional shape of the straight-through MC is next discussed based on the types and balance of the forces acting on a single droplet from a channel.

A circular straight-through MC has a droplet formation behavior similar to that in a circular capillary (Peng and Williams, 1998). A droplet growing at the channel tip with circular section is mainly subjected to external forces, consisting of the drag force from the continuous phase flow, the interfacial tension force, the buoyancy force, and the inertial force from the dispersed phase (Peng and Williams, 1998). The interfacial tension force acts against droplet detachment, while the other forces induce the droplet detachment. A droplet growing at the channel tip in this straight-through MC swung along the continuous phase flow due to the drag force. When the droplet diameter reached a critical volume, the swing caused by the drag force made the droplet detach from the channel tip. This droplet formation demonstrates that the drag force works as the driving force to detach the droplet. However, the drag force from the continuous phase flow on a micron scale fluctuates, resulting in the formation of polydisperse droplets from this straight-through MC. Additionally, smaller droplets tend to be forced to detach by the stronger drag force from a faster continuous-phase flow velocity (Peng and Williams, 1998), since the droplet detachment from the circular straight-through MC is determined by the balance between the interfacial tension force and the drag force from the continuous phase. This is the reason for why the resultant droplet size depends on the continuous phase-flow velocity. The circular straight-through MC therefore had a difficulty in stably forming size-controlled monodisperse emulsion droplets.

The oblong straight-through MC exhibited the formation of monodisperse emulsion droplets with and without a continuous phase flow. Monodisperse emulsion droplets would be obtained in this straight-through MC because of a driving force different from that for droplet formation using a circular straight-through MC. The effect of the continuous phase flow in this case is negligible since the oblong straight-through MC yielded monodisperse droplets without the continuous phase flow. The interface near the channel tip was forced to elongate during the droplet growth from the oblong straight-through MC. In general, such an elongated interface tends to be unstable. The growing droplet also had a spherical shape for its upper portion. At the point where the droplet diameter attained a critical value, the droplet was sheared and detached from the channel tip without any turbulent flow. We consider that instability from the elongated interface may play an important role in forming the monodisperse emulsion droplets. Sugiura *et al.* (2001) have proposed the spontaneous droplet formation mechanism from a grooved MC with elongated section caused by interfacial tension. This droplet formation mechanism may be applicable to the droplet formation from the oblong straight-through MC as well. That is, the force to restore the interfacial tension force gradient of the elongated interface at the channel tip may shear the droplet from the channel tip. Further study is required to make clear in detail the droplet formation mechanism from the oblong straight-through MC.

5.5 Conclusions

In the present chapter, we have succeeded in developing an ingenious emulsification device, called the silicon straight-through MC plate with uniform through-holes by rapidly developed micromachining technology. The results in this chapter found that the oblong straight-through MC has excellent performance in preparing monodisperse emulsions by forcing the dispersed phase through the simply elongated cross-sectional shape of the straight-through MC. The elongated cross-sectional shape of the straight-through MC allowed spontaneous formation of monodisperse oil droplets even without any turbulent mixing. This provides a new insight into applicable nozzle-based dispersing systems. The average droplet diameter and coefficient of variation of the emulsions prepared using the oblong straight-through MC remained almost constant in a range of the examined applied pressures below 10.8 kPa. This micromachined emulsification device has the potential for preparing functional microspheres and microcapsules that require monodispersity. It can also be used as size-controlled membrane filters.

We will investigate how the geometry of the oblong straight-through MC, such as the channel elongation and size, affects the straight-through MC emulsification characteristics in the next chapter.