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Investigation of Microchannel Wettability on the Formation of Droplets and Efficient Mixing in Microfluidic Devices

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Abstract

This study is an experimental investigation of a microfluidic method for the formation of droplets and mixing efficiency in continuous microfluidic channels. Droplet size strongly depends on the total aqueous flow rate under a fixed oil flow rate. In the case of different wetting properties, a hydrophobically homogeneous microfluidic channel produces smaller droplets than that of a heterogeneous microfluidic channel because of the different wettability of the formed aqueous droplets. However, high mixing efficiency in the two types of microfluidic channel is achieved by droplet recirculation. Although an increase in droplet size demands a longer mixing time, the microfluidic approach provides rapid mixing and no reagent dispersion. This mixing method in microfluidics can be applied to a variety of chemical syntheses or biochemical reactions at the nanoliter scale.

Keywords: Microfluidics, Droplets, Mixing, Dispersion

Introduction

Microfluidics has become a rapidly growing area due to the miniaturization of analytical apparatuses and (bio)chemical reactors[1,2]. The main advantages of microfluidics have been the consumption of a small amount of sample or reagent, rapid reaction time, application of hazardous reagents, lower operational costs than conventional instruments, and an increase of throughput. One of the most important applications, chemical reaction in a microfluidic reactor, is attractive because a microfluidic reactor can be easily fabricated and used to manipulate small volumes of reagents. But inherent problems in microfluidics can occur. First, mixing is too slow due to the laminar flow in microfluidics. Second, the dispersion of solutes along the channel is large because the profile of a pressure-driven flow is parabolic[3,4].

Recently, a droplet-based microfluidic system is presented to solve two critical problems, mixing and dispersion[5]. The design of the microfluidic device is based on the different properties of two immiscible liquids, water and oil. The aqueous liquids formed droplets surrounded and transported by the immiscible oil fluid. The formation of droplets in microfluidic devices is a promising tool because it can produce droplets including multiple aqueous reagents in an immiscible carrier fluid, transport the droplets with a minimized dispersion of reagents, and rapidly mix the reagents of the droplets by chaotic advection in serpentine microchannels. Basically, the droplet press against all four walls of the microchannel, but it still prevents any intimate contact with the channel walls due to thin film of carrier fluids[6-8]. Previous studies have characterized the formation of droplets and the mixing within them using immiscible fluids that have matched viscosities equal to that of water[9]. In addition, the effect of viscosity on droplet formation in microfluidic channels have also been studied[10,11]. However, there are few studies concerning the effects of microchannel wettability on droplet formation and mixing, although the wettability of a formed droplet onto a wall is a critical factor for the stable formation of droplets in microfluidic devices[12].

In the present study, we have investigated the effects of microchannel wettability on the relationship between droplet size and flow rate for the formation of droplets. Mixing efficiency was also investigated according to droplet size, as rapid mixing in a microchannel is essential to reduce analytical and reaction times. This microfluidic system will be useful for a wide range of multi-step chemical and biochemical reactions.

Results and Discussion

Principle of Droplet Formation

The formation of droplets at a junction is governed by competition between viscous stress and surface tension stress. The size of a droplet is mainly dependent on the flow rates of the aqueous and oil phases.

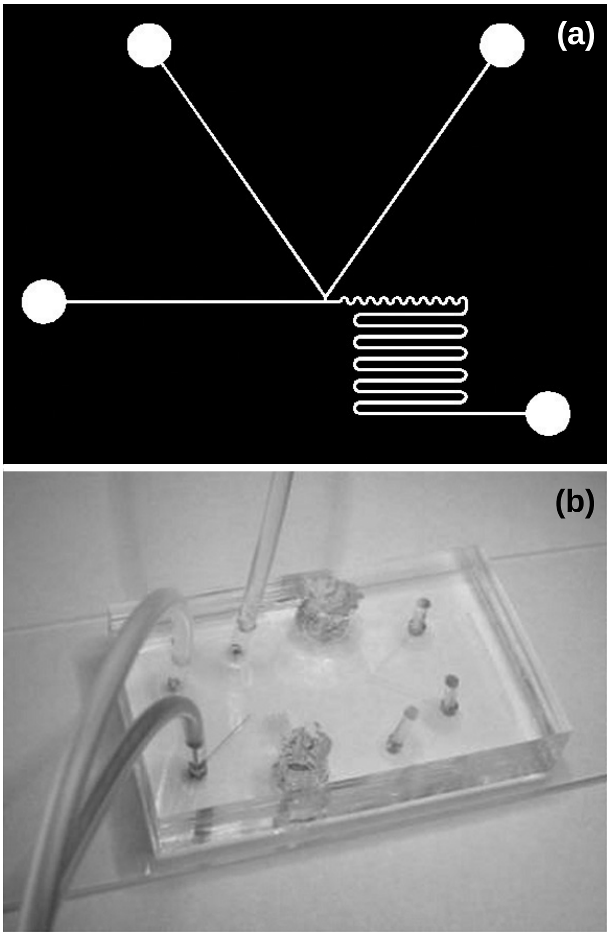

Figure 1. The design of a microfluidic device for the generation of droplets; (a) a schematic diagram of the microfluidic device, (b) a finally assembled microfluidic device.

The design of a microfluidic device for the generation of droplets is shown in Figure 1.

A dimensionless number, capillary number (*Ca*), which is the ratio of viscous to interfacial tension stress, can be used to predict the droplet size.

$$Ca = \mu\nu / \gamma, \tag{1}$$

where μ is the viscosity of oil phase flow, γ is the interfacial tension between the oil and water, and ν is the velocity of the total flow rate.

According to the mechanism of a cross-flow droplet rupture, the droplet diameter is then described by the simple equation

$$D \approx D_i / Ca, \tag{2}$$

where D_i is the hydraulic diameter of the intersection of the microchannel ($D_i = D_{capillary} = 50\ \mu m$). From equation 2, we can predict the droplet size.

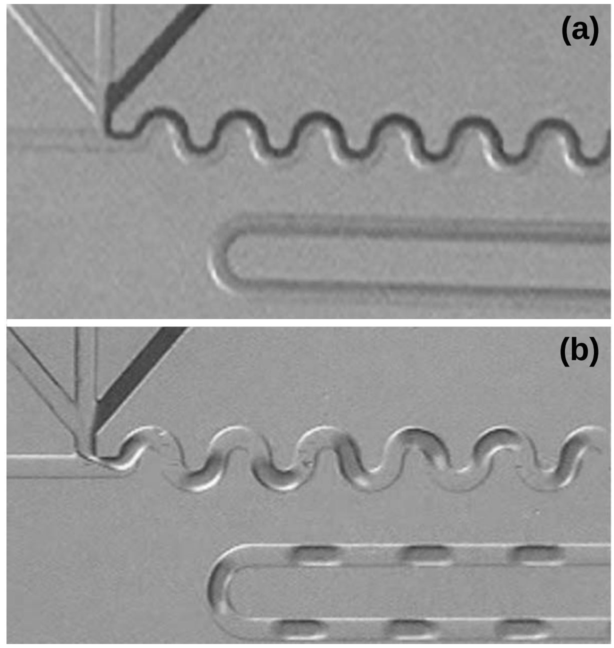

Figure 2. (a) Laminar flow mixing, (b) rapid mixing by recirculation of generated droplets.

Mixing in Microfluidic Channel

A microfluidic tool is a promising technique for the rapid analysis of distance-to-time transformation. Flow in a microchannel is laminar because it has a low Reynolds number value (0.01-100). However, this laminar flow in microfluidic devices has difficulty in achieving a simple analysis of distance-to-time transformations[13]. First, mixing has been the critical problem because when two microfluids are introduced into a microchannel they do not mix immediately. Thus, mixing in a laminar flow occurs only by diffusion between the interfaces of two streams (Figure 2a). Ideally, a turbulent flow can render a rapid mixing and low dispersion. However, these are difficult to achieve in a microfluidic channel because the turbulent flow occurs at a higher Reynolds number value ($Re > 2{,}000$). Although higher flow rate in a microfluidic channel could generate a turbulent flow, achieving a high flow rate compensates for the higher consumption of sample and high-pressure problem. In addition, as shown in Figure 2a, the inherent problem of dispersion of a sample along a microchannel is a critical issue because the property of pressure-driven flow always has a hyperbolic profile, which leads to maximum velocity at the center stream but minimum velocity at the microchannel walls[10].

Recently, several studies have presented microfluidic technologies that produce droplets in immiscible fluids. The process of droplet formation involves basic physics with the geometry of a microchannel, surface chemistry that strongly affects the formation of a droplet by viscous forces, and capillary force so as to minimize the interfacial energy between two immiscible fluids. Based on these approaches, droplet size can be controlled by the flow rates of two immiscible

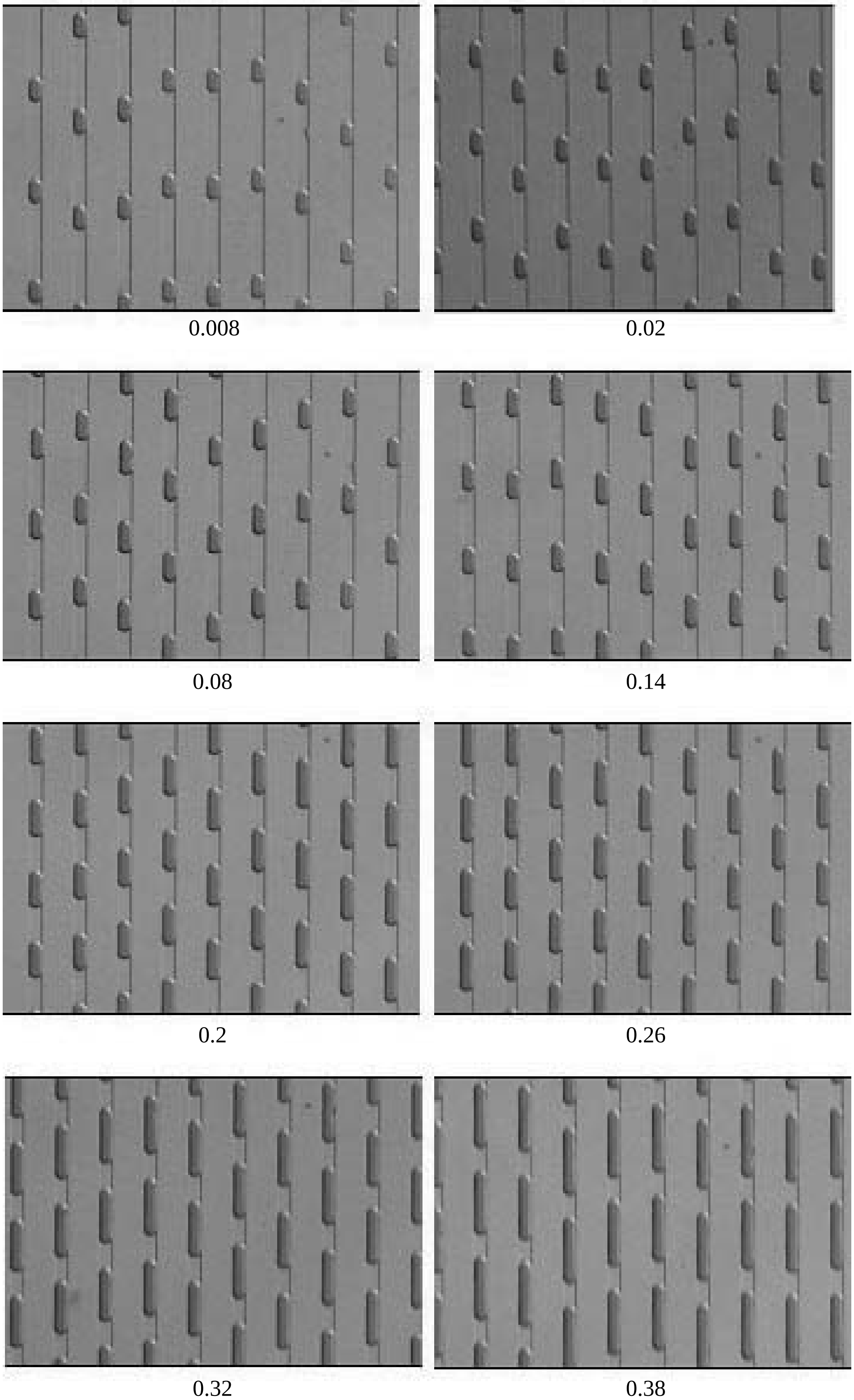

Figure 3. The formation of different sized droplets by a varying of total aqueous flow rates (μL/min) with a constant continuous oil flow rate.

fluids or by the surface property of the microchannel. However, there have been few studies focusing on mixing in these approaches. We first investigated the efficiency of mixing using a high viscous glycerol solution and dye as an aqueous stream as it is difficult to conduct a mixing analysis when a lower viscous solution is used for two aqueous streams (Figure 2b). Contrary to that of a laminar flow, mixing by recirculation of generated droplets is successfully achieved by immediate mixing of two reagents in a microfluidic device using winding channels to rapidly mix the reagents into a single droplet.

Effect of Flow Rates on Droplet Size in Homogeneous and Heterogeneous Microchannels

The effect of droplet size on flow rate is studied for homogeneous (all the walls of the channel are composed of PDMS) and heterogeneous (the bottom layer of the channel is hydrophilic glass and the remaining walls are composed of PDMS) channels. Figure 3 shows images of the effect of droplet size on various flow rates at a constant oil flow rate. A quantitative analysis of the images indicates that the size of the droplets linearly increases with an increase in total aqueous flow rate, which is consistent with previous studies[10]; in particular, smaller droplets are formed when the flow rate of the water stream is less than that of the oil stream, and larger droplets are formed when the flow rate of the water stream is higher than that of the oil stream. In the case of a variation of oil flow rate, this has little influence on droplet size. Therefore, we can successfully control the size of a produced droplet with a variation of total aqueous flow rates.

Figure 4 indicates the effect of droplet length on aqueous flow rates under constant oil flow rates on both homogeneous and heterogeneous channels. It was observed that the droplet length increased with an increase in aqueous flow rates and decreased with an increase in the constant oil flow rates. Also, the distance between the generated droplets decreased in both the channels, as shown in Figures 5. But the generated droplets in the homogeneous microchannel were smaller than those in the heterogeneous channel. This is mainly attributed to the different wetting of fluids, i.e., the hydrophilic glass surface provided higher wettability than that of the hydrophobic PDMS channel[14].

Effect of Flow Rates on Degree of Mixing

Mixing efficiency is an intrinsic property of each microfluidic device, especially in a droplet-based microfluidic system. It occurs by a recirculating flow

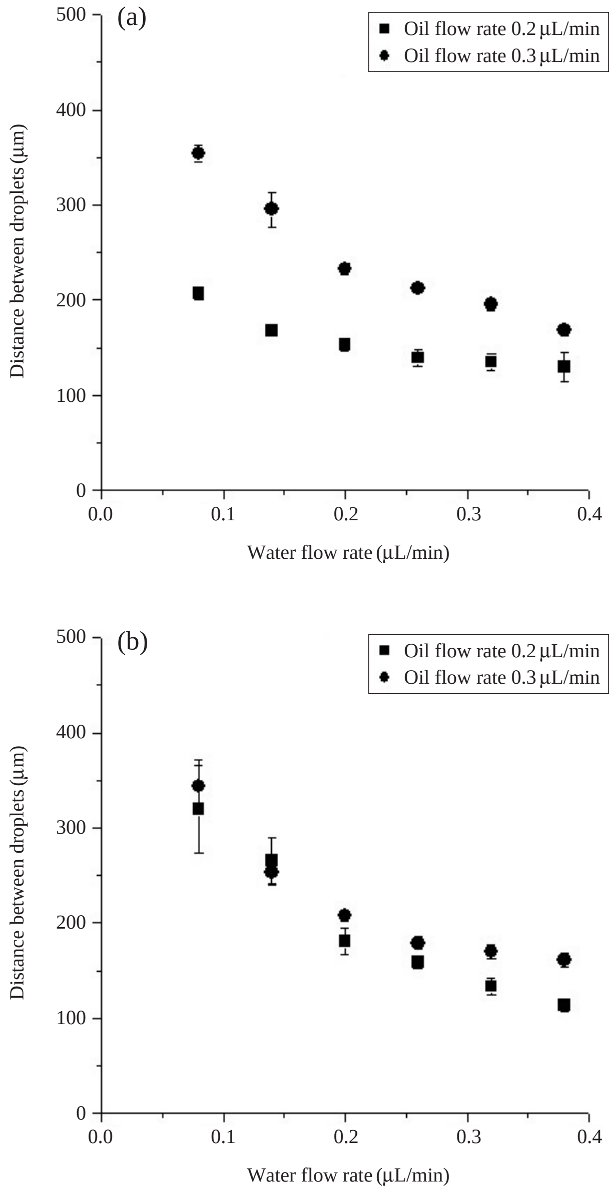

Figure 4. Effect of droplet length on aqueous flow rates under constant oil flow rates in (a) homogeneous and (b) heterogeneous channels.

caused by the shearing interactions of the fluid inside the droplet with the stationary walls of the microchannel. The closed recirculation is localized in the front- and back-halves of the droplet from the junction in the microfluidic device, i.e., there are two vortices of flow in a drop moving through a straight microchannel, one in the upper-half of the drop and another in the lower-half.

A theoretical investigation on the ideal conditions indicates that the recirculating flow reduces the striation length, $st(d) = st(0) \times l/d$, where d (m) is the

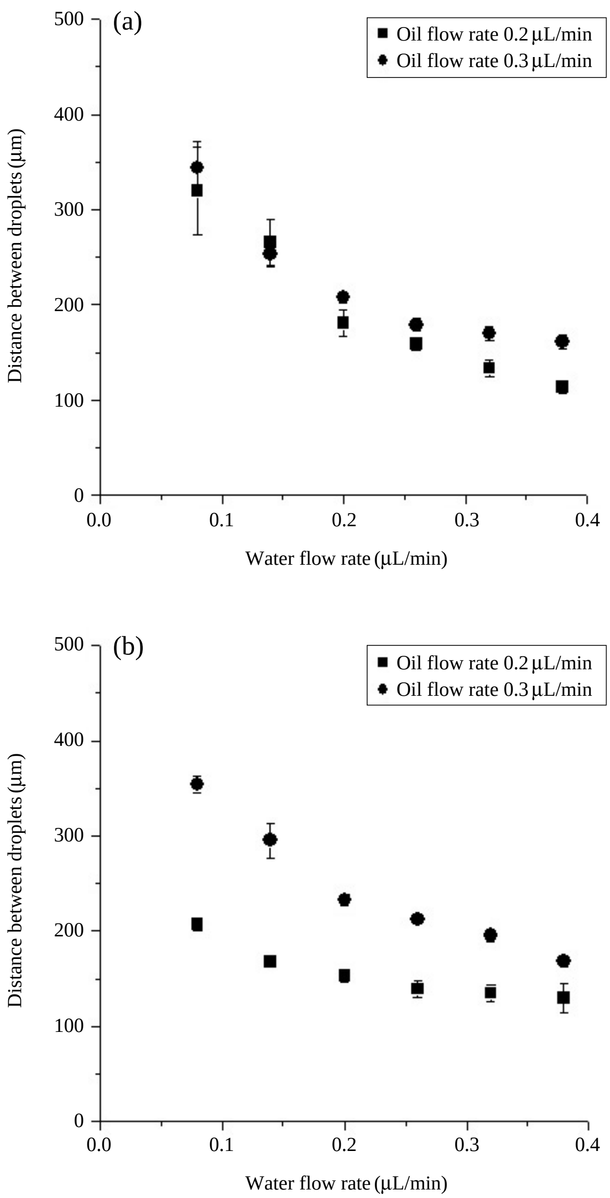

Figure 5. Relation of the distance between droplets and aqueous flow rates under constant oil flow rates in (a) homogeneous and (b) heterogeneous channels.

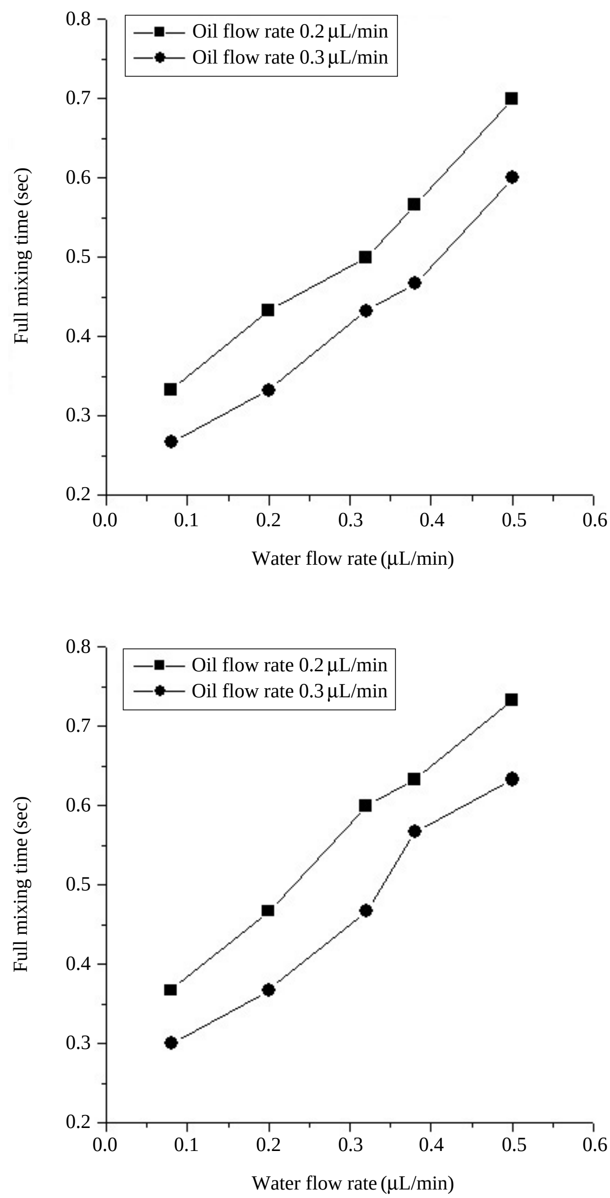

Figure 6. Effect of full-mixing time on aqueous flow rates under constant oil flow rates in (a) homogeneous and (b) heterogeneous channels.

distance traveled by a droplet, l (m) is the length of the droplet, st (0) is the initial striation length in the droplet, and st (d) is the striation length after a plug has traveled distance (d) through the channel. The mixing efficiency in the microfluidic channel mainly depends on the initial distribution of reagents in each half of the droplet. And a higher degree of mixing is also achieved by recirculation. The above equation predicts that a shorter droplet will mix within a shorter distance and a shorter mixing time at a constant flow rate. This prediction matches well with our experimental results, as shown in Figure 6, which suggests that initial droplet formation as an eddy in a microfluidic channel is extruded into the stream of the oil fluid, and that the eddies are a well-distributed reagent, such as the use of a red dye in a droplet.

Conclusions

We examined the influence of flow rate and wetting on the mechanism of droplet formation and rapid mixing in homogeneous and heterogeneous microchannels. The size of the droplet can be easily controlled by the combination of flow rate and wetting property. A rapid mixing can be obtained by the recirculation of a droplet and the geometry of the channel design. The smaller droplets show a higher mixing efficiency in microfluidic channel. This microfluidic system with rapid mixing and no dispersion is useful for controlling chemical and biochemical reactions. We are developing this microfluidic system for applications in chemical syntheses and biochemical analysis.

Materials and Methods

Microfabrication of Microfluidic Device

Microfluidic devices were fabricated with polydimethylsiloxane (PDMS) using replica micromolding, and a silicon master was fabricated with an SU-8 photo resist using conventional photolithography. The microfluidic device was fabricated by replica micromolding techniques. A mixture of PDMS, prepolymer, and curing agent (10 : 1, Sylgard184, Dow Corning Co.), was thoroughly stirred then degassed in a vacuum oven. The degassed PDMS mixture was then poured onto the silicon master and cured at 65 °C. After curing, the PDMS replica was peeled away from the silicon master. Finally, the PDMS was bonded with a slide glass after oxygen plasma treatment for the heterogeneous channel. For the homogeneous channel, the PDMS replica was exposed to an oxygen plasma treatment and then bonded to a precured PDMS spin-coated glass device (Figure 1).

Analysis of Droplets

A red aqueous stream is made of red food dye diluted with water, and a colorless stream is an 85% glycerol-water solution. The water immiscible stream as an oil phase is made of soybean oil. The mixing images were grabbed using a color CCD camera, and the mixing analysis was performed using imaging software (Image J and Photoshop 6.0). Image J was also used to measure droplet length and the distance between droplets. The interfacial tension was measured using a ring method.

Acknowledgements

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