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## SOLID-LIQUID OPERATIONS IN MICROCHANNELS

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### KEYWORD

polymer microparticles – flow manipulation – fluid injection and withdrawal

### ABSTRACT

*This paper deals with solid-liquid operations in microchannels. Polymerisation processes have developed in microreactors. But once droplets are polymerized, further operations are needed in order to obtain more complex structures. A microparticle management unit system, completely built with Plexiglas plates and chromatography capillary tubing, is presented here. The device includes droplet generation, polymerisation and microparticles flow manipulation. These three different process operations are connected thanks to larger capillaries and glue without leakage or clogging. After droplets polymerisation, this management unit under evaluation is either able to increase or reduce distance between microparticles or inject or withdraw liquids by using secondary channels and pumps. With 180 microns inner diameter capillaries, monodisperse microparticles are obtained with different size and shape. They are either round or bullet-shaped and in the range of 130 to 200 microns. Carrier fluid withdrawal is studied and flow manipulation is lightly different with particles or droplets. Nevertheless, distance between particles can easily be regulated until particles touch each other. Fluid injection is tested with miscible or non-miscible liquids but only miscible fluid appears to be effective in order to change solvent around particles. The number of secondary channels and parameters of aspiration necessary to change carrier fluid have been determined.*

### 1. INTRODUCTION

Microreactors are receiving a growing interest in polymerisation processes. The micron-size dimension is directly used for precise size distribution of the solid obtained [1, 2]. The use of microfluidic allows obtaining polymeric particles with different shapes and compositions. Directly derived from the shape of the droplets, polymer beads [4-6], disks and plugs [5, 6] were thus synthesized. Moreover, microfluidic enables to form multiphase droplets [7] from which partial polymer spheres [8], Janus [9] and ternary polymer particles [10] were obtained. In each case, synthesized polymeric particles have an extreme regularity and a broad range of size is available.

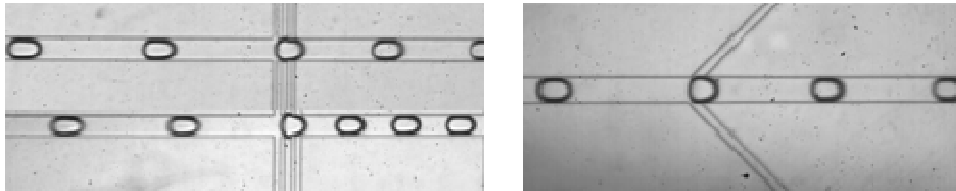
Microparticles are usually collected just after polymerisation. After the generation itself, an important issue is now to be able to perform operation on the solids in the channels. This should be use to obtain interesting and more complex structures such as polymer necklaces or onion-structured microparticles. In a process engineering point of view, further operations are then needed such as multiple operation connection, addition of a secondary fluid, solvent change or increase or decrease of interval length

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between two particles. This study is focused on the description of a multi-operation microfluidic system implementation. Three operations will be considered: (i) droplet generation, (ii) polymerisation reaction, (iii) secondary fluid injection and withdraw.

The last part microfluidic system is derived from previous studies on secondary channels [11] which have shown to be possible to act on the continuous phase without disturbance on the dispersed phase (fig. 1a and 1b). The secondary channels will either extract continuous phase or inject a second fluid. Fluid extraction has to face the respective pressure drop within main or secondary channels. A right balance to be found for effective aspiration.



**Figure 1:** Continuous phase extraction on droplet flow by use of secondary channels [11]

The chosen chemical system is the polymerisation of tripropylen-glycol diacrylate. The reaction occurs in presence of an initiator of photo-induced polymerisation (Hydroxyl-cyclohexyl-phenyl ketone).

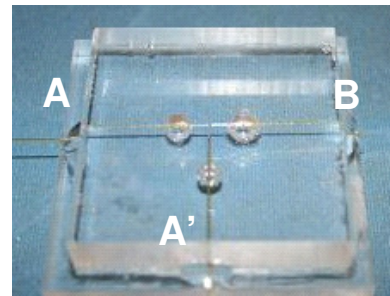
## 2. MATERIAL AND METHODS

### 2.1 Microfluidic units

The microparticles management unit system is divided into three parts providing three different process operations: droplet generation, polymerisation part and secondary fluid injection and withdraw.

#### 2.1.1 Droplet generation unit

The droplet generation unit (Figure 2) can either be a T or a cross junction. It is composed of two Plexiglas plates and standard 360 microns outer diameter capillaries (OD), different inner diameters (ID) can be used. The first plate is worked with a micromilling machine and a 300 microns drill. The channels thus created hosts the capillaries that are put in contact all together at the T junction and fixed with glue when correctly set. The second plate is then sealed upon to close the generator thanks to chloroform. 180 microns inner diameter capillaries and a T-junction are used in this study.



**Figure 2:** Droplet generator in a T-junction. A and A' are the injection point and B the outlet point. Capillaries are inserted in the milled channels and sealed with glue.

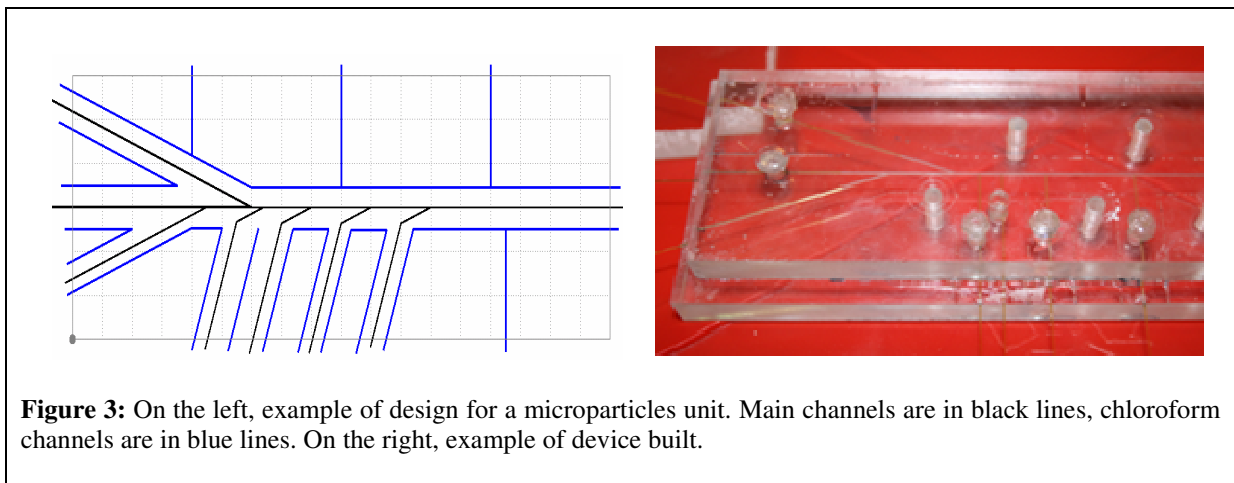
#### 2.1.2 Connections and polymerisation block

The polymerisation unit is composed of a single capillary whose length can vary to ensure the good exposure time to the UV light. Standard 360  $\mu\text{m}$  capillaries made out of fused silica have 20 microns-thick polyimide coating. This coating is useful to protect against capillary breaking but absorbs UV light avoiding polymerisation so it has to be removed. The connection between the different units is possible thanks to larger capillaries (320  $\mu\text{m}$  ID 465  $\mu\text{m}$  OD). Polyimide coating is to be removed from 360  $\mu\text{m}$  capillaries, in order to be inserted into the larger ones. Capillaries from both units are set

in straight contact in the middle of the larger one and glued with it. No leakage is observed and there is neither droplet deformation nor clogging due to polymer particles.

### 2.1.3 Microparticles management unit

As for the droplet generator, two Plexiglas plates and standard 360  $\mu\text{m}$  OD capillaries are used to produce this unit. First plate is milled with 300  $\mu\text{m}$ . Figure 3 gives an example of design used to mill the bottom Plexiglas plate. When all the capillaries are in place, the second plate is added and both plates are sealed with chloroform. All the channels have a square section of 380x380  $\mu\text{m}$  so that they can host 360  $\mu\text{m}$  capillaries. The angle between main and secondary channels has been fixed to 20°. This value is the minimum possible to ensure a good design during the milling process. Furthermore, low angle values are favourable to avoid droplets formation when injecting [12].



## 2.2 Chemical system

Tripropylen-glycol diacrylate is used as the organic phase liquid. An initiator of photo-induced polymerisation (Hydroxyl-cyclohexyl-phenyl ketone) is added to the monomer to produce a (5.0 wt.% mixture [5]. This chemical system is described in previous studies on polymerisation in microchannels. It has the advantage to be very reactive thanks to two acrylate groups and thus interesting to produce microparticles with short exposition time.

## 2.3 Surrounding equipment

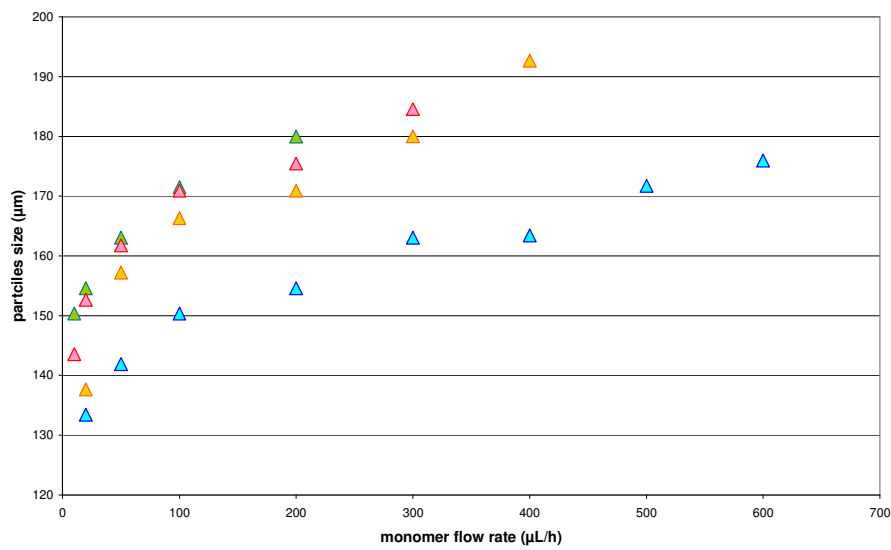
The fluids are stocked into 1 to 20 ml syringes (Terumo, BD) placed on syringe pumps (Harvard 2000, Picoplus). The connection with the capillaries is made with 22G needle (Terumo) directly glued on them with cyanolithe glue. The observation is made with a fast CCD Camera (NV1000) coupled with a microscope (Nikon SMZ-10). Images acquisition rate is 900 frames per second. Exposition time is chosen in order to have enough light for contrast distinction and short exposition for the droplets edges sharpness. A 100W spot lamp is used to provide necessary light. The images are acquired with transmission light through Plexiglas.

### 3. RESULTS AND DISCUSSION

The device, (connections and sealing) is resistant up to  $15 \text{ mL.h}^{-1}$  which can be evaluated as a  $0.1 \text{ bars.m}^{-1}$  pressure drop. In the experimental domain studied, no leakage are observed but sensible points concern the glue which ensure the sealing between capillaries and Plexiglas channels. The management unit used for experiments is the left design exposed on Figure 3.

#### 3.1 Monomer droplets generation and polymerisation

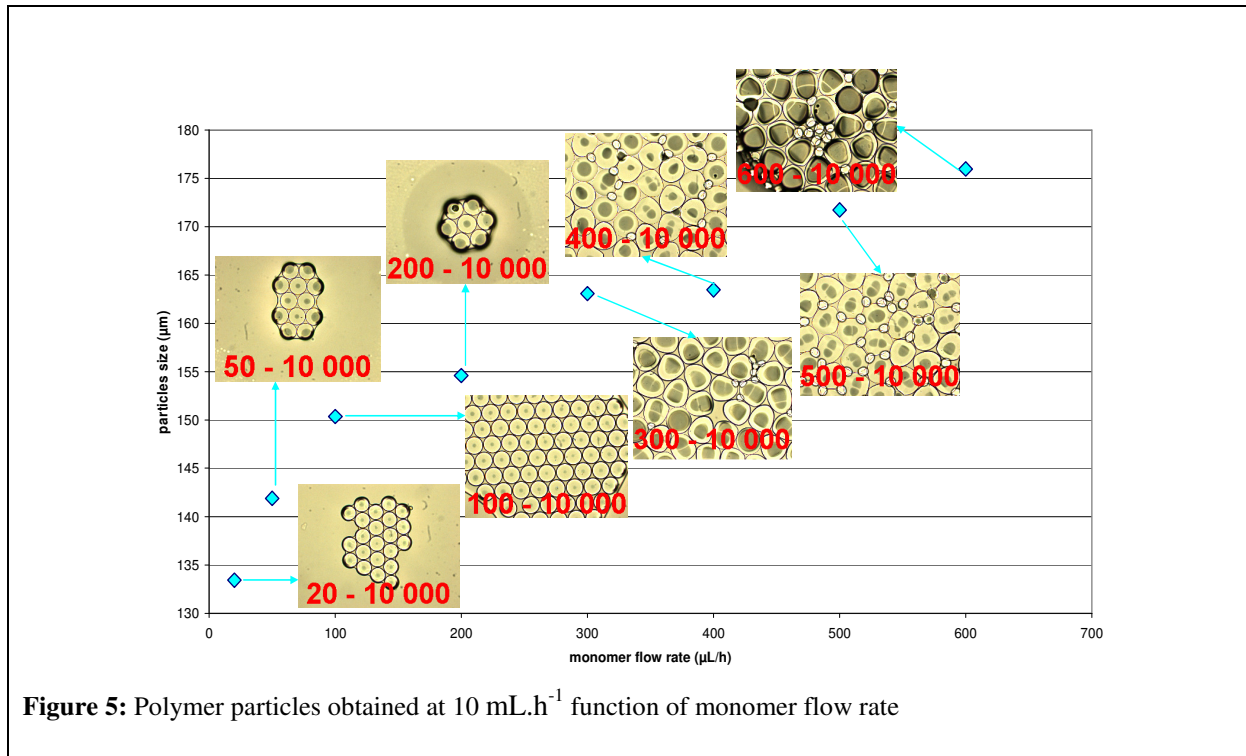
Due to the very low thickness of the fluid in the capillary submitted to the UV lamp, the residence time necessary to obtain solid particles is reduces down to about 5 s. Several experiments have been performed in order to choose an operating domain which allows having spherical particles. Dispersed phase varies from 20 to  $600 \mu\text{L.h}^{-1}$  and continuous phase from 4 to  $10 \text{ mL.h}^{-1}$ .



**Figure 4:** Particles size distribution function of monomer flow rate with different water flow rates: (▲)  $4 \text{ mL.h}^{-1}$ , (▲)  $6 \text{ mL.h}^{-1}$ , (▲)  $8 \text{ mL.h}^{-1}$ , (▲)  $10 \text{ mL.h}^{-1}$

Figure 4 shows the particles size distribution through the operating conditions. Monodisperse particles of different size and shape are obtained in the range of 130 to 200 microns. Although it is not much noticeable at lower flow rates, particles size decreases with the increase of continuous phase flow rate, and increases when dispersed phase is raised. Particles shape varies with monomer flow rate. An example is given in Figure 5. At low monomer flow rate (inferior to  $200 \mu\text{L.h}^{-1}$ ), particles are spherical and satellites are not visible; they set themselves in regular hexagonal structures. At higher monomer flow rates, particles assume a bullet shape and satellites are numerous and visible.

For the rest of the experiments, flow rates are fixed at  $4 \text{ mL.h}^{-1}$  for the continuous phase and  $100 \mu\text{L.h}^{-1}$  for the dispersed phase.

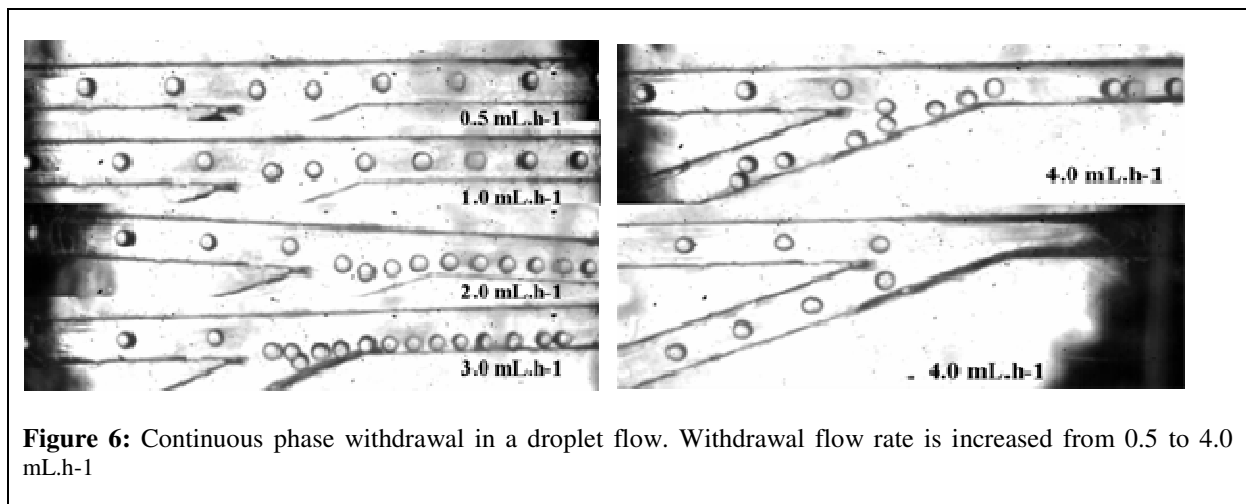


### 3.2 Carrier fluid withdrawal

This part is preliminary to second fluid injection. It can be useful to choose the distance between particles before injection. It may also be interesting to reduce flow velocity. The carrier fluid withdrawal is studied with droplets and particles.

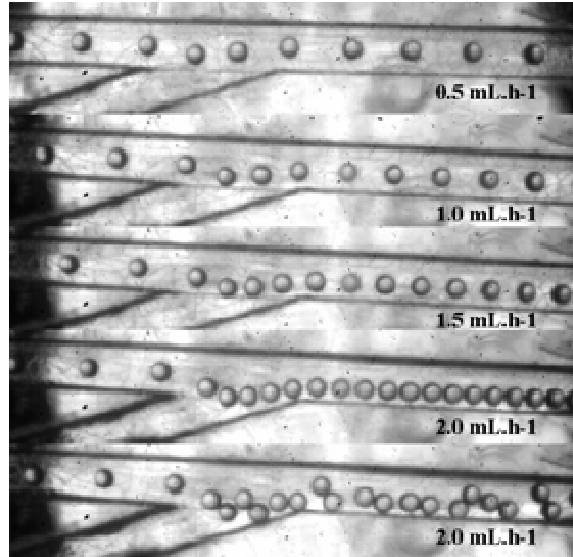
#### 3.2.1 Droplet flow

Before testing solvent aspiration with particles, withdrawal is tested with monomer droplets to define operating conditions. Particles may indeed clog the withdrawal channel if aspiration is excessive. The withdrawal flow rate is increased (Figure 6) until all the droplets are drained into the secondary channel. The distance between droplets and walls slowly decreases until some may explode with the shock. At  $3 \text{ mL}\cdot\text{h}^{-1}$ , flow starts to be chaotic and droplets can switch to secondary channel. At  $4 \text{ mL}\cdot\text{h}^{-1}$ , droplets move into secondary channel after a few seconds, then flow is regular in the withdrawal channel and droplets do not touch the walls. An aspiration flow rate of  $2.5 \text{ mL}\cdot\text{h}^{-1}$  is then a limit to prevent droplets from directing into the secondary channel.



### 3.2.2 Particle flow

With a particle flow, withdrawal flow rate is increased cautiously (Figure 7). Distance between particles decreases progressively until they touched each other at  $2 \text{ mL.h}^{-1}$  but this state is unstable and particles begin to put themselves in staggered rows. At  $2.5 \text{ mL.h}^{-1}$ , particles move into withdrawal channel. The aspiration flow should then be lower than  $2 \text{ mL.h}^{-1}$ .



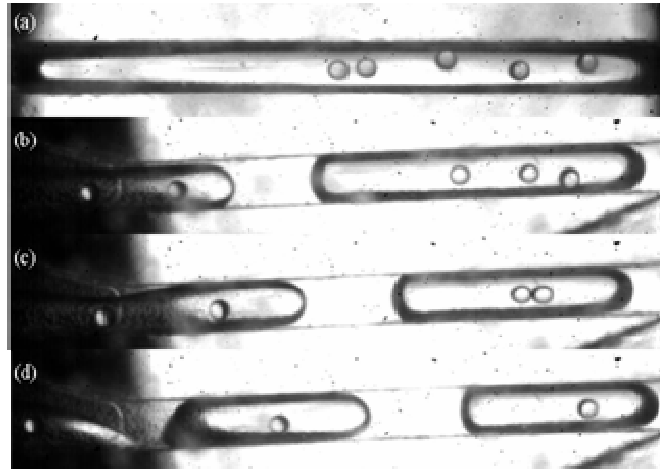
**Figure 7:** Continuous phase withdrawal in a particle flow. Withdrawal flow rate is increased from 0.5 to 2.0  $\text{mL.h}^{-1}$

## 3.3 Secondary fluid injection

Secondary fluid injection is tested with either non-miscible or miscible fluid. The aim is to find operating conditions where carrier fluid can easily be replaced by a second fluid. The angle between injection and main channel is  $20^\circ$ . First aspiration channel is set at 20 centimetres from injection channels and second at 40 centimetres.

### 3.3.1 Non-miscible fluid injection

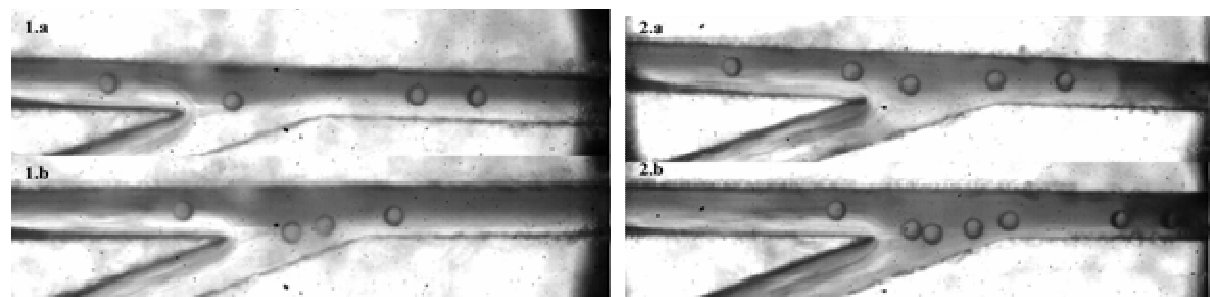
1-Octanol is the non-miscible fluid chosen for injection. Different flow rates are tested (figure 8) but in each case water slugs in octanol were generated. The number of particles in water slugs varies with the second fluid flow rate. As laminar flow is impossible, solvent withdrawal is ineffective to separate particles from first carrier fluid. Direct injection of non-miscible fluid is thus excluded in order to change carrier fluid.



**Figure 8:** Injection of 1-Octanol at different flow rate: (a) 1 mL.h<sup>-1</sup>, (b) 2 mL.h<sup>-1</sup>, (c) 3 mL.h<sup>-1</sup>, (d) 4 mL.h<sup>-1</sup>

### 3.3.2 Miscible fluid injection

A solution of bromothymol blue is used as miscible fluid and flow rate is fixed at 4 mL.h<sup>-1</sup> to test carrier fluid withdrawal. As flow is laminar, half of the channel is occupied by bromothymol blue and half by water so that any change of level can be noticeable. Water withdrawal is first studied with only one aspiration. Flow rate is increased until particles start moving in the secondary channel: the limit is at 2 mL.h<sup>-1</sup> (Figure 9). Water level has decreased of a half. Due to wall effects, some bromothymol blue is aspirated through withdrawal channel.



**Figure 9:** First carrier fluid withdrawal with particles in a laminar flow. On the left, pictures are taken at the first withdrawal channel (1.a no aspiration, 1.b aspiration flow 2 mL.h<sup>-1</sup>). On the right, pictures are taken at the second withdrawal channel when first aspiration flow is fixed at 2 mL.h<sup>-1</sup> (2.a no aspiration, 2.b aspiration flow 2 mL.h<sup>-1</sup>).

A second aspiration is then added with first withdrawal flow rate set at 2 mL.h<sup>-1</sup>. Flow rate is again raised until particles are aspirated through secondary channels. The limit flow rate is still at 2 mL.h<sup>-1</sup> and main channel is practically full of bromothymol blue after the second aspiration (Figure 9, 2.b). It seems then that two aspiration channels are necessary to remove first carrier fluid after the injection of a new miscible fluid. This number may be reduced if carrier fluid is aspirated before secondary fluid injection and second fluid flow rate is increased. In order to reduce diffusion phenomena, withdrawal channels should be placed closer to secondary fluid injection.



## 4. CONCLUSION

A micromanagement unit system including droplet generation, polymerisation part and secondary fluid injection or withdraw is reported here. Polymer particles generated are monodisperse and in the range of 130-200 microns. This range can easily be widened by changing inner diameter of capillaries composing the device. Solvent withdraw before secondary fluid injection has been efficient to regulate the distance between particles. Only miscible fluid injection can lead to changing fluid around polymer particles by withdrawing the first carrier fluid. This preliminary study has given encouraging results on the route to produce more complex polymer structures.

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