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Droplet size modulation through controlled swelling of PDMS.

J. H. Gonzalez-Estefan,[a,b] G. Chastanet*[a,b] and M. Gonidec*[a,b]

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Hereby, we present a new method to modulate the droplet size in microfluidic PDMS chips that is based on the geometrical changes of the device when it is exposed to different concentrations of a solvent that causes swelling PDMS. Hereby, we present a new method to modulate the droplet size in microfluidic PDMS chips that is based on the geometrical changes of the device when it is exposed to different concentrations of a solvent that causes swelling of the PDMS. Hereby, we present a new method to modulate the droplet size in microfluidic PDMS chips that is based on the geometrical changes of the device when it is exposed to different concentrations of a solvent that causes swelling of the PDMS.

Introduction

The precise control and manipulation of fluids achieved by microfluidics has greatly attracted the attention of the scientific community.[1] In particular, droplet microfluidics – the generation and manipulation of droplets in microfluidic channels – has been used for a myriad of applications, ranging from the synthesis of metal-organic frameworks[2] and CdS nanoparticles,[3] to protein crystallization,[4] drug delivery[5] and even single-cell barcoding and sequencing.[6] Typically, in such devices, droplets of an aqueous phase are dispersed and carried by a hydrophobic continuous phase inside channels which critical dimensions (width and height) vary from tens to hundreds of micrometres. Inside these systems, the viscous forces dominate over the inertial ones and the flow is predominantly laminar with secondary flows usually appearing with disturbance obstacles or curvatures in the channels.[7]

The degree of precision in the generation and manipulation of the droplets in these systems depends sharply on the accurate control over the flows involved. Within this scope, the droplet size is a dominant parameter because the drag force on a droplet carried by a laminar flow, as well as all the secondary flows, depend on it.[7] Moreover, in the use of droplet microfluidics for the crystallization of proteins, the nucleation rate is proportional to the droplet volume in case of homogenous nucleation, and to the droplet surface in case of heterogeneous nucleation;[4] the droplet size is also critically important in the microfluidic synthesis of micro-particles for controlled drug delivery, because the rate of drug release is proportional to it;[5] and the ease to merge droplets depends on their size as well.[8]

Droplets with narrow size distributions can be generated during extended periods of time by passive methods. For this reason, there is a growing interest in controlling the size of droplets accurately and many studies have been devoted to the prediction of the size of droplets in such systems.[9–11†] There are still opportunities for improvements in this direction, especially in the development of new models that effectively combine simplicity and accuracy without the need of empirical parameters.

Experimentally, a few strategies are available to control the diameter of droplets. A simple strategy could consist in maintaining operational parameters constant (nature of the fluids, flow rates, temperature) and changing only the geometry of the chip, iteratively, until the desired droplet size is achieved. Unfortunately, this approach requires the manufacture *ab initio* of a new chip at each iteration, and even then, minor fabrication defects could alter the behaviour of the chip and the achieved nominal droplet diameter could thus deviate from the desired one.

A more pragmatic approach is that of leaving the geometry of the chip constant and to change the other parameters that influence the droplet size: flow rate,[10,12,13] surface tension,[12] viscosity of the fluids[14] or temperature[13] (which in turns affects the latter two parameters). These techniques, together with active droplet generation methods (like those based on the manipulation of electric fields,[15,16] mechanical forces[17–21] or channel deformation[22–25]) build the set of tools by which the droplet size can be efficiently modulated in microfluidic devices. Each one of these methods presents unique advantages and drawbacks. For example, active droplet generation methods require specialized equipment[15–21] or complex chips with multiple layers;[22–25] changing the flow rates of the dispersed and the continuous phases leads to changes in the dwell times and production rate;[ref?] and changing the temperature of the system will alter the kinetics

[a] CNRS, ICMCB, UPR 9048, F-33600 Pessac, France
[b] *Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France*

† The articles mentioned here refer to models to predict the droplet size in the squeezing regime, a more extensive list of the models used to predict the droplet size in other regimes can be found in reference 34.

Electronic Supplementary Information (ESI) available: Details about the geometry of the microfluidic mixer and about the damage of thin PDMS walls, the behaviour of the T-junction using the conventional configuration and the calculation for the capillary number during the experiment. See DOI: 10.1039/x0xx00000x

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of the reactions occurring inside each droplet. Moreover, the properties of some nano- and micro-particles, like the coordination polymers displaying spin-crossover behaviour, are strongly influenced by the reaction time,[26] the temperature[26,27] and the presence of surfactants.[27] For all of those reasons, it would be highly convenient to dispose of an easy method to control the size of droplets generated in a microfluidic channel without resorting to the use of surfactants and without changing the flow rates or the temperature of the system.

Here, we present a simple method to control the size of droplets generated in a single layer chip, with passive methods, and without the need of additional equipment. It is based on the controlled swelling of poly(dimethylsiloxane) (PDMS) in the presence of some solvents and the subsequent effect that the geometrical changes of the chip has on the droplet size. While a few recent studies have been dedicated to this phenomenon,[refs] generally speaking, the swelling of PDMS with organic solvents is still considered as an issue to be avoided, and solvents that lead to swelling are often described as "incompatible with PDMS".[28,29] We show here that this effect can be controlled and that the controlled deformation caused by swelling can then be used as a way to modulate the size of droplets in a microfluidic T-junction droplet generator.

Results and discussion

Experimental design

The swelling of PDMS (and other polymers) by organic solvents is a well-known phenomenon, but little is known about its effect on the deformation of the geometry of PDMS micro-channels inside a microfluidic chip.[ref deformacion] In order to establish how the swelling of PDMS can be used to modulate the behaviour of a microfluidic chip, we had to first gain control over the swelling process and then to apply it to the control of the behaviour of functional chips.

We postulated that the deformations of micro-channels could be controlled by tuning the nature and composition of the fluid flowing through them, and in particular by diluting a solvent known to cause significant swelling into one that is known to be inert towards PDMS. We chose to use a mixture of mineral oil (a hydrophobic mixture of hydrocarbons commonly used as carrier oil in microfluidics) and a swelling agent, toluene (which is known to swell PDMS significantly).

To perform this study, we designed three chips: i) a zig-zag mixer (see Fig. SXX) designed to homogenise the solvent mixtures before entering the functional chips, ii) a model chip (Chip A, see Fig. 1) designed to study solvent-induced channel deformation as a function of the concentration of swelling agent, and iii) a T-junction droplet generator (Chip B) to study the effect of swelling on droplet sizes.

For all experiments, the volume percent of toluene in the experimental setup was set by controlling the relative flow rates of two solutions: pure mineral oil, and a 50% (V/V) solution of toluene in mineral oil, that were mixed using the inline mixer before entering the test chips.

Controlled Swelling in PDMS Micro-channels

One could expect the deformation of PDMS microstructures to depend on the concentration of swelling agent, but it should also depend on the geometry of the microstructures themselves. For example, a thin, 10-µm wide PDMS barrier sandwiched between two micro-channels is essentially a membrane, and can be expected to swell differently than the two opposing walls of an isolated microchannel (separated from other structures by a few millimetres or centimetres) which can instead be considered as semi-infinite walls. Since functional chips usually consist of microstructures separated by barriers of different critical thicknesses, understanding properly the behaviour of microfluidic chips subject to swelling therefore requires studying such size-dependent properties. Chip A (see Fig. 1) was designed for this purpose, and consists of a zigzagged channel of 500 µm in width and 75 µm in height encompassing a series of parallel barriers with different widths ranging from 30 to 770 µm.

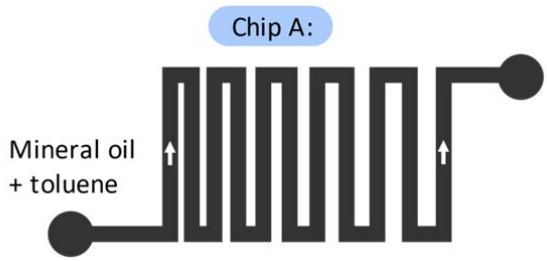

Fig. 1 Simplified geometry of Chip A showing the zig-zag test structure with increasing channel separations.

We dispensed mixtures of mineral oil and toluene through the chip with toluene concentrations ranging from 0-48% (V/V). The volume fraction of toluene was increased stepwise every 40 minutes in 6% increments, maintaining a total flow rate of 1.5 mL/h. To quantify the chip deformation, we then measured the separation between channels by optical microscopy – for each concentration of toluene – and determined the effect of swelling by calculating the absolute change in lateral dimensions δw as a function of the toluene concentration C_T:

$$\delta w(C_T) = w(C_T) - w_0 \qquad (1)$$

where w_0 is the width of the structures when flowing pure mineral oil, and $w(C_T)$ is the width of the structures at a toluene volume percent equal to C_T.

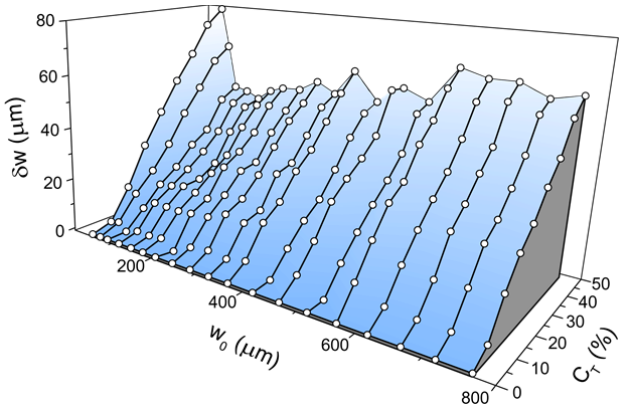

Fig. 2 Change in microstructure dimension δw due to the swelling of PDMS as a function of the initial width w_0 and the concentration of toluene C_T.

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We took pictures 20, 30 and 40 minutes after each increase in toluene concentration in order to assess the time dependency of the swelling process. We did not observe a significant change in the values of δw between 30 and 40 minutes of exposure to the swelling media (see SI?), and we concluded that the former time was long enough to reach practical equilibrium.

As expected, the effect of swelling is different for different initial barrier widths w_0. For the thinnest structure (w_0 = 30 µm), we observed a clear damage of the material, as shown in figure SIYYY. For all the other microstructures, the barrier widths increased with increasing concentration of toluene, as shown in Fig. 2. We also observed that the lateral growth δw is a linear function of the concentration of toluene C_T for all of the studied dimensions, with similar slopes for all of the structures, but with clear outliers for values of w_0 below 70 µm. Three regimes could be distinguished, by comparing the rate of growth with increasing concentration of toluene Δδw defined as:

$$\Delta\delta w = \frac{d\,\delta w}{dC_T} \qquad (2)$$

For channels separated by a barrier which width is shorter than its height (~75 µm) – corresponding to the first two data sets (w_0 = 50 µm and w_0 = 70 µm) – Δδw is considerably larger than for all the other cases. It then reaches a minimum for $w_0 \approx$ 100 µm before increasing slowly until it stabilizes for values of $w_0 \geq$ 570 µm.

This behaviour can be seen more clearly by plotting Δδw as a function of w_0 (see Figure 3). For the thinnest barriers (which widths are shorter than their heights), the expansion of PDMS in the vertical direction caused by swelling can be expected to be larger than that occurring in the horizontal direction. This is likely to cause buckling of the PDMS barriers, which could explain the high response coefficient observed for the smallest structures.

Outside of a chip, and therefore in the absence of structural constraints, PDMS soaked in toluene increases 31% in size.[28] This means that, without constraints, the size variation of a PDMS structure due to swelling should depend directly on its dimensions. In this sense, thin PDMS structures should behave like free PDMS because the strain generated by their expansion is minimal. For larger widths, as w_0 increases, the deformation generates more strain, and the interplay of forces that promote and hinder the swelling induced displacement slowly reaches an equilibrium, corresponding to the plateau we observed for w_0 > 570 µm, and corresponding to a response coefficient Δδw ≈ 1.34 µm/toluene %(V/V). We do not expect Δδw to deviate dramatically from this value for bigger structures. Moreover, a single isolated channel can be conceived as two parallel PDMS walls with a semi-infinite width. For this reason, PDMS swelling should make a channel shrink linearly as the concentration of toluene increases, and have a response coefficient close to *c.a.* 1.34 µm/toluene % (V/V). Nevertheless, it must be considered that PDMS swelling depends on the curing temperature, the curing time, and the amount of curing agent used.[29] Chips fabricated with different procedures might therefore exhibit different response coefficients.

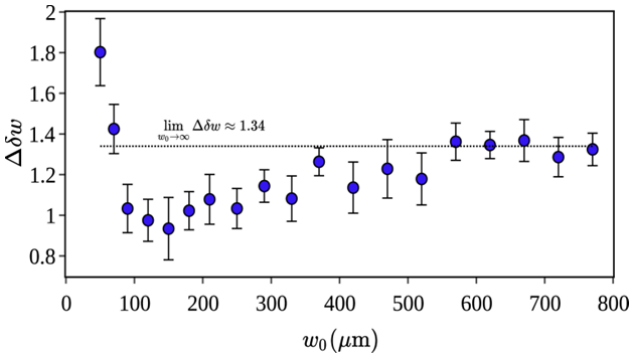

Fig. 3 Swelling response to toluene in mineral oil, Δδw, for PDMS barriers with different initial widths (w_0).

Droplet size change due to PDMS swelling

Once established that the swelling behaviour of model channels could be controlled by the concentration of a modulating agent in a carrier oil, we wanted to apply this concept to the active control of a functional chip. For this purpose, we designed Chip B (see Fig. 4) that consists in a T-junction droplet generator which inlets and outlets were all 50 µm wide, and with a height of 75 µm. We chose this configuration over more complex ones (flow-focusing junctions, Y junctions, … other examples Juan?) because their simple geometry makes it easier to rationalize their behaviour, and because – based on the calibration experiments – we expected the channel dimensions to be modified in a rather homogeneous fashion upon swelling, thus making the analysis of the influence of swelling on the chip performance more straightforward.

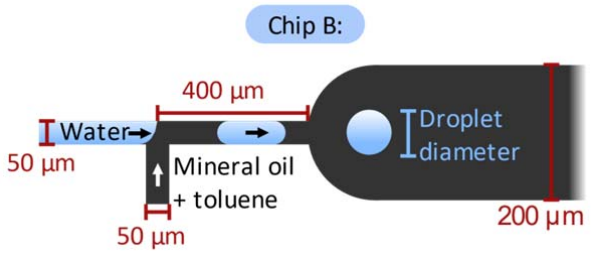

Fig. 4 Design of the T-junction droplet generator used for droplet size modulation.

The T-junction produced droplets by intercepting a straight flow of water laterally with the solvent mixture, as shown in figure 4. There is scarce research about the droplet formation in T-junctions with this configuration, *i.e.* with the continuous phase being inserted from the side channel (as shown in figure 1), which we will refer to as *alternative configuration*. To our knowledge, the only example of generation of droplets using the *alternative configuration* is reported by J. H. Xu and co-workers,[31] nevertheless the nozzle proposed by L. Frenz and co-workers[32] consists, *sensu stricto*, of two T-junctions in the *alternative configuration* as well. We performed experiments in both conventional and alternative configurations with similar results. Nevertheless, in the conventional configuration, irregular swelling prevented us from performing a refined analysis – such as estimating the capillary number – and those results are therefore only included in the SI.

For all of the experiments, we maintained a flow rate of 1.5 mL/h for the continuous phase (mixture of mineral oil and

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toluene) and a flow rate of dispersed phase (water) of 100 µL/h which corresponded to reasonable initial droplet diameters of *ca.* 72 µm, slightly smaller than the channel height, thus ensuring no contact between the droplets and the channel walls.

In a first experiment, in order to assess the required time to reach a stable regime, the toluene content was increased from 0 to 20 % in a single step and pictures were taken every 5 minutes to measure the temporal evolution of the droplet size. After stabilization of the droplet size, the reversibility of the process was assessed by setting the toluene concentration back to 0% in a single step and, again, pictures were taken every 5 minutes to characterize the process.

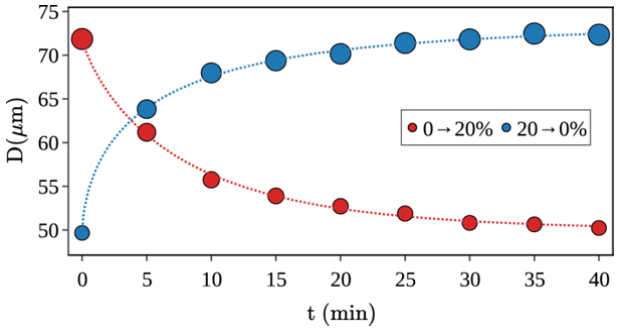

Fig. 5. Reversible change in the droplet size as a function of time upon stepping the concentration of toluene by 20% (V/V). The diameter of the markers is proportional to the droplet diameter for easy comparison. The continuous line corresponds to the best fit to a stretched exponential model.

Upon stepping the toluene content from 0 to 20% in chip B, we observed a slow reduction in the droplet size, from an initial diameter of 72 µm to a diameter of *c.a.* 50 µm after 30 minutes. After this time, no significant further evolution in droplet size was observed (figure 5). The variation of droplet-size *vs.* time does not follow a single exponential decay but instead follows very-well a stretched exponential modal, which points at a complex phenomenon. The fitted saturation value is with a fitted saturation value of 49.9 µm, which corresponds to an error of less than 1 % with respect to the value obtained after 30 minutes, which we therefore used as a reference stabilization time for the rest of the study. A similar behaviour was observed when the toluene content was stepped down from 20 to 0%: after 30 minutes, the droplet diameter returned to *c.a.* 72 µm, demonstrating the reversibility of the process, and no significant evolution was observed beyond that point.

In order to study quantitatively the effect of swelling on the operation of the T-junction droplet generator, we measured the size of the droplets generated with this junction for carrier oils containing a different concentration of toluene, while maintaining the total flow rates constant. To do so, the toluene content was increased stepwise (2% every 30 minutes) from 0% to 42% and pictures were taken after 30 minutes of stabilization.

Upon swelling the chip, the width of the channels reduces gradually and as a consequence the diameter of the droplets is reduced by a factor of 3 between 0 and 42% of toluene content (see Fig. 6). The main factor governing the mechanism of droplet generation in microfluidic junctions is the capillary number of the continuous phase, Ca_c, a

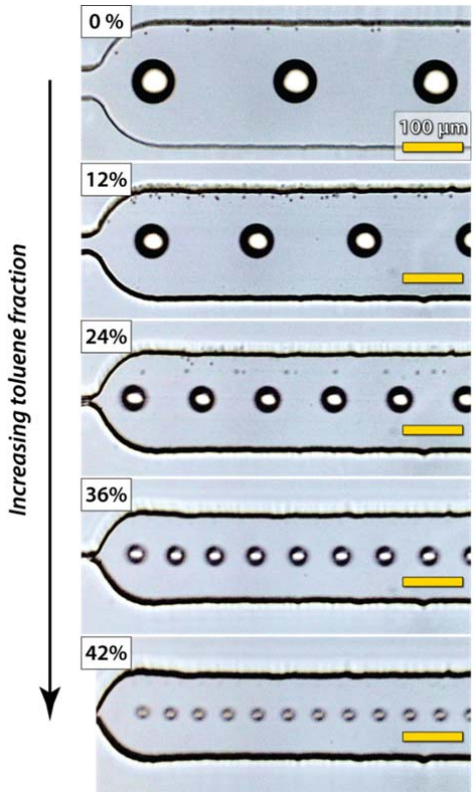

Fig. 6. Optical microscopy images showing the operating T-junction droplet generator for different concentration of toluene in mineral oil after a stabilization time of 30 minutes.

dimensionless number defined as:

$$Ca_c = \frac{\eta_c u_c}{\gamma_c} \qquad (3)$$

where η_c is the dynamic viscosity of the continuous phase in mPa.s, u_c is the linear velocity of the continuous phase in m/s and γ_c is the interfacial surface tension between the two phases in mN/m.

In this experiment, we expected the capillary number of the continuous phase to be low, which would imply that the droplet breakup should be in the squeezing, geometry-controlled regime and we therefore expected the droplet diameter to depend essentially on the dimensions of the channels. If this assumption were wrong, the changes of viscosity of the carrier oil would have an effect on the droplet breakup. It is commonly assumed that in this case the diameter of the droplets should be proportional to the inverse of the capillary number, that is, proportional to the interfacial tension between the two phases and inversely proportional to the dynamic viscosity of the continuous phase. In the present case, mixing toluene with mineral oil causes only a small change in interfacial tension, and a big change in dynamic viscosity (the mineral oil we used has a dynamic viscosity of about 28 mPa.s at room temperature against 0.55 mPa.s for toluene). If the non-geometrical effects were dominating, we should observe an increase in droplet size with increasing

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amount of toluene. Instead, the diameter of the droplets decreases with increasing toluene content, which indicates that we are likely in a squeezing regime.

Under the experimental conditions we used, the dead time should be around 4-5 minutes, and upon changing the composition of the dispersed phase, we would therefore expect to the change of viscosity and surface-tension to affect the system by an abrupt change of droplet size after about 5 minutes. Instead, we observed a gradual change of droplet size over 30-40 minutes which corresponds well to the kinetics of the swelling process.

Altogether, the droplet size was reduced from 72 µm with pure mineral oil to about 23 µm for a continuous phase containing 42% (V/V) of toluene. Beyond this point, the chip is so distorted that the droplet production becomes unstable (see SI). Similar results were obtained using petroleum ether and xylene instead of toluene (see SI).

When the toluene concentration exceeded 32%, the channels appeared to be almost collapsed. We therefore decided to limit further analysis to the generation of droplets for a composition of the continuous phase varying between 0 and 32%. In that range, the droplet diameter varies linearly with the concentration of toluene, with only minor deviations from the linear trend at high concentrations (see Fig. 7).

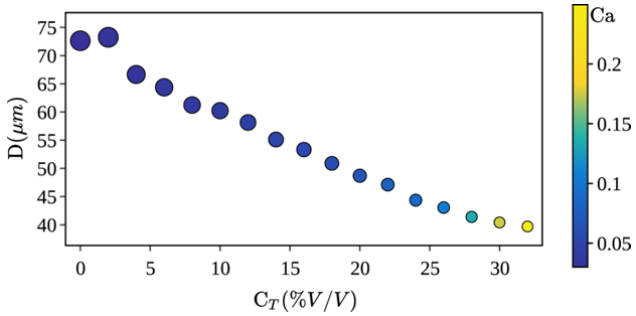

Fig. 7. Evolution of the droplet diameter with the concentration of toluene. The geometry of the chip changes as the PDMS swells, thus changing the size of the droplets. The diameter of the markers is proportional to the droplet diameter for easy comparison. The colour of each marker corresponds to the estimated capillary number of the continuous phase.

The contraction and expansion of the channels are in good agreement with those observed for the model channels with large barrier widths, which allowed us to estimate the capillary number for the different concentrations of toluene. The details of this calculation – which we provide in the SI – is based on the linear geometrical deformation predicted with the response coefficient observed for Chip A, and the predicted changes in viscosity and interfacial tension for the corresponding binary mixtures of toluene and mineral oil.

When the concentration of toluene remains below 25% (V/V) the capillary number is lower than 0.1 which should correspond to a squeezing regime,[REF Zhu] and we observed that the droplet diameter changes linearly with the concentration of toluene in the continuous phase. To rationalize this apparent linear behaviour – which we did not expect – we predicted the droplet diameter by using the model of van Steijn *et al.*[ref] for T-junctions operating in the squeezing regime (see SI for detailed calculations). While our deformed chips are likely to depart significantly from an idealized rectangular cross-section, in our experimental conditions, the model predicts an almost perfect linear trend (see Fig. SXXX) up to a concentration of toluene of 24% (V/V). After this point, the trend deviates from linearity, but the model should not be valid at such concentrations, as the system is most likely transitioning to a dripping regime.

The experimental data also deviates from linearity beyond 25% (V/V) which corresponds to an estimated value of the capillary number of the continuous phase of 0.1. This observation seems to support a change of breakup mechanism at higher toluene concentrations and a more complex interplay of experimental parameters (including viscosity and interfacial tension). Nevertheless at such concentrations, the chip is already highly deformed, and another potential explanation for this deviation from linearity could be found in the fact that its geometry is likely to be significantly different from that of an idealized T-junction consisting in 3 inter-connected channels of rectangular cross-section.

Conclusions

We present a simple, reversible method to modulate the geometry of microfluidic chips through the geometrical changes that arise from the controlled swelling of its PDMS parts. We showed that PDMS swells linearly as the concentration of swelling agent increases. Nevertheless, we also showed that the response coefficient for this process is not independent from the dimensions of the PDMS structure to be deformed (which is likely due to some partitioning mechanism between the carrier fluid and the PDMS structures). For this reason, uneven swelling is to be expected for chip designs containing internal microstructures with critical dimensions below 600 µm. We also demonstrate that, while conventional wisdom considers PDMS swelling as an issue, taking into account the expected magnitude of swelling while designing a microfluidic chip can lead to practical applications. In particular we exploited the controlled swelling of PDMS to modulate the size of droplets generated in a T-junction operating in the squeezing regime. We expect that PDMS swelling could be used to modulate droplet generation in other configurations as well, but we showed that in the configuration we used here, the change in droplet diameter can be directly related with the geometrical changes of the chip and not with the changes in physical properties of the continuous phase. In our hand, this method afforded over 3000% change in droplet volume, and since our methodology should be compatible with other droplet modulation and generation methods, we expect that further development and combination with active techniques could extend significantly the range of droplet sizes that can be generated with a single chip design. It also presents unique advantages: i) it does not require the use of surfactants or changes of temperature (that could affect the reactions occurring inside the droplets in a materials synthesis), ii) the infrastructure requirements are minimal, and iii) there is no clear limit to which degree a PDMS channel could be modified using this technique.

Finally, we hope this study can motivate the scientific community to consider PDMS swelling as a potentially useful phenomenon. As it is the case with many complex behaviours, when analysed deeper, PDMS swelling can become a useful tool to control and modulate the geometry of microfluidic chips, which applications are still to be unveiled.

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