Thesis:
Designing droplet microfluidic systems: from chemistry of surfaces, through rheological properties of fluids to geometries of the channels
submitted by PhD candidate:
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1. Objective
The thesis focuses on the methods to control the multiphase flow at the microscale. As the flow in microfluidic devices occurs at small length scales (usually sub-millimetres), surface stresses – including the interfacial tension effects, the shear stresses and elastic effects associated with deformations of the fluid – dominate over the inertial forces, which can typically be completely neglected. As a consequence the wettability of the walls of the channels, and of the interfacial tension between liquids are of outmost importance. In case of oils and polymer solutions the value of viscosity coefficient depends on shear stress what becomes crucial for the dynamics of microfluidic systems. These effects are profoundly discussed in the thesis, and a possibility to take advantage of non-Newtonian fluids behaviour to effectively modulate the flow has been demonstrated.

The aim of this thesis can be extracted from the introduction as the attempt to demonstrate possibility of controlling dynamics of multiphase microfluidic systems by applying:

i) modification of the surface chemistry of the channels wall,

ii) use of rheological effects of liquids used,

iii) modifying geometry of the microchannels.

In the thesis the candidate presents (i) a new method of modification of the surface chemistry of microchannels fabricated in polycarbonate and the use of this
modification to stabilize flow and generation of oil-in-water emulsions, (ii) performed a study of the effect of viscoelasticity of the continuous liquid on the process of formation of droplets in a microfluidic flow-focusing system, and (iii) developed a set of innovative geometric modules for passive and precise controlling of droplets merging and trapping in microfluidic systems.

Thus the present study is an important step in the correct direction. A new approach of controlling wettability of the microchannel surface is demonstrated. It offers original methodology of producing well defined, mono-dispersed droplets within the channel, important issued for those using microfluidic devices for controllable chemical and biological reactions. The results obtained indicate that there are good prospects for the continued advancement of designing microfluidic devices designated to complex experiments involving multicomponent fluid flows.

The objectives of the thesis were met.

2. Originality and Results

Stable formation of droplets can be obtained only if the continuous phase completely wets the walls of the channels and the to-be-dispersed phase does not wet them even partially. Even a small partial wetting may cause disordered droplets patterns and difficulties with controlling droplets formation. It is well known that partial wetting can be overcome by adding a small amount of surfactants to one of the phases. Surfactants lower the interfacial tension between the walls of the channels and the droplet phase and can avoid partial wetting. On the other hand, use of surfactants is undesirable in systems where droplets need to be merged. Moreover, they can undesirably modify chemical and physical properties of both phases. For generation of double or multiple emulsions one meets additional problems. In particular, in planar designs it is necessary for the devices to comprise both hydrophilic and hydrophobic sections of the channels. Usually part of the device's surface is rendered hydrophilic and simultaneously the other part is rendered hydrophobic by chemical modification, where the two treatment protocols must be compatible with each other (i.e. modification agents shouldn't react with
each other, temperature and exposure times of both methods should be the same or similar).

In the thesis proposed substrate material for fabrication of the microdevices is polycarbonate and up to date a stable formation of oil-in-water emulsion in such substrate has not been reported. The candidate developed original modification technique for channel walls that renders the surface of the polycarbonate hydrophilic and allows the formation of oil-in-water (O/W) emulsion. The hydrophilic character appears stable against polar and non-polar solvents over weeks or months. Hence, the formation of O/W emulsion became possible in the absence of surfactants. Additionally, with the combination of another (hydrophobic) modification technique pattern of the microfluidic channels formation of W/O/W and/or O/W/O double emulsion is demonstrated.

The results of the surface modification technique that uses polyelectrolyte multilayers (PEMs) and enables the use of the aqueous liquids as the continuous phase for formation of organic droplets without the use of surfactants was published in the journal Lab On A Chip (2011) with the candidate as the first author. Another hydrophilic modification technique is proposed, that uses tin-chloride and allows the formation of O/W emulsion in microfluidic channels, and enables formation of W/O/W double emulsion. The result of this study was published in the journal Microfluidics & Nanofluidics (2013).

In his experimental comparative study on the use of the viscoelastic liquid as a continuous phase to produce Newtonian droplets the candidate found similar regimes of operation in both viscoelastic flow-focusing system and in Newtonian flow-focusing system used as the reference. It is rather informal study presenting discrepancies between non-Newtonian and Newtonian fluids, mainly observed as difficulty to maintain stable droplet generation for non-Newtonian liquids.

In the third part of the thesis the candidate describes attempts to use of bypass channels/areas (also with the combination of obstacles and/or contractions) for droplets handling or trapping. It is demonstrated that bypassing the T-junction succeeded to generate droplets of which length (volume) is determined by the geometry (bypassed section of the outlet channel) and is mostly independent on the flow rates of both phases. Using the bypass in straight channels the candidate
succeeded to lock droplets at position, and found that by using an obstacle to stop
the droplet it can be used for modifying drops volume (cutting them into sizes
determined by the length of the bypassed channel). The use of a contraction shorter
than the bypassed area permits to lock and release droplets in a well controllable
way. According to this principle the candidate fabricated the original complex
system using such modules for serial dilution of droplets in a controlled
manner.

The presented in the thesis work is original and its scientific findings are worth
publication, both in terms of the new methods developed, as well as in terms of the
possible applications given. As a matter of fact the main objectives of the thesis are
subjects of the two candidate's journal papers already published.

3. Presentation

The text of the thesis consists of almost 180 pages. The main part of the thesis is
composed to three major parts. Comprehensive chapters with conclusion,
appendices and a list of 255 references follow it. Each part of the thesis is divided
into chapters and includes independent introductions and conclusions. The overall
construction of the thesis is typical for textbooks. The effect of this is that sometimes
it is difficult to distinguish original contributions from the textbook information given.

The text starts with a list of abbreviations. It is useful approach, however another list
usually called Nomenclature is missing. It would be useful for readers, specifically in
places where dimensional variables are given. In addition, silicon oil used as working
liquid and polydimethyl siloxane used for building channels are commonly
abbreviated in several places as PDMS, what is confusing.

First part of the thesis considers surface treatment. It includes a well written
introduction to the problem, the basic idea behind the problem formulation, a
discussion of existing approaches, the description of the free surface formulation. It is
however unclear how surface tension is quantified, in some places we find mJ/m²
units, in other classical dyn/cm. There is number of results presented in form of
graphs and illustrations. However, it is not always made clear which of them comes
from them is original contribution of the candidate, which are reproduced from other resources.

The second part of the thesis dealing with rheology reminds part of the textbook. Most of the obvious information on non-Newtonian liquids is repeated and demonstrated using data from the literature. Presented flow-focussing experiments with viscoelastic liquid seem to have preliminary character, their interpretation is rather confusing. General conclusion coming out states that flow focussing with viscoelastic liquids is unstable and leads to generation of satellite droplets.

The last two chapters of the thesis demonstrate original idea of bypassing flow in order to control behaviour of droplets transported in micro channels. This part is clearly done with a vast number of drawing exemplifying the leading idea of the chapter.

The thesis is prepared in English. Generally style of writing is clear and free of errors. There are only few misprints and spelling errors, which could be easy tracked using standard spell-checking program. Hopefully, the text will be verified in future publications.

The overall opinion on the thesis form and organization is positive. Taking into account huge material presented and diversity of problems touched, obviously the candidate had difficulties in adopting a uniform style to his work.

4. Methods

This is purely experimental work. The candidate investigated experimentally large number of cases, made exhaustive parametric studies to evaluate effects of surface modification, liquids rheological properties or channel geometry modification. In fact most of the studies concerning microfluidic system are based on experimental data. However, in the thesis such approach results in some places with number of data difficult to interpret (e.g. confusing Fig. 7.4). Specifically in Chapter 6 dealing with non-Newtonian liquids, despite of exhaustive theoretical introduction, there are no attempts to evaluate expected shear stresses and to interpret expected changes of the flow structure. Simplicity of the geometry could allow to perform simple analytical
or numerical evaluations of the flow structure and compare it with obtain experimental data. Similarly in the next chapters, which deal with proposed modifications of the channel geometry by using bypasses and obstacles, one may miss any numerical/analytical analysis allowing for interpreting observed flow behaviour. Clearly, having set of numerical results could help to optimize shape and position of the channel modification. By the way, the statement saying that turbulence may occur for viscoelastic liquids at the outlet (chapter 7.8) cannot be truth. First of all it is not possible to obtain turbulent flow in microfluidic systems, and even if so, it is well known that viscoelastic liquids rather damp than amplify turbulent fluctuations.

5. Conclusion

My overall opinion on the thesis is good. The candidate was able to formulate the physical basis for the problem of controlled generation of microdroplets, to discuss tools used to chemically modify the micro channel surfaces, verify consistency of the approaches, and to develop and demonstrate use of original procedure based on multilayer surface treatment. He also developed original microfluidic system for droplets trapping and modifying/mixing. Both achievements have great value for further applications of microfluidic systems.

Taking into account that the candidate has solved original scientific problems and demonstrated his good knowledge of the experimental methods used in the surface chemistry I propose to let him defend his thesis at the public presentation.

Rozprawa spełnia wymagania określone w art. 13, ustawy z dnia 14 marca 2003r o stopniach i tytuły naukowy (Dz. U. Nr. 65/2003 poz. 595 z późniejszymi zmianami).

- Prof. dr hab. Tomasz Kowalewski -

Warszawa, 25/03/2013.