CRITICAL REVIEW OF THE DOCTORATE DISSERTATION

Entitled: „Designing droplet microfluidic systems: from chemistry of surfaces, through rheological properties of fluids to geometries of the channels”

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Introduction

The beginning of the age of modern human engineering can be characterised by constructing bigger and bigger monuments of technology. The most significant designs appeared at the turn of the century. As examples we can point out the Eiffel Tower (erected 1889) and passenger liner Titanic (launched 1912). After that time engineers started to work on a bit smaller systems, what resulted in miniaturisation of commonly used devices, in the development of small mechanical systems, micro – fluidic systems, semiconductor electronics, microscopy, micro analytical devices and finally nanotechnology. This interest in miniaturised systems came from the fascination of living organism, where in cells, micro fluidics, micromechanics and nanorobots are employed widely. Miniaturisation of technologies not only makes our devices smaller, it opens the door to completely new physical and chemical phenomena to act. Presented thesis falls nicely into this field of engineer’s activity.

The Dissertation

Microfluidics is a new branch of engineering which deals with the production and manipulation of small, micro litre volumes of fluids, which are usually constrained by small, typically sub-millimetre sized channels. Ladislav Derzsi in his dissertation focuses mostly on two phase systems composed of two immiscible liquids. He describe devices designed to
generate and to manipulate droplet of one liquid in the continuous phase flow of the other liquid, usually described systems are composed of organic liquid and water. Due to that fact, surface properties of the channels where droplets are formed and manipulated, are very important.

Dissertation started with a broad introduction to microfluidics. Author described the principles of microfluidics, methods of production of fluidic microchips, and basic "units" of microfluidic systems. Principles of droplet formation from two immiscible liquids in T-junction, and in flow focusing and co-flowing systems were also described. Then methods of droplet manipulation in microluidic systems, droplet fusion and fission, droplet separation and sorting were well described and depicted with various illustration and literature positions.

Second part of the dissertation contains analysis of inner surface properties of channels and its influence on liquid behaviour in microfluidic systems. It should be stressed out that surface properties are crucial for proper droplet formation and control. For proper operation of droplet based microfluidic device it is absolutely crucial that the droplet phase do not wet the walls even partially while the continuous phase wets them perfectly. Even partial wetting of the walls can completely disrupt droplet formation or manipulation process. Because of the importance of the surface properties this part also contains description of chemical and physical modifications of the channels inner surface. Two methods which were applied by the author are explained in details, application of polyelectrolytes starting from the first layer formed by polyallilamine (PAH), and application of tin (2) chloride.

In the next part Author describes the influence of fluids theology on the behaviour of microfluidic devices. Few types of non Newtonian fluids and their behaviour in micro channels are presented. This part also contains description of flow focusing and droplet formation from viscoelastic fluids.

The last part presents geometry of various microfluidic subunits, problems associated with their shape and geometry. It also shows fabrication techniques of various shapes from few typical materials. Basic principles of microfluidic systems design are also described.

At the end dissertation contains appendixes with detailed description of surface treatment techniques and measurement protocols.

Critical Remarks

Dissertation is well written, with interest and passion, the subject is very well presented and interesting as well. Unfortunately the structure of the whole dissertation is a bit chaotic. The classical structure of scientific publication is missing or is not clearly introduced. There is no proposition of scientific thesis at the beginning of the dissertation, which can be then
proved. This is a typical error of "project report writers", since philosophy and scientific discussions started to extinct at universities this omission became a common mistake of contemporary doctorate in applied sciences. Unfortunately the rest of the chapters are also not well arranged. Classical structure of any scientific publication, including doctorate, should consist of introduction, description of materials and methods, results and discussion / conclusions. This structure is not clearly introduced and sometimes it is difficult to find out what was done by the author and what was a part of someone else work (if it was). Missing "materials and methods" brings a lot of problems when someone wants to repeat experiments performed by the Author, some chemicals are not described, there is no type and source of applied substances, also polymers applied to make microfluidic devices are not properly described. Other missing element is a lack of measurement error analysis of a large part of presented graphs. Among other critical remarks I have to mention some minor mistakes in literature citation numbering and misspellings, however I have to say that dissertation was prepared in a language foreign for the Author and the number of linguistic errors is rather small.

The part describing chemical and physical methods of surface modification, both introductory and the work done by Ladislav Derzsi contains few errors. In the introductory part Author present a hypothetical reaction between polyallylamine and polycarbonate. The structural presentation of polyallylamine is wrong, there is one carbon missing between amine group and a polymer backbone, allylamine contains 3 carbons, not 2. This mistake is present in all drawings dealing with polyallylamine structure. Author claims that the chemical bonding between polyallylamine and polycarbonate can be observed. This conclusion is supported by the literature and by his own experiments. Since polycarbonates are chemically inert, I think that observed bonding are of physical nature and are based on the hydrogen bonds formation only. Cited publications deals with different chemical reagents and completely different reaction conditions (150 °C, hours; in the case of this work: 10 minutes ambient temperature). In my opinion data and experiments presented in the dissertation does not prove that the covalent bonding between polyallylamine and polycarbonate are obtained. It would be enough to perform FTIR ATR analysis to check this, water contact angle analysis is not enough. Actually, reviewed dissertation contains proves that only hydrogen bonds are present. On the page 52, it is said that washing with a weak HCl solution can bring water contact angle of the polyallylamine treated surface back to the same value as untreated PC surface, also long exposition to ambient air (CO2, page 49) can make polyallilamine layer “removable”. In acidic conditions amine is ionised (protonated) and strongly hydrated what breaks hydrogen bonds. Otherwise protonated amine groups present at the coated surface will be much more
hydrophilic then non-ionised. However the lack of covalent bonding does not diminish overall quality of the performed experimental work. Another method of PC treatment with Tin (2) chloride is also not finished. Author claims that Tin Chloride works as catalyst of polycarbonate hydrolysis, but on the other hand the contact angle of treated surface is correlated with the concentration of tin atoms at the surface. To prove the catalyst properties of tin, reaction products should be detected and hydrolyzed/altered surface of PC should maintain its properties also after the removal of catalyst.

Final Remarks

Doctorate dissertation “Designing droplet microfluidic systems: from chemistry of surfaces, through rheological properties of fluids to geometries of the channels” prepared by Ladislav Derzsi is an original scientific work. The Author of this work proved to be an independent researcher able to plan, conduct and describe the results of scientific research. The range of presented experimental research and theoretical analysis is wide, and parts of the results have already been published by the Author of the dissertation. I think that obtained results are scientifically sound. I conclude that the demands of Polish legal act about academic degrees from 14 March 2003 (with later amendments) are completely fulfilled. Hereby I lodge a statement that Ladislav Derzsi should be admitted to the next steps of the doctorate degree procedure.

Tomasz Ciach Ph.D.