

APPLICATION OF FERROFLUID AS A VALVE/PUMP FOR POLYCARBONATE MICROFLUIDIC DEVICES

NSF Summer Undergraduate Fellowship in Sensor Technologies 2006

Helen Schwerdt (Biomedical Engineering) - Johns Hopkins University

Advisors: Professor Haim H. Bau, Jason Thompson

ABSTRACT

Integrated pumps and valves make up an essential part of most microfluidic devices and produce increased control in the device. Some existing micro-pumps and valves utilized in microfluidics involve electrical, pneumatic, and thermal actuation. However, electrical micro-pumps and valves generally entail a complicated and expensive fabrication process, and are limited to samples free of any ions or charges. We attempt to create a phase-changing pump/valve out of a mixture of ferrofluid and paraffin wax, called “ferro-wax”, that is operated by magnetic force. We utilize oil based ferrofluid solution, which is made up of magnetic iron nanoparticles and surfactant. Ferrofluid may be used as immiscible slugs that are able to separate and pump water based samples in a polycarbonate (PC) channel modified to exhibit hydrophilic properties, without leaving noticeable film. We treat different polycarbonate samples using oxygen and argon plasma, spin-on-glass (SOG), and polyvinylpyrrolidone (PVP) to find the optimal procedure to produce low contact angles with water, while maintaining high surface energy and resistance to heat. Although most of our experiments involved using ferrofluid alone, melting the ferro-wax allows it to become a fluidic pump that can be easily manipulated with an external magnet. This same procedure allows the ferro-wax to operate as a valve, by directing the fluid across a branching side channel. We work on finding the most effective ratio of ferrofluid to wax, what properties the substrate require for this pump/valve to function properly, and how to create such a microfluidic device that integrates these ferrofluid based pumps/valves.

TABLE OF CONTENTS

1. INTRODUCTION	3-4
2. BACKGROUND AND PRELIMINARY PROCEDURE	4-7
3. SURFACE PROPERTIES OF CHANNEL SUBSTRATE	7-14
3.1 Observations	7-8
3.2 Surface Treatment	8
3.3 Oxygen Plasma	9-10
3.4 Argon Plasma	10
3.5 PVP	11-13
3.6 Spin-on Glass	13-14
4. FUTURE APPLICATIONS OF FERROFLUID VALVE AND PUMP	14-16
4.1 Ferro-wax Valve	14
4.2 Ferrofluid Pump	15-16
5. RESULTS AND DISCUSSION	16
6. RECOMMENDATIONS	16-17
7. ACKNOWLEDGEMENTS	17
8. REFERENCES	17

1. INTRODUCTION

Microfluidics incorporates the study and application of precise control and manipulation of micro to nano liter volumes of fluid. Common materials that form the basis of microfluidic chips include silicon, polymers (PDMS, PMMA, PC), and glass. Handling liquids at a micro level differs greatly from a macro scale in that factors such as surface tension, energy, and fluidic resistance start to dictate the behavior of the fluid. Additionally, due to a low Reynold's number,

$$\text{Re} = \frac{v_s L}{\nu},$$

where v_s denotes fluid velocity, L is the characteristic length of the channel, and ν is kinematic fluid viscosity defined as

$$\nu = \frac{\mu}{\rho},$$

where μ is the dynamic viscosity, and ρ is the fluid density, fluid flow remains laminar. Microfluidic chip applications include detection within a solution, biological assay operations (such as protein or DNA analysis), and Lab-on-a-Chip (LOC) systems.

Most microfluidic chips integrate pumps and valves in order to produce increased control of the device. Common microfluidic control elements utilize electromechanical or electrokinetic effects such as peristaltic micro-pumps, which are operated by piezoelectric disks [1], or an electromagnetic actuator for a microvalve [2]. However, such devices generally entail a complicated fabrication process and are uneconomical, and therefore a pump/valve that can be driven simply by a magnet is more favorable. Electrically actuated pump/valves limit the device's functionality by disallowing electrically sensitive samples from being tested; such as solutions containing a noticeable charge or pH. Another example of a micro-pump/valve is a hydrogel valve that closes as liquid approaches it because the liquid causes the hydrogel to swell and shut the chamber. The valve opens again when heated [3]. An example of a liquid phase change valve is one that closes as a liquid is cooled below its freezing temperature and opens when heated [4]. In our experiments we chose polycarbonate (PC) because it is an inexpensive, transparent, biocompatible material that is easily machined into chips. Additionally, surface treatments of PC, an essential part of our design, necessitate less complicated procedures than those of other polymers.

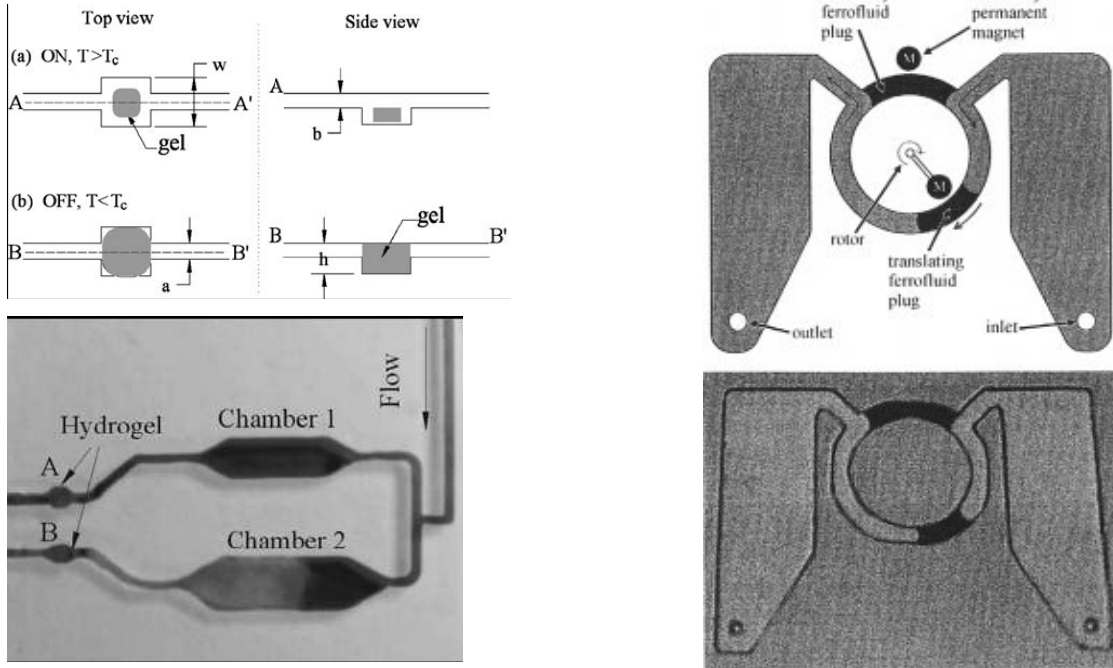


Figure 1. Hydrogel valves in microfluidic channels (left) [3]. **Figure 2.** Ferrofluid valve controlled by rotating magnet and stationary magnet (right) [5].

2. BACKGROUND AND PRELIMINARY PROCEDURE

Part of the ferro-wax valve/pump we employ consists of an oil based ferrofluid, a magnetic fluid consisting of nanoparticles of 5% magnetic solid mixed with a 10% surfactant and 85% carrier, manufactured by FerroTec Corp (Lot#F021606A). The nanoparticles of ferrofluid behave like molecules in a paramagnetic gas, where in the absence of a magnetic field, the particles are randomly oriented [6]. When a magnetic field is applied, the tendency for dipole moments to align with field lines is somewhat overcome by thermal agitation. Magnetization of ferrofluid can be described by the following equations

$$\frac{M}{\Phi M_d} = \coth \alpha - \frac{1}{\alpha} \equiv L(\alpha),$$

$$\alpha = \frac{\pi \mu_0 M_d H d^3}{6 kT},$$

where Φ is the volume fraction of magnetic solids ($\pi d^3/6$), M is the magnetization of

ferrofluid (A m^{-1}), M_d is the domain magnetization of the particles (A m^{-1}), $L(\alpha)$ is the Langevin function, d is the particle diameter ($\sim 10 \cdot 10^{-9} \text{ m}$), H is the applied magnetic field (A m^{-1}), k is Boltzmann's constant ($1.38 \cdot 10^{-23} \text{ N m K}^{-1}$), T is the absolute temperature (degrees Kelvin), and μ_0 is the permeability of free space ($4\pi \cdot 10^{-7} \text{ H m}^{-1}$). The ferrofluid exhibits saturation magnetization at $L(\alpha) = 1$. There are two mechanisms by which ferrofluid magnetization relaxes after modification of the applied field. Relaxation can take place by particle rotation in the liquid, which is represented by a Brownian rotational diffusion time τ_B . *Extrinsic superparamagnetism*, where the Brownian mechanism dominates, occurs when

$$\frac{\tau_N}{\tau_B} \gg 1$$

It may also occur by rotation of the magnetic moment within the particle, which is known as the Néel mechanism, with a time constant, τ_N . *Intrinsic superparamagnetism*, where the Néel mechanism dominates, occurs when

$$\frac{\tau_N}{\tau_B} \ll 1$$

Microfluidic devices have employed the use of ferrofluid in the past for various applications. Some noteworthy examples include using ferrofluid to mix different solutions as well as to guide proteins or other molecules. Oil based ferrofluid is an attractive substance, as it is cheap, easily manipulated, immiscible with aqueous solutions, and conforms to the shape of the channel geometry.

The other portion of our valve/pump is made up of ordinary paraffin wax (Acros Organics, Lot#A017441501), such as may be found in birthday candles. This wax helps resolve any leakage difficulties ferrofluid has by itself. At room temperature the wax will remain solid and operate as an exemplary seal in most channels, and when heated above 50°C its melted form combined with ferrofluid can be easily repositioned along a channel with an external magnet.



Ferrofluid by itself may also function as a pump and ideally we would like to make a train of fluids separated by immiscible slugs, propagated by one magnet. However, with this mechanism leakage issues need to be considered.

Figure 3. Ferrofluid in vial, with square magnet on side.

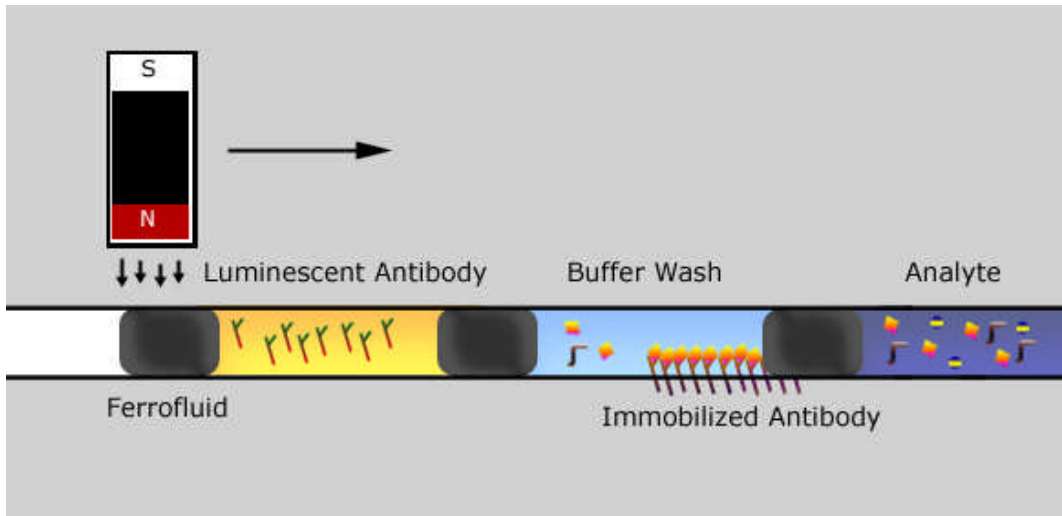


Figure 4. Fluid train prototype design.

To create ferro-wax we heated paraffin wax pellets on a Thermolyne hotplate at 50°C to 80°C. When the pellets had melted, we added ferrofluid and stirred the solution. We then let the ferro-wax cool and examined the stiffness of the solid for different ratios of ferrofluid and wax.

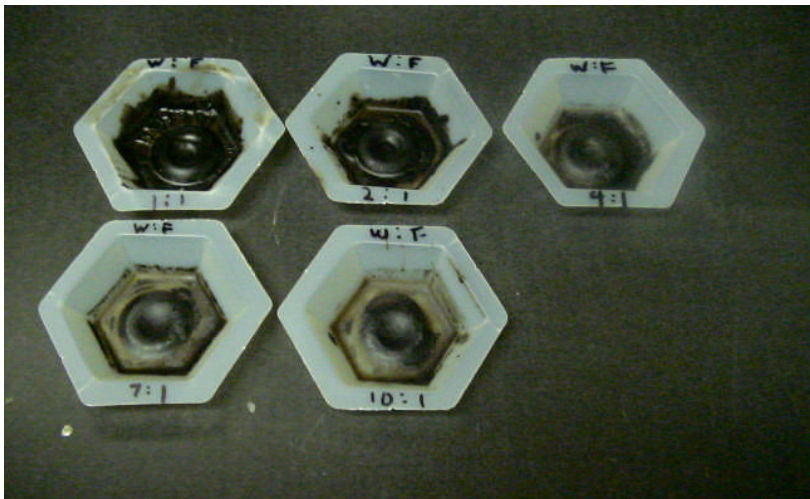


Figure 5. Ferrowax (wax : ferrofluid) solidified to shape of an external ring magnet at different mix ratios.

We tested ferrofluid and ferro-wax separately in glass capillaries to observe their pumping capability at the macro scale. The glass capillaries had square cross sections of approximately 2.2 mm on a side. Water was placed in between ferrofluid slugs and dyed liquids were used to note any leakage. Samples were inserted into the tube using a syringe and a magnet was placed directly above the surface of the channel. Advancing the slugs at slow velocities showed clean pumping action with no observable film or leakage. However, at faster speeds, we detected traces of film and some leakage.

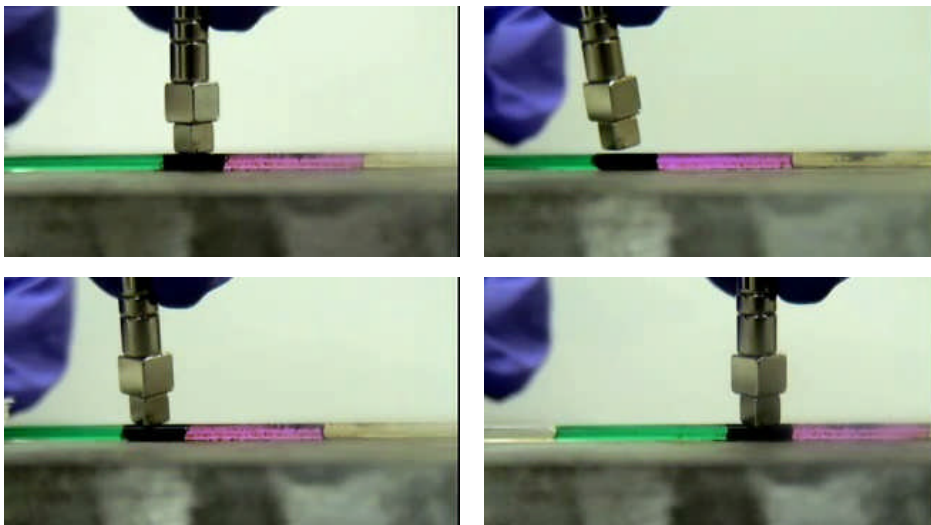


Figure 6. Ferro-wax was inserted between two dyed aqueous solutions in a square shaped glass capillary and controlled by a magnet as shown above. The device was placed on top of a heating plate at 85°C.

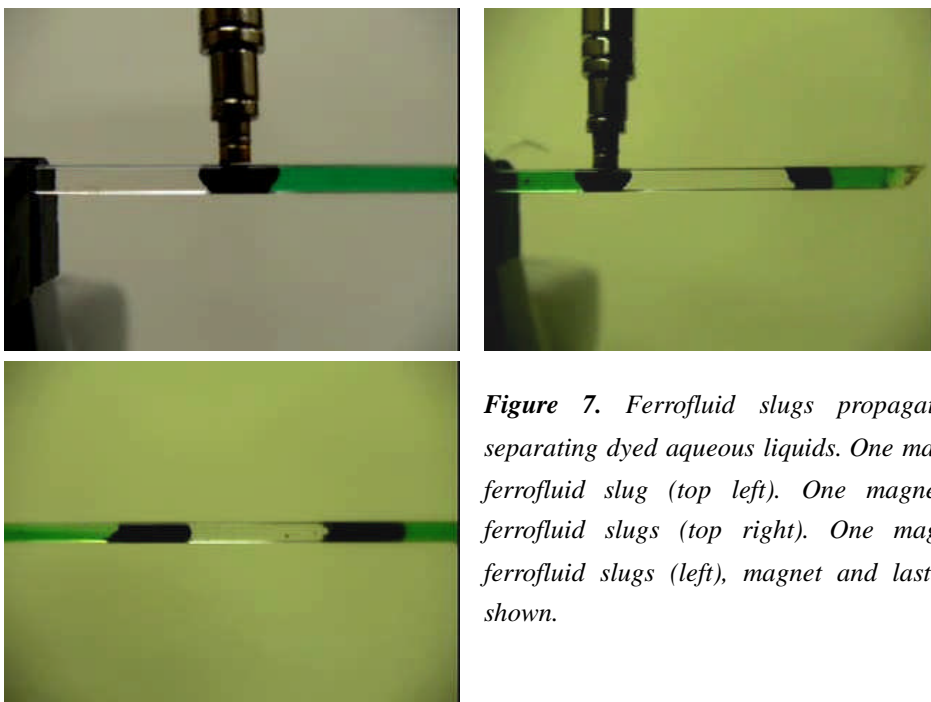


Figure 7. Ferrofluid slugs propagated by a magnet, separating dyed aqueous liquids. One magnet controlling one ferrofluid slug (top left). One magnet propagating two ferrofluid slugs (top right). One magnet propagating 3 ferrofluid slugs (left), magnet and last ferrofluid slug not shown.

3. SURFACE PROPERTIES OF CHANNEL SUBSTRATE

3.1 Observations

We used contact angle estimates of water droplets as a measurement of hydrophilicity/hydrophobicity on the surfaces of glass, polycarbonate without any

treatment, and polycarbonate with various surface modifications. Polycarbonate and glass retain contact angles of about 80° , and 35° respectively [7]. Higher contact angles correspond to more hydrophobic materials whereas hydrophilic surfaces express low contact angles. Ferrofluid slugs in hydrophilic channels, such as glass, left no observable film during slow movement. However, in hydrophobic substrates, such as polycarbonate, apparent film deposition occurred.

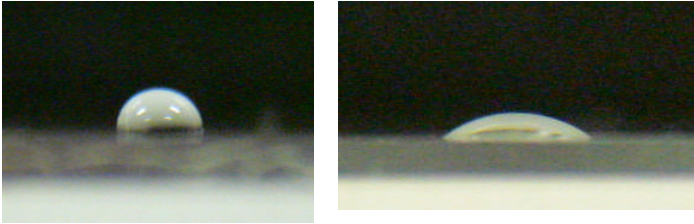


Figure 8. Contact angle differences can be observed on PC (left) vs glass surfaces (right).

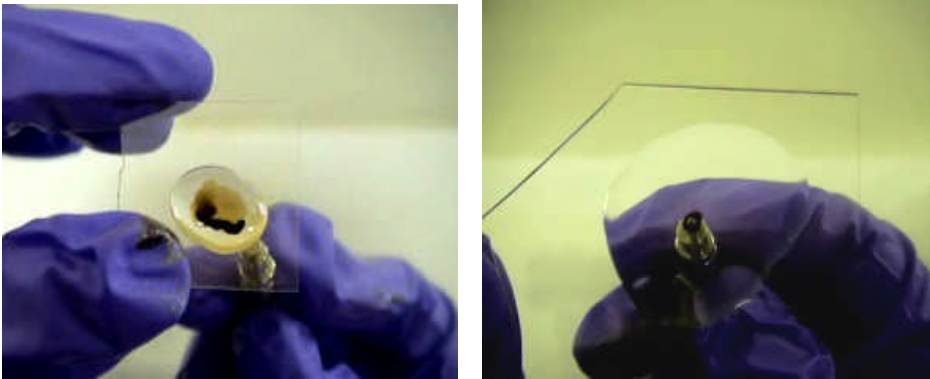


Figure 9. Because of differences in wetting properties of PC vs glass, ferrofluid floats above the surface on glass, creating a thin film of water underneath, and preventing a film from depositing (right). However, this is not the case for PC (left).

3.2 Surface Treatment

To make the channels fabricated in polycarbonate hydrophilic, such that ferrofluid slugs matched or surpassed the pumping action in glass tubes, we tested treatments by oxygen and argon plasma, PVP (polyvinylpyrrolidone), and SOG (spin-on-glass). Some issues arising with plasma treatment include complications with bonding. Bonding is a process in which a PC chip containing milled channels and another flat piece of PC are pressed together and heated to generate an enclosed microfluidic chip. Presently, our procedure for PC bonding involves the use of a bonding press in which chips must be heated to 145°C . However, plasma treatments are reversed at temperatures higher than approximately 50°C [8]. Therefore, some research and experiments were conducted to bond PC chips at low temperatures.

3.3 Oxygen Plasma

Oxygen plasma activation can yield surface contact angle measurements of 10° or less on PC [8]. However, difficulties arise from its limited stability towards washing, heating, and time extent of maintaining these low contact angles. Basic plasma treatment settings include power (watts), gas flow rate (sccm), and duration of treatment. At the most intense settings, corresponding to the highest W/F (power : flow rate) ratio, modified PC could be stored up to six months in aluminum foil before contact angles approached 20° [8].

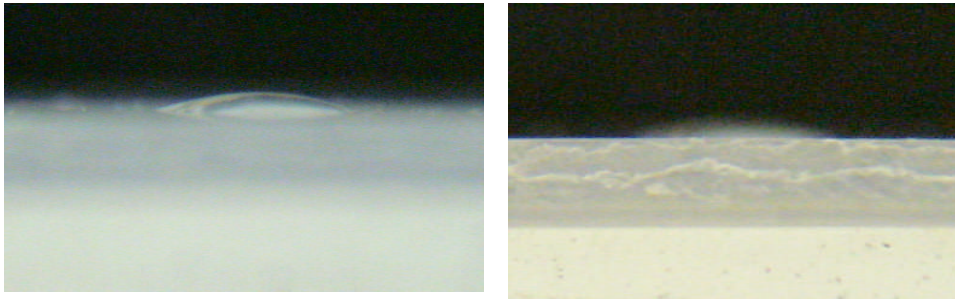


Figure 10. Water droplets on oxygen plasma treated PC surface (50 W, 10 minutes, 3 sccm).

We tested our PC chips at various settings and our results agreed with earlier studies. Higher W/F ratios resulted in the lowest contact angles and greatest resistance to washing with ethanol. Our initial best two treatment settings were found to be 270 W, 3 sccm, for 3 minutes ($W/F = 90$), and 406 W, 3 sccm, for 3 minutes ($W/F = 133$). However, the latter treatment slightly melted the chip. In later PC channel treatments, to test our ferrofluid pump, we would use power in the range of 300-350 W for 3-5 minutes at the same flow rate. We based our conclusions on how hydrophilic a particular treatment was by visually estimating contact angles with the aid of a protractor. However, using too much power for extended periods warped the shape of the PC because higher power introduces more heat that can begin to melt the chip.

Finally we applied this treatment to a PC chip with a channel about $800 \times 800 \mu\text{m}$ and fixed it to another piece of treated PC using a vice (to avoid thermally bonding the chip and maintain previous plasma treatments) to observe ferrofluid and dyed water in the modified channel. Ferrofluid surrounded by aqueous solutions left no noticeable film or leakage when manipulated carefully and slowly by an external magnet. Successful pumping action was also observed.

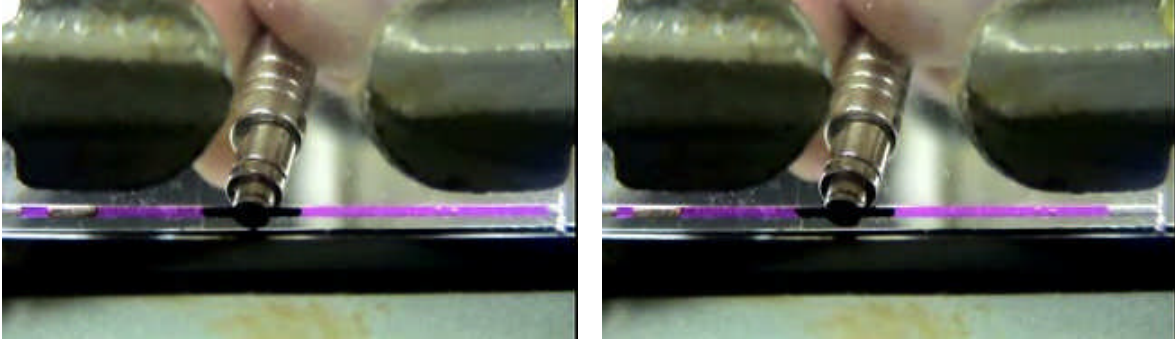


Figure 11. Oxygen plasma treated PC channels, bonded temporarily by vice. Ferrofluid guided by external magnet, surrounded by aqueous dyed liquid.

3.4 Argon Plasma

Argon plasma activates the surface of PC with physics similar to oxygen, and was performed in the same machine with comparable settings. However, Ar plasma does not activate the surface as well as oxygen and therefore film deposition was an issue. Water contact angles on argon plasma treated PC have been measured to be around 47° [9].

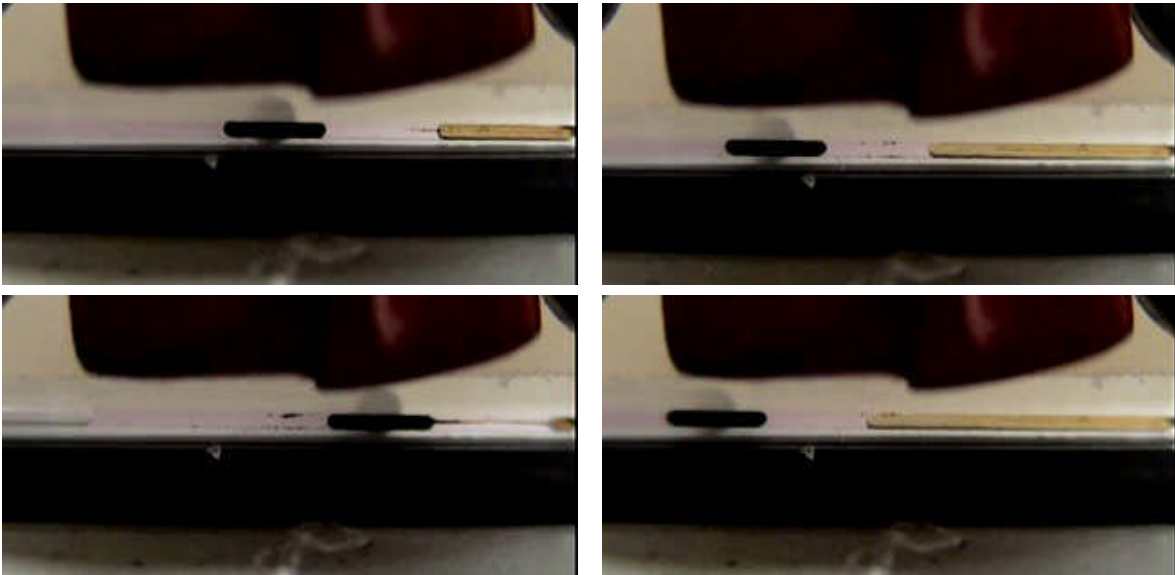


Figure 12. Argon plasma treated PC channels, temporarily bonded by a vice. Ferrofluid deposited some film, especially when moved at faster speeds.

Argon and oxygen plasma together have been used to successfully bond silicon to PC and is known to increase adhesion properties on the surface of PC [10]. Argon by itself has been shown to improve adhesion of PC to SiO_2 [11]. However, both of these methods were ineffective in PC-to-PC bonding in our experiments.

3.5 PVP

PVP (polyvinylpyrrolidone) is a polymer material used in many biomedical applications because of its biocompatibility within the human body [9]. It is used in toothpaste and can even be eaten in some cases. A powder form of PVP (Fluka K90, EC No. 2018004) was combined with water to form a homogeneous solution (1%, w/v). This solution can be used to further enhance the hydrophilic properties of a surface. Without previously activating PC, the PVP solution will not adhere to the surface because of its hydrophobicity. Therefore, in order to obtain a wetting surface, argon plasma (50 W, 5-10 minutes) was used to activate the surface, and afterwards, the chips were dipped in PVP solution a few times. Spinning the chips guaranteed a thin layer through the channel and on the surface. To dry and let the PVP solidify on the surface, the chips were heated at 50°C for approximately one hour.

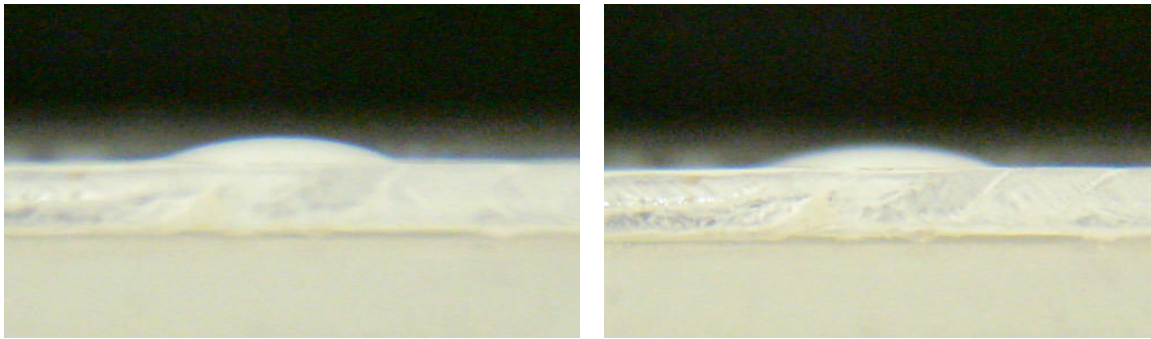


Figure 13. Water droplets on PVP coated PC surface.

We observed the cleanest pumping action of ferrofluid between aqueous solutions with this treatment. Furthermore, pumping multiple slugs of ferrofluid was possible with PVP coated PC channels. With previous treatments, our attempts to create a pumping mechanism with multiple immiscible slugs and one ferrofluid slug controlled by a magnet failed due to leakage across slugs not influenced by the magnetic field.

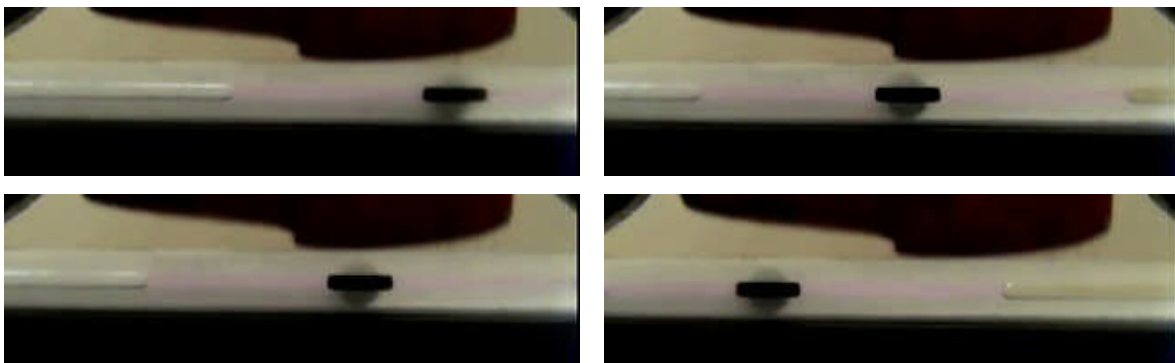


Figure 14. Pumping action of one ferrofluid slug in argon treated, and PVP coated channel.

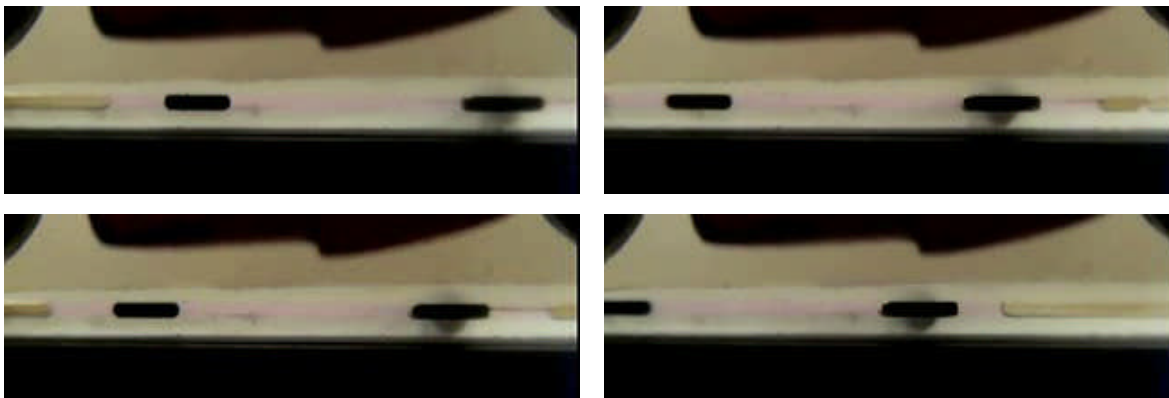


Figure 15. One magnet pumping 2 ferrofluid slugs and 3 water slugs in same channel as above.

A method of temporarily activating the surface of PC was by application of acetone prior to dipping in the PVP solution. Although acetone eats through PC, depending on the amount applied, PVP creates a coating that seems to cover pores and dents smoothly. Additionally with the acetone application, hydrophilic modification of a microfluidic channel in PC can be achieved following thermal bonding of the PC chips.

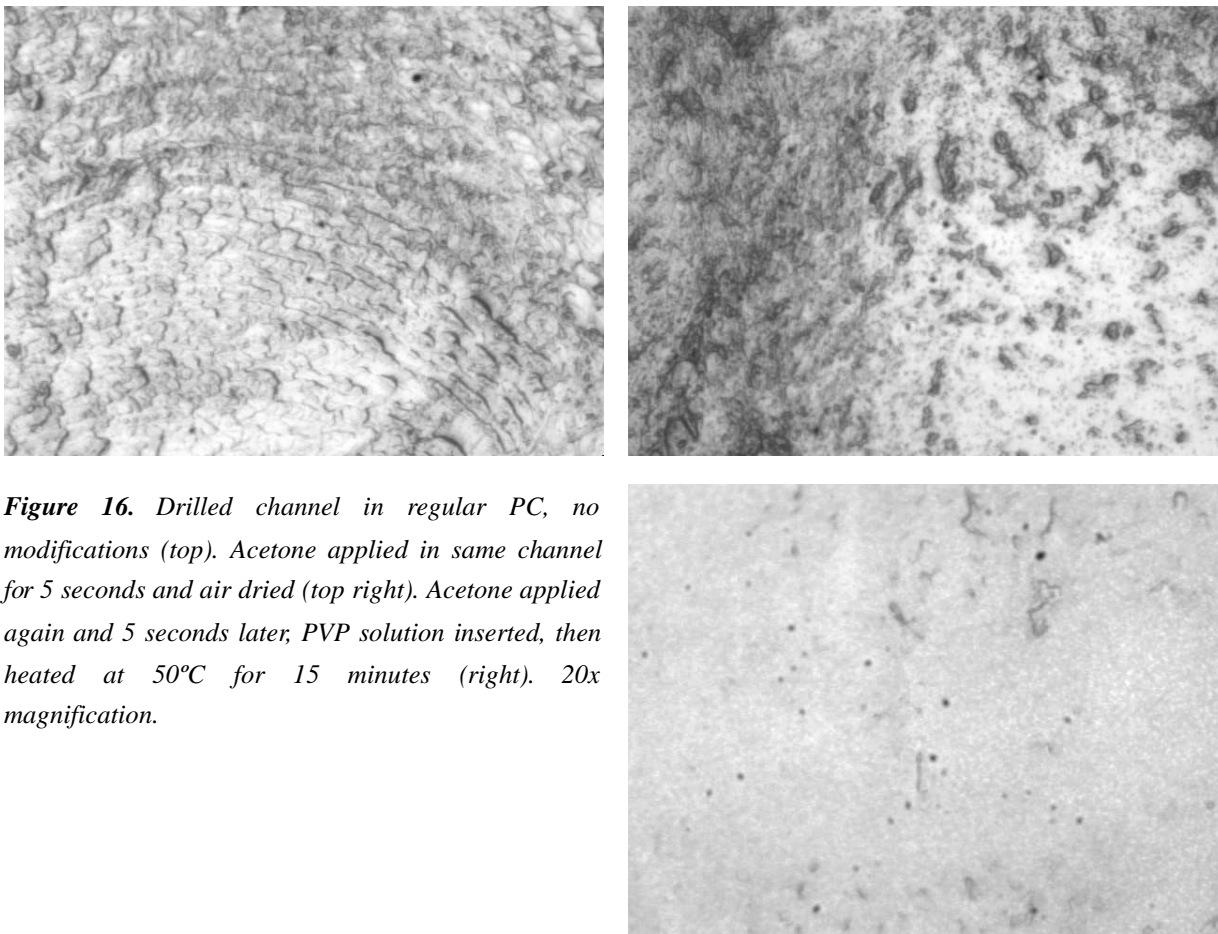


Figure 16. Drilled channel in regular PC, no modifications (top). Acetone applied in same channel for 5 seconds and air dried (top right). Acetone applied again and 5 seconds later, PVP solution inserted, then heated at 50°C for 15 minutes (right). 20x magnification.



Figure 17. Same channels as above in order: unmodified, acetone applied, PVP treatment (from left to right). 2x magnification

A potential low temperature bonding approach for PC was found by directly bonding PVP dipped, argon plasma treated PC chips, and pressing them together with 300 lbf at 50°C. Although the seal in between the PC chips was very weak, the bond successfully enclosed the channel. Additional modifications could be made to better fasten the PC microfluidic chip following PVP sealing, such as screwing or taping the two pieces together.

Another possible low temperature bonding technique was to wet both surfaces with acetone and immediately press them together, before acetone could evaporate. This could be done at room temperature. However, complications arose in attempting to apply enough acetone on both sides of PC while simultaneously shielding the modified channels.

3.6 Spin-on Glass Treatment

Spin-on glass (SOG) is mainly used to coat silicon wafers with hard films of pure SiO₂ and was generously donated to us by Filmtronics (silicate, 700A). Generally SOG is cured at temperatures of 750°C to 1000°C, and thin coats of 1000Å-1500Å are applied in order to avoid cracking. However, polycarbonate surfaces were heated up 140°C to prevent warping the PC. SOG was pipetted on to the PC surfaces and spun in order to create an even, thin layer (1600 rpm, 30 seconds). The PC was heated gradually to 140°C (about 30-45 minutes to heat) and maintained at this temperature for about 90 minutes.

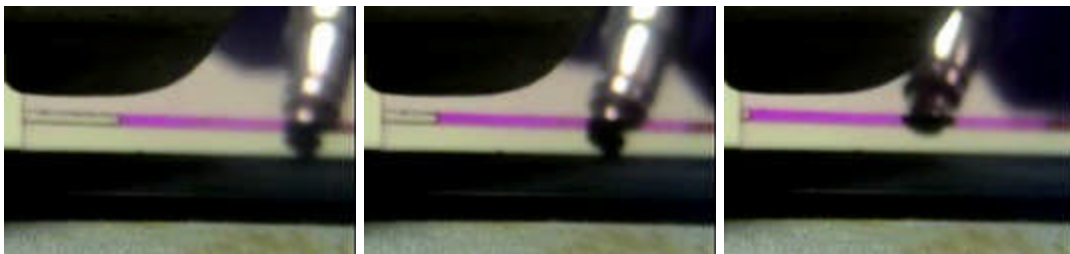


Figure 18. Ferrofluid slug guided by magnet in between two aqueous dyed liquid in SOG coated PC. Channel held together temporarily by vice.

Channels treated with SOG displayed similar results as the macroscale glass capillaries. Although the ferrofluid slug left no noticeable film, very slow movements were necessary.

4. FUTURE APPLICATIONS OF FERROFLUID VALVE AND PUMP

4.1 Ferro-wax Valve

Although most of our experiments dealt with ferrofluid as a pumping device, ferro-wax can be applied to function as a prospective valve in microfluidic chips. As shown below, in this mechanism, a heating pad would be required to heat above 80°C, the region in which the ferro-wax valve will be situated and transfer itself by a magnet. However, with this technique, heat sensitive solutions could not be located in the vicinity of the heating pad.

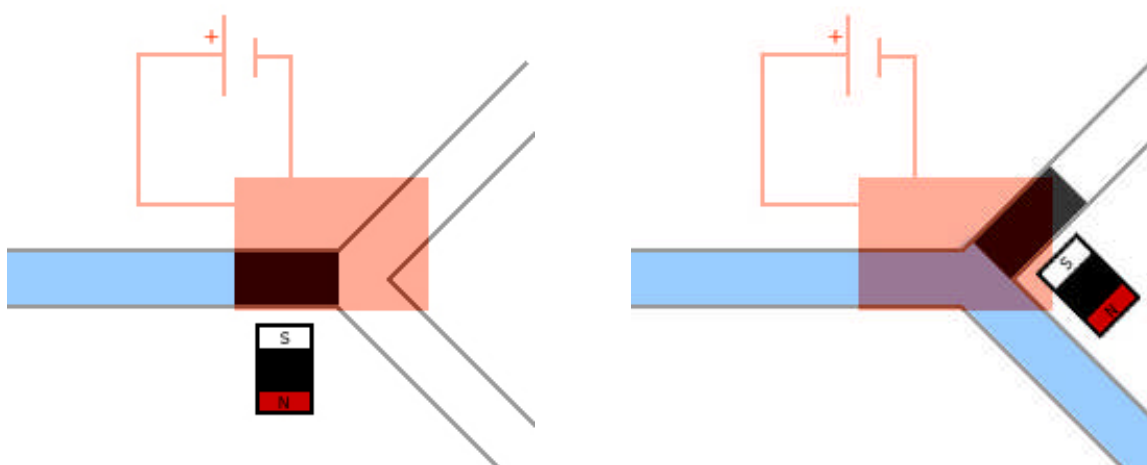


Figure 19. Ferro-wax valve prototype design, closed valve (left), open valve (right).

4.2 Fluid Train

As modeled in figure 4, ferrofluid can be used to direct fluids separated by immiscible slugs (possibly ferrofluid). In this example, a fluid train operates as a protein detection device utilizing chemiluminescence technology. This cost efficient technology is advantageous for microfluidic devices because it has a high level of sensitivity, does not generate hazardous waste, and the light produced by the chemical reaction lasts for a substantial duration. Such a device could be used to detect a particular protein which may suggest the presence of cancer. First, an aqueous buffer solution slug flows through the section containing immobilized antibodies or a membrane of antibodies directed against the target protein. The second slug contains the sample, possibly a body fluid, being investigated. As the sample flows across the antibody section, corresponding target protein molecules bind to these antibodies if they are present in this sample. To wash out any remaining molecules in the sample not attached to the immobilized antibodies, another buffer flows through this area. Next, tagged antibodies directed against the target protein bind to the available target protein sites, followed by another buffer. Finally, a slug of chemiluminescence detection reagents at the end of the train activates the tagged antibody sites to emit light. Using a camera suitable to detect very low intensity light signals, the light emitted by the chemiluminescent reaction can be captured. If no light is emitted, the target protein was not present in this sample, and the test would yield a negative result. Initially this chemiluminescence procedure was tested on a small piece of membrane outside of the microfluidic device. To test whether ferrofluid had a negative effect on the immobilized biological system, a small amount was applied on the membrane and rinsed off after a few minutes. Even after applying ferrofluid, light was detected from the membrane (this membrane was prepared and known to contain target proteins and their corresponding tagged antibodies). Pictures were taken of the membrane at different exposure times following application of the detection reagents, as seen in figure 20.



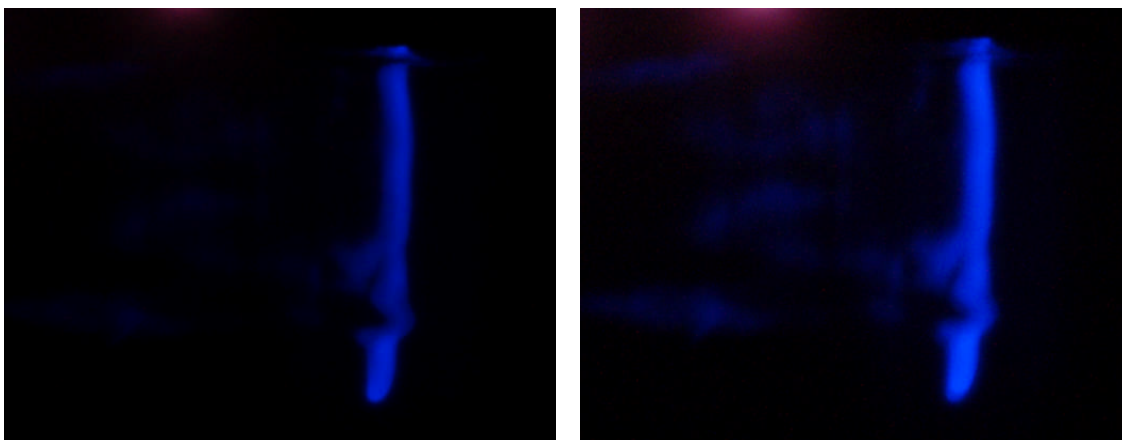


Figure 20. Membrane with antibodies and chemiluminescence emitting light at 38.2 s exposure (top left), 65.0 s (top right), 182.8 s (bottom left), 423.2 s (bottom right).

5. RESULTS AND DISCUSSION

Ferrofluid was shown to effectively pump aqueous solutions in a hydrophilized PC channel. Although ferrofluid could also pump in an unmodified PC channel, it coated the walls of the channel, which may be undesirable in a microfluidic device because of contamination of biological entities or inability to see through the surface of the device. Even though this may be true, initial experiments demonstrated that ferrofluid does not adversely affect the chemiluminescence procedure. The most appealing results were found using argon plasma or acetone activation, followed by a coating of PVP solution. Only with this treatment did ferrofluid have the ability to pump successive aqueous solutions and ferrofluid slugs without noticeable leakage. Additionally this treatment could be performed following thermal bonding of the PC chips by flowing acetone in the channel directly followed by PVP solution. For these reasons, fabricating a device that incorporates a fluid train, with the capability of utilizing chemiluminescence for protein detection, shows promise.

6. RECOMMENDATIONS

Although PVP treatment seemed to yield the best ferrofluid pump in polycarbonate channels, the duration of this modification should be tested. Additionally, further experimentation of bonding PC chips using PVP or plasma should be conducted. PVP seemed to seal the chips under certain conditions, but the bond was so weak that supplementary screws or adhesives to fix the two pieces together would be necessary. However, PVP application was only tested following argon plasma or acetone activation. Oxygen plasma also hydrophilizes PC and should therefore be investigated for PVP bonding. Our plasma bonding trials were limited to testing a few different settings, while

higher power (around 1000 W) that was used in previous research of plasma bonding [10] was not tested. After finding the best method of hydrophilizing and bonding PC channels, exact leakage amounts across ferrofluid plugs should be measured and the maximum leakage permitted for applications of these pumps should be studied.

7. ACKNOWLEDGEMENTS

I would like to thank the SUNFEST coordinator, Professor Jan van der Spiegel, and my advisor, Professor Haim H. Bau, for giving me the opportunity to conduct research in a microfluidics laboratory at the University of Pennsylvania. I would also like to thank my mentor, Jason Thompson, for all of his guidance in this research and in the lab. In addition, I would like to thank Joseph Grogan for his help in the microfabrication lab. Furthermore, I would like to thank Erica Falls for constructing numerous chemiluminescence membranes for us to test. Finally, I would like to thank everyone else in Dr. Bau's lab for their support.

8. REFERENCES

1. J. G. Smits, *J. Sensors Actuators*. **A 21** (1990) 203–206.
2. D. Bosch, B. Heimhofer, G. Muck, H. Seidel, U. Thumser and W. Welser, *J. Sensors Actuators*. **A37-A38** (1992) 684-692.
3. J. Wang, Z. Chen, M. Mauk, et al., *Biomedical Microdevices*. **7:4** (2005) 313-322.
4. Z. Chen, J. Wang, S. Qian, H. Bau, *Lab Chip*. **5** (2005) 1277-1285.
5. A. Hatch, E. Kamholz, G. Holman, P. Yager, K. Bohringer, *J. Microelectromechanical Systems*. **10:2** (2001) 215-221.
6. R. Rosensweig, *Ann. Rev. Fluid Mech.* **19** (1987) 437-463.
7. H. Shadpour, H. Musyimi, J. Chen, S. A. Soper, *J. Chromatogr.* **A1111** (2006) 238-251.
8. A. Larrson, H. Derand, *J. Colloid and Interface Science*. **246** (2002) 214-221.
9. L. Kessler, G. Legeay, et al., *J. Biomater. Sci. Polymer Edn.* **10** (2003) 1135-1153.
10. S. Kitova, M. Minchev, G. Danev, *J. Optoelectronics and Advanced Materials*. **7** (2005) 2607-2612.
11. S. Vallon, B. Drevillon, F. Poncin-Epaillard, J. Klemberg-Sapieha, L. Martinu, *J. Vac. Sci. Technol.* **A14:6** (1996) 3194-3201.