Hydrophilic polycarbonate chips for generation of oil-in-water (O/W) and water-in-oil-in-water (W/O/W) emulsions

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Received: 13 July 2012 / Accepted: 6 October 2012 / Published online: 9 November 2012 © The Author(s) 2012. This article is published with open access at Springerlink.com

Abstract Modification of the surfaces of polycarbonate (PC) with the use of a solution of tin (II) chloride renders them hydrophilic. The surface draping is stable against exposure to water and to alcohols. Exposure to alkanes reduces but does not diminish the effect. The method is compatible—in using the same solvent and temperature—with the hydrophobic modification of PC (Jankowski et al. in Lab Chip 11:1151–1156, 2011). The combination of these methods makes it possible to generate single and multiple monodisperse emulsions with the use of flow-focusing junctions in systems made in PC—a material that is suitable for fabrication of multilayer, high-throughput microfluidic devices.

Keywords Microfluidic · Hydrophilic · Double emulsions · Tin

1 Introduction

We report a new technique for modification of surfaces of polycarbonate (PC) that yields these surfaces hydrophilic. Our method uses tin (II) chloride. The procedure is compatible (i.e., in using the same solvent and temperature) with the hydrophobic modification of PC (Jankowski et al. 2011). This compatibility makes it possible to produce microdevices comprising both hydrophilic and hydrophobic regions needed, e.g., to generate multiple emulsions. The presented method of modification of PC can be also useful for “Lab-on-a-chip” systems, e.g., for “Lab-on-a-CD”. The hydrophilic surface of centrifugal microfluidic platforms, which have the potential to become a standard tool for mainstream diagnostics, allows to change the surface tension and can improve the efficiency and cost-effectiveness of the processes (Gorkin et al. 2010). The ability to perform these modifications in PC is important because PC is one of materials that (a) allow for facile construction of multilayered systems for parallel (i.e., high throughput) formation of emulsions and (b) are compatible with mass production via injection molding. The disadvantage of PC is its poor chemical resistance to most organic solvents. Although PC is compatible with a wide range of organic oils (including hexadecane, silicone oils, mineral oils, and fluorocarbons), it is incompatible with aggressive solvents (e.g., acetone, benzene, or dichloromethane). Concentrated acids and bases destroy the surface of native PC via hydrolysis of the carbonate bonds. Only a handful of solvents can be used, including, water, dilute solutions of acids and bases, alcohols and cyclohexane (Jankowski et al. 2012).

Double emulsions comprise droplets encapsulated in immiscible liquid shells, e.g., water drops in organic shell in a continuous aqueous phase (W/O/W) or an oil droplet inside an aqueous shell suspended in a continuous oleic phase (O/W/O). Double emulsions are useful in: medicine (especially in drug delivery) (Davis and Walker 1987; Nakano 2000; Vasiljevic et al. 2006), biology (Kelly et al. 2007), cosmetology (Yoshida et al. 1999; Lee et al. 2001) and food industry (Weiss et al. 2005; Lobato-Calleros et al. 2006; Muschiolik 2007). The uses in medicine and cosmetology typically center around encapsulation of active substances inside double emulsions for targeted drug delivery and for control of the temporal profile of their release. Conventional (bulk) schemes of generation of double emulsions present numerous challenges, making it
particularly difficult or impossible to control the number of embedded droplets and the distribution of volumes of the cores and shells (Muschiolik 2007; Nakashima et al. 2000; Van der Graaf et al. 2005; Vasiljevic et al. 2006).

Such control is readily available via the use of microfluidic devices that form emulsions one droplet at a time (Muschiolik 2007; Engl et al. 2008; Shah et al. 2008). The use of microfluidic devices to formulate double emulsions yields an easy and unlimited ability to design the size and number of embedded droplets (Wang et al. 2011) and to place distinct surfactants at each of the interfaces which can be used to increase their stability. Generation of double emulsions imposes specific requirements on the design of the microfluidic chips. In particular, in planar designs it is necessary for the devices to comprise both hydrophilic and hydrophobic sections of the channels. This can be realized in two ways. Either by proper selection of hydrophilic and hydrophobic materials (Shah et al. 2008) that are later snapped together to form the heterogeneously wettable device. Another possibility is to use one kind of polymer—or more generally, one material—to build the chip and then to modify selected regions of the microchannels using appropriate chemistry (Okushima et al. 2004; Nisisako et al. 2005; Abate et al. 2008, 2010; Bauer et al. 2010). For example, Nisisako et al. (2005) presented a glass microfluidic device with serially connected hydrophobic and hydrophilic microchannels to form aqueous and organic drops consecutively. A hydrophobic channel was prepared using a silane-coupling agent. Abate et al. (2010) proposed both hydrophobic and hydrophilic modifications of monolithic microchannels fabricated in PDMS using polyacrylic acid and photoreactive sol–gel mixture containing fluorosilane. Bauer et al. (2010) used sequential layer-by-layer deposition of polyelectrolytes yielding hydrophilic microchannels in PDMS-based microfluidic devices. PDMS is a material of choice in academic use, yet industries typically use thermoplastics that can be mass-produced by injection molding. This motivates the search for appropriate schemes of modification of the surface chemistries of popular plastics. We have recently developed two methods to modify PC: one that coats the polymer with dodecylamine (DDA) to render a hydrophobic and lipophilic surface (Jankowski et al. 2011) and one for sequential deposition of electrolytes to render PC hydrophilic (lipophilic) (Derzsi et al. 2011). These two methods, however, although suitable for production of single emulsions are not fully compatible with protocols for heterogeneous modifications. The coating with polyelectrolytes requires multiple operations of sequential flushing with different solutions. Each of changes of the solution requires equalization of pressures and flow to avoid undesired cross-modification of the regions of the chips. A procedure involving multiple such operations would be prohibitively difficult in execution.

Here, we demonstrate a method for rendering PC hydrophilic in a procedure that is compatible with the hydrophobic draping of PC with DDA. We first detail the procedure of the new modification with tin (II) chloride and then demonstrate a microfluidic system suitable for production of (O/W) and (W/O/W) emulsions.

2 Experimental

2.1 Materials

We used tin (II) chloride (Sigma-Aldrich, Germany), DDA (Sigma-Aldrich) and ethanol (Chempur, Poland) to modify the surface of PC (Bayer, Germany). All chemicals were analytical grade and were used without further purification. For preparation of aqueous solutions we used doubly distilled water (Millipore, 18 MΩ).

Fabrication of the chips in PC (Makrolon, Bayer) included micromilling of PC plates (Ergwind MSG4025, Poland) and bonding them (Ogoriczky et al. 2010). We found it critical that the channel surfaces were well cleaned prior to modification. For this purpose, we cleaned the PC plates in an ultrasonic cleaner in isopropanol for 1 h at 40 °C before bonding.

2.2 Procedure for surface modification

Ethanolic solution of SnCl_2 [20 % (w/w)] was introduced into the microchannels and passed through them for 2 h (at a flow rate of 4 mL/h for channels of 400 × 400 μm cross-section). During the process of modification the microdevice was thermostated at 60 °C. After flushing the channels with water (5 mL/h) for 20 min at room temperature the devices were ready to use. The life-span of the modification can be increased by storing the chips with micro-channels filled with water.

2.3 Surface analysis

The XPS spectra were recorded on a PHI 5000 Versa-Probe™ scanning ESCA Microprobe using monochromatic Al-Kα radiation (hν = 1,486.6 eV) from an X-ray source operating at 200 μm spot-size, 50 W and 15 kV. Elemental quantification was done using Casa XPS ver. 2316 software.

Contact angle (CA) measurements were done using static sessile drop method. In the case of CA of water in air (water/PC/air) we took images of a 2-μL droplet of distilled water on the surface. We also measured the CAs of hexadecane in surrounding water (oil/PC/water) by placing the PC plates in a reservoir filled with distilled water and putting a droplet of hexadecane on the plate from underneath, using a syringe
and a 100-μm internal diameter capillary. We used a camera (UI-1120SE, uEye, Germany) to record the shape of the droplet and measured the value of the CA with ImageJ (Fiji).

3 Results and discussion

3.1 Nature of the hydrophilic modification

Tin (II) chloride (SnCl₂) is known as an effective catalyst for thermal decomposition of PC. It is characterized by extremely strong activity of degradation (Chiu et al. 2006). We observed that the treatment of PC with a solution of tin (II) chloride in ethanol at elevated temperatures yields a strongly hydrophilic surface. We found that there is a close correlation between the contact angles of water on the plate in air and the content of tin in the surface layer of modified PC (Fig. 1).

XPS analysis was used to verify this assertion and results are presented in Table 1 and Fig. 2. The analysis of the O 1s XPS spectra revealed that in addition to oxides also hydroxide compounds were detected. This confirms the assertion that the hydrophilic character is likely associated with the presence of SnO-nH₂O on the modified surface (Table 1).

In order to finally confirm the chemical state of tin oxide on the surface, we compared the XPS spectra of the modified surfaces of PC with the corresponding XPS spectra obtained for commercially available (Alfa Aesar GmbH), standard samples of SnO and SnO₂ (Fig. 2). The BE values detected for XPS states of tin (II) and tin (IV) oxides indicate SnO to be the dominant form of tin compounds on the modified PC. The surface layer of the standard SnO sample was partially contaminated by SnO₂, which was removed after 1 min Ar⁺ sputtering (Fig. 2). The results allow us to conclude that the surface modification of PC with SnCl₂ yields the surface draped with SnO with the atomic content of tin in excess of 20 % (Table 1).

Interestingly, none of the other metal chlorides (MgCl₂, ZnCl₂, AlCl₃ and SnCl₄) we tested under similar conditions for modification of PC increased the hydrophilic character of the surface.

3.2 Optimization of the procedure

We have varied a number of parameters of the procedure of draping PC with SnO in order to find possibly optimum conditions. For each type of modification we first inspected the quantitative content of tin atoms on modified plates of PC using XPS. We also measured the contact angles of water on these plates. Then, we repeated the experiments to modify the surface of microchannels in preassembled chips.

The most general finding of all these experiments is that the higher amount of tin on the modified surface makes the lower values of the contact angles of water (Fig. 1). We selected ethanol as a solvent because of good solubility of tin (II) chloride and because it is also used in the procedure of rendering PC hydrophobic by draping it with DDA (Jankowski et al. 2011). In the screens of parameters of modification we found that the content of tin in the modified surface area depends on the concentration of tin (II) chloride in the solution (Fig. 3a). The atomic concentration (AC) of tin on the surface increases with concentration of the solution and saturates at the coverage of approximately 25 % of tin at the surface of a modified PC for solutions of concentration of 10 % (w/w) or higher. Nonetheless, in

Table 1 XPS measurements conducted on the modified PC surfaces

| Element Core level | BE (eV) | FWHM (eV) | AC (%) | Remarks |
|--------------------|---------|-----------|--------|---------|
| O 1s               | 529.9   | 1.3       | 21.4   | SnO     |
| 1s                 | 530.9   | 1.3       | 7.4    | SnO₂, O₂ |
| 1s                 | 531.7   | 1.3       | 5.1    | –C=O    |
| 1s                 | 533.2   | 1.3       | 1.5    | R–OH    |
| Total O            |         |           | 35.5   |         |
| Sn 3d₃/₂           | 486.2   | 1.4       | 13.0   | SnO     |
| 3d₅/₂              | 494.6   | 1.4       | 8.6    | SnO     |
| 3d₃/₂              | 487.1   | 1.6       | 0.7    | SnO₂    |
| 3d₅/₂              | 495.5   | 1.6       | 0.5    | SnO₂    |
| 3d₅/₂              | 493.1   | 2.0       | 0.3    | Sn      |
| 3d₅/₂              | 493.1   | 2.0       | 0.2    | Sn      |
| Total Sn           |         |           | 23.3   |         |
| Other elements     |         |           | 41.2   |         |

Data obtained from the analysis of the Sn 3d and O 1s XPS spectra (see top spectra in Fig. 2). Remarks give the most likely chemical state of the detected elements.

BE binding energies, AC atomic concentration, FWHM full width at half maximum of deconvoluted peaks of oxygen and tin with SnO with the atomic content of tin in excess of 20 % (Table 1).
modifications of the surfaces of microchannels we often continued to use a 20% solution of SnCl₂ to make sure that all the nooks in the corners of the milled channels are saturated with the salt.

We found that the quality of the modification depends strongly on the temperature at which the modification was done (Fig. 3b). In order to get a sufficiently large concentration of tin on the surface of PC, it is necessary to conduct the modification at relatively elevated temperatures (≥60 °C). Finally, the interval over which the surfaces are exposed to the solution of tin chloride should not be less than 1 h (Fig. 3c). We found that in the case of modifications of microchannels it is optimum to conduct the procedure for 2 h. Increasing the interval more does not result in any further improvement of the modification.

In conclusion, we determined the best set of conditions comprise CSnCl₂ = 20% (w/w) in ethanol, T = 70 °C and t = 2 h.

3.3 Stability of the modification

It is well known that the surface properties may deteriorate (or simply change) over time of exposure of the surface to various media. The stability of the coating and of the desired character of the surface is one of the more important criteria in a judgment of applicability of any method to either academic or industrial use.

We tested the evolution of the CA of water on the treated planar substrates of PC. In all these trials we used the optimized procedure of modification: we used 20 × 40 mm PC plates of a thickness of 0.75 mm. Cleaned PC plates were swelled in vacuum with dichloromethane vapors and heated in an oven at 130 °C for 30 min prior to use in order
to mimic the conditions of the sealing process (Ogończyk et al. 2010). Then we treated them with a 10 % (w/w) ethanol solution of SnCl$_2$ at 70 °C for 2 h and then thoroughly washed with water and dried with pressurized air.

In order to quantify the stability of the hydrophilic character of the modified surfaces, we immersed each set of substrates in one of four different media: two hydrophobic (air and hexadecane) and two polar (water and isopropanol). Then, at various instants over the course of 3 weeks we took the plates out, dried with pressurized air (and in the case of immersion in hexadecane, first thoroughly washed with ethanol). Finally, the contact angles of water on the substrate in air, and of hexadecane on the substrate immersed in water were measured.

Figure 4 graphs the CAs of water on the modified PC substrates. The plates that were exposed to polar solvents sustained the hydrophilic character with typical values of the CA of water in air equal ca. 15°–20° for samples exposed to water and 10°–15° for plates exposed to isopropanol. These values did not show any statistically significant change over the course of the 3 weeks of the experiment. Exposure of the plate to hexadecane immediately shifts the CA of water to values typical to slightly hydrophilic substrates (ca. 70°) and stabilized at this value. The value of the CA of water on the plates exposed to the atmospheric air showed slow recovery of the original hydrophobic character.

In microfluidic applications comprising formation of droplets of oil in water in the microchannels, it is necessary to use a surface that is not only hydrophilic but also lipophobic. For example, the hydrophilic surface of PC after exposition to oxygen plasma or UV is equally well wetted by water and by oil and thus cannot serve the purpose. Thus, in order to verify the applicability of the modified surfaces to formation of O/W emulsions, we measured the contact angles of oil (hexadecane) drops deposited on the modified plates in the continuous phase of water (Fig. 5). The native (untreated) PC is lipophilic, with the CA of hexadecane in water (oil/PC/water) equal to ca. 40°. In a stark contrast, the treated substrate, immediately after the modification yielded CA of hexadecane in water exceeding 150°. Exposure of the substrates to air or hexadecane slightly deteriorated this lipophobic character, decreasing the CA of hexadecane in water to 120°–125°. Exposure to either water or isopropanol preserved the strongly lipophobic character with the CAs of oil on the plates in excess

![Fig. 4](image-url) Evolution of the wettability of the modified plates of PC by water over the course of 3 weeks of immersion in various fluids. Each value is an average of at least eight independent measurements of the contact angle of water on a cleaned and dried surface in the atmosphere of air.

![Fig. 5](image-url) Contact angle of water in atmospheric air environment (water/PC/air) and of hexadecane in surrounding water (oil/PC/water). The volume of water droplets was 2 µL, oil droplets were produced by spontaneous breakup from a steel capillary (ID = 100 µm) based on the principle used pedant drop technique. The capillary was placed under the PC substrates in water bath and was connected to a syringe of a small diameter (ID = 4.7 mm). The oil was injected manually via the syringe and controlled optically. The volume of the droplets were 11.95 µL with repeatability of CV = 4.2 % (defined as CV = (σV/V) × 100 %, where CV coefficient of variation, σV standard deviation of the volume of the droplets, V mean volume of the droplets). Left row text indicates the solvent in which the PC plates were immersed for up to 3 weeks before taken out and dried prior to the water/PC/air and oil/PC/water CA measurement. Native is unmodified PC plate.
of 150°. We note that these values may be even higher: droplets of hexadecane were freely rolling on the modified plates immersed in water.

3.4 Formation of single organic droplets in water

We tested the applicability of the modification to microfluidic generation of O/W emulsions. We used a standard cross-junction chip with all the channels having square 400 × 400 μm cross-sections. We tested formation of droplets of hexadecane, FC-40 (Fluorinert), silicone oil and soya oil, all in the continuous phase of water (Fig. 6). For all types of oils we did not observe any evidence of wetting of the modified surface by the oil phase in the experiments conducted over a period longer than 8 h each.

3.5 Fabrication of chips for generation of double emulsions

The method that we described can be used to prepare microfluidic chips for generation of double emulsions. Such a system should have sections of channels presenting hydrophilic (and—at the same time—lipophobic) character and sections that are hydrophobic (and lipophilic) (Bauer et al. 2010). Figure 7a shows the schematic diagram of the double cross-junction systems designed to generate W/O/W emulsions.

As an example, we fabricated a chip for generation of W/O/W double droplets. For generation of O/W/O all the regions of different wettability should simply be inverted. In the system that we fabricated (for generation of W/O/W emulsions), the channel between the first and the second cross-junction has to have hydrophobic character and the channel between second cross-junction and the outlet needs to be hydrophilic.

In order to prepare these selective wettabilities we need to use two modifications: one that we described here, that generates a hydrophilic surface; and second that dapes the surface of PC with DDA to render it hydrophobic (Jankowski et al. 2011). Simultaneous execution of these two protocols proved impossible because of precipitation of complexes [SnCl₂][H₂NC₁₂H₂₅] or [SnCl₂][H₂NC₁₂H₂₅]₂ at the interface of the streams carrying solutions of DDA and tin chloride. Because both the procedures use the same solvent, we could use ethanol to prime the surface before the first modification to wash the system before the second step and to use the same (pure) solvent as a blocking agent that prevents modification or contamination of the regions that are not to be modified within the first or second step. During the exchange the syringe with ethanol with the syringe with solution of tin chloride (inlet 2), ethanol is continuously passed through an inlet 1 to prevent the SnCl₂ solution entering to the hydrophobic part of the channel. This is sufficient to keep the coating agent away from the surfaces that we do not wish to modify. In the first stage we introduced the
hydrophobic character to a section of channels by passing a 5 % (w/w) solution of DDA from inlet 1 and pure ethanol from inlet 2 (Fig. 7b). Both liquids were passed through the channels at the same rate of 4 mL/h at 60 °C for 2 h. Then we washed the device with pure ethanol for 15 min (4 mL/h). In the second step of modification, we run a 20 % (w/w) solution of SnCl₂ in ethanol (at 3 mL/h, via inlet 2) and pure ethanol (3 mL/h, inlet 1) for 2 h at 60 °C. For practical reasons we decided to use the same temperature for both modifications in order to run them quickly one after the other in the same temperature bath. As 70 °C degrades the surface of PC in the DDA treatment (Jankowski et al. 2011), we decided to use 60 °C to run the two modifications. Next, the chip was removed from the thermostat and allowed to cool while the liquids continued to flow through to preserve the selective exposure of the walls to tin chloride. When the temperature decreased to room temperature, we washed the channels with water (5 mL/h, inlets 1 and 2) for 30 min. We stored the chip with channels filled with water. Reverse sequence modification is also possible, but requires additional steps. After reaction with SnCl₂ the device should be cooled to room temperature, the channels flushed with water, dried and then again placed in a thermostat for further modification with DDA. It should be noted that the modification with SnCl₂ is more sensitive, and therefore, better results are obtained by performing it as a final step. Figure 7c shows an exemplary micrograph of the selectively modified double cross-junction producing double W/O/W droplets.

4 Conclusion

In this report we have detailed a new method of modification of PC. Treatment of PC with an ethanolic solution of tin (II) chloride at elevated temperatures gives the surface strong hydrophilic properties. These properties are stable and can withstand weeks of storage in polar solvents. Storage in non-polar fluids reduces the originally strong hydrophilic character to slightly hydrophilic properties.

The hydrophilic modification of PC can be used to fabricate chips for generation of oil-in-water emulsions of alkanes (e.g., hexadecane), natural oils (e.g., soya oil), fluorocarbons (e.g., fluorinert FC-40), and silicones (e.g., PDMS).

To the best of our knowledge, this is the first demonstration of selective modification of PC to render sections of this material hydrophilic and other regions hydrophobic. The fact the two modifications (using SnCl₂ and DDA) are, respectively, also lipophobic and lipophobic makes the procedure ideal for fabrication of microfluidic chips dedicated to controlled generation of double emulsions. The proposed method is convenient in that it requires a single step for the hydrophilic modification and only two steps for the heterogeneous draping of PC. Both procedures use readily available and inexpensive reagents.

The important point to note is that we found it critical that the surfaces of native PC are properly cleaned before the modification with SnCl₂. We have also found that PC from other sources not always modified equally reproducibly—unknown additives to the commercial brands of PC may interfere with the procedure.

Finally, the fact that the method uses PC as a substrate makes it potentially applicable to both academic and industrial uses in controlled generation of double emulsions and in preparative applications for targeted or controlled release of active substances in pharma, cosmetic and food industries.

Acknowledgments Project operated within the Foundation for Polish Science Team Programme co-financed by the EU European Regional Development Fund. The research was partially supported by the European Union within European Regional Development Fund, through an Innovative Economy grant (POIG.01.01.02-00-008/08).

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