

Stable hydrophilic surface of polycarbonate.

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Abstract

In this report we present a simple method for preparation of stable hydrophilic surface modification of polycarbonate. The method yields the polymer surface rich in carboxylic acid groups and may thus be also useful for further surface modification protocols (e.g. immobilization of enzymes on the surface of the polymer). The method has been designed particularly for use in microfluidics applications. The surfaces obtained via the method are extremely durable and can be stored without any special conditions for at least one year.

1. Introduction

In this paper we report a new procedure for preparation of hydrophilic surface of polycarbonate (PC). The method was specifically developed to modify the surface of channels in microfluidic systems. The new technique is based on the chemical modification of the polymer surface with branched polyethyleneimine (BPEI) and poly(ethylene-alt-maleic anhydride) (PEMA) polymers as the reagents. As a result of the modification we obtain a highly hydrophilic surfaces (with contact angle of water less than 20°) characterized by exceptional durability and stability against storage over months.

Polycarbonate is an attractive material for the construction of microfluidic devices because of its high impact resistance, low moisture absorption, good machining, high glass transition temperature ($T_g = 145\div 148^\circ\text{C}$), transparency in the visible, biocompatibility, and relatively low cost [1, 2]. PC is one of materials that allow for facile construction of multilayered systems for parallel (i.e. high throughput) formation of emulsions and compatible with mass production via injection molding and hot embossing [3, 4].

The use of polycarbonate for the production of microfluidic systems designed for generation of oil-in-water (o/w) or water-in-oil (w/o) droplets, requires that the surface of the microfluidic channels is adequately hydrophilic or hydrophobic. The native contact angle (CA) of water on unmodified PC is 84° making this material neither decisively hydrophobic nor hydrophilic. Further, it is of interest in constructing microfluidic devices for heterogeneous assays that the surface of the channels presents chemical groups that allow for a wide range of chemical or biochemical modifications for specific capture of biomolecules. Thus, a method for hydrophilic modification of polycarbonate, that allows for further

processing and is stable against prolonged storage is of high interest to the microfluidic community.

The literature describes several methods for hydrophilic modification of the surface of PC. The known and often used modifications of PC include exposure to UV light (alone[5, 6] or in combination with an atmosphere of ozone[7, 8]) or to oxygen plasma[9-11]. to generates high concentrations of polar groups on the surface and effectively increases the surface energy of the material. That modification induces a decrease of CA of water on PC to 20°–55° depending on the time of irradiation The hydrophilic character has, however, very limited stability against washing, heating and storage. Ion beam irradiation[12, 13] increases the population of C–O and C=O groups on the surface of PC leading to a reduction the CA of water on irradiated PC to 16°–18°, but recovers to 78° within two weeks in air. A range of surface reactions were also reported. For example TiO₂ coating creates highly hydrophilic, self-cleaning surface of PC with a CA of water of 20°, unfortunately, the CA recovers to 50° in two weeks, when left in air.

We have recently developed two methods for rendering the surfaces of microchannels fabricated in polycarbonate hydrophilic: one using sequential deposition of polyelectrolytes[14] and another that treats the surface of PC with an ethanolic solution of tin (II) chloride[15]. Both methods allow to obtain highly hydrophilic surfaces. The hydrophilic character of such modified surfaces of PC remains stable if the material is stored in polar solvents. However, storage in non-polar fluids (as e.g. storage of dry chips in air) reduces the originally strong hydrophilic character to only slightly hydrophilic properties.

Here we demonstrate a procedure for modification of polycarbonate microchannels that renders them stably hydrophilic. The surfaces obtained via the method that we here describe are extremely durable and can be stored without any special conditions for at least one year. The method is simple to use, does not require neither specialized equipment nor expensive reagents. The modified surface contains a high surface density of carboxylic groups, opening it to a wide range of further surface modification protocols.

2. Material and methods

2.1 Materials

We used branched polyethyleneimine (BPEI), poly(ethylene-*alt*-maleic anhydride) (PEMA) and sodium hydroxide from Sigma-Aldrich. Solvents (isopropanol and acetone) were obtained from Chempur (Poland). All chemicals were of analytical grade and were used without further purification. For preparation of aqueous solutions, we used doubly distilled water (Milipore, 18 MX). Polycarbonate was manufactured by Bayer (Germany). In preliminary experiments and measurements of contact angles we used polycarbonate plates of sizes 40x20x0.75 mm.

2.2 Fabrication of the chips

We fabricated the microfluidic chips in polycarbonate by micromilling in plates of thickness of 5 mm and then bonded them[16] with plane 0.75 mm plates.

2.3 Surface modification

In the procedures of modification we used syringe pumps (PHD 2000, Harvard Apparatus, US), a thermostat (ED3, Julabo, Germany) and laboratory drying oven (SLN 115 ECO, POL-EKOAPARATURA). For modification of microchannels we introduced continuous flow of the solution of 10% (w/w) of BPEI in isopropanol at 2÷4 mL/h. During the modification we kept the microfluidic chip in a thermostat at 70 °C for 2.5 h. After completion of this step we cooled the chip to room temperature and washed the channels with isopropanol (flushed at 4 mL/h) for 0.5 h. Then we dried the microchannels by blowing air through them and placed the chip in an oven at 100 °C for 3 hours. Then we filled the channels with a solution of PEMA (PEMA:acetone:water – 0.5:20:5.5 parts by weight) and after a few seconds we removed this solution with compressed air. Next we incubated the chip in the oven at 100 °C for 2 h. After cooling we passed the solution of HCl (0.2M) for 1h followed by NaOH (0.1 M) for additional hour (at 2÷4 mL/h) through the channels. Then we washed the channels with water (at 2÷4 mL/h) for 0.5 h and dried them with air.

2.4 Contact angle measurements

Contact angle (CA) measurements were done with the use of a 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 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 The chemistry of the process of modification

The surface modification comprises three main steps: (i) reaction of the carbonate groups on the polycarbonate surface with branched polyethyleneimine (BPEI) leading to the formation of strong urethane bonds, (ii) reaction of the free amine groups with anhydride groups of poly(ethylene-alt-maleic anhydride) (PEMA) to create amide bonds and (iii) hydrolysis of the remaining anhydride groups consequently leading to generation of large amounts of carboxyl groups on the surface (Fig. 1).

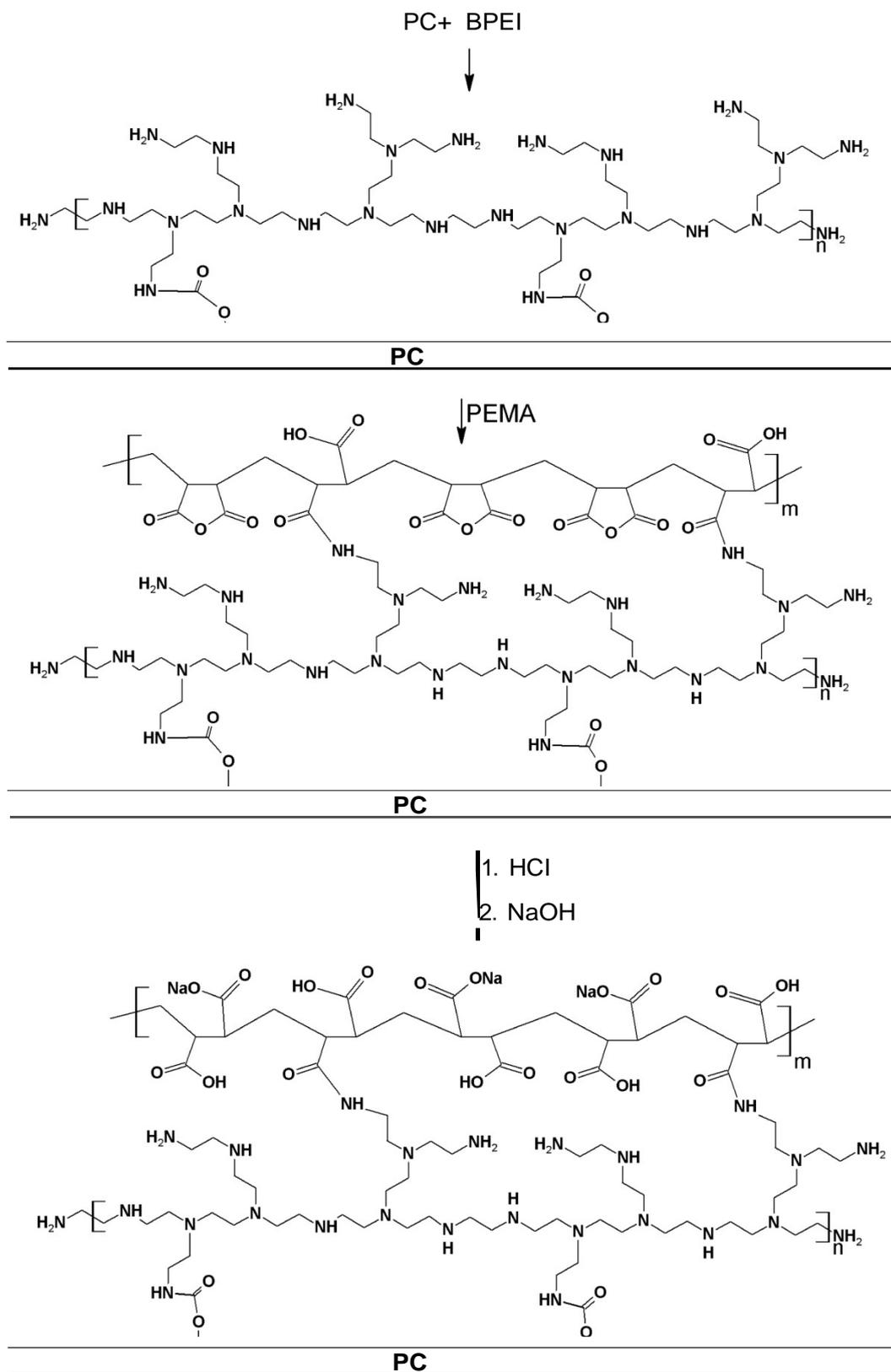


Fig.1 Chemical reaction scheme used for the modification of polycarbonate surfaces.

We have recently presented the method to modify polycarbonate with the use of BPEI as a first step to protection of polycarbonate microchannels against the normally destructive action of common organic solvents[17]. We found that the content of nitrogen at the surface depends on the concentration of BPEI, the type of solvent, temperature and time. Achieving a high concentration of amine groups on the surface is particularly important because it allows permanent bonding of the poly(ethylene-alt-maleic anhydride) in the subsequent stage of modification. We performed the optimization of reaction and found that the highest concentration of amino groups can be obtained by using 10% (w/w) of BPEI in isopropanol at 70° C for at least 2h. Additional annealing the plates in the oven further enhances the durability of the coating by increasing the number of urethane linkages. In the next step we treated these surfaces with acetone/water solution of PEMA (PEMA:acetone:water – 0.5:20:5.5 parts by weight). Channels were filled with a solution of polymer and after a few seconds the solution was removed by compressed air in order to obtain a thin film of PEMA on the surface of PC. It should be noted that the native polycarbonate is incompatible with aggressive organic solvents such as acetone. However preliminary coating of PC with branched polyethyleneimine (BPEI) renders the surface resistant to this aggressive solvent[17]. Next we incubated the chip in an oven at 100 °C for 2 h to enhance the degree of cross-linking of the layers of polyimine with poly(ethylene-alt-maleic anhydride). The contact angle of water on the resulting surface was about 69° (Fig. 2).

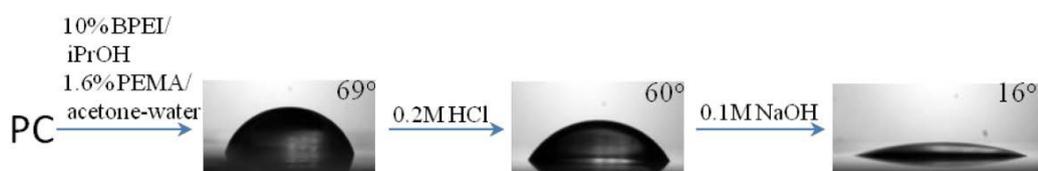


Fig. 2 Optical images of a water droplets on the surface of the polycarbonate in the subsequent stages of modification. The value of the contact angles are given in the upper right corner of the micrograph

We assume that only a very small number of anhydride groups of PEMA react with amino groups to form amide bonds. In order to make the surface highly hydrophilic the rest of anhydride groups should be hydrolysed. We found that the best results (lowest contact angles of water) can be obtained by treating the surface first with a dilute hydrochloric acid (0.2M) followed by a solution of sodium hydroxide (0.1M). The contact angles of water measured on such surfaces were all well below 20 ° (Fig. 2)

3.2 Formation of O/W emulsions in modified microchannels

The method that we described can be used to prepare microfluidic chips for generation of oil in water emulsions. We used a standard cross-junction chip with all the channels having square 400 x 400 μ m cross-sections. The experiment was first performed with the use of hexadecane as a dispersed phase. In some cases, we observed a slight wetting of the surface by the oil droplets. Addition of small amount of surfactant (0.25% SDS) to the aqueous phase completely solved this problem (Fig. 3). We did not notice any signs of wetting even after several hours of continuous operation of the microfluidic droplet generator.

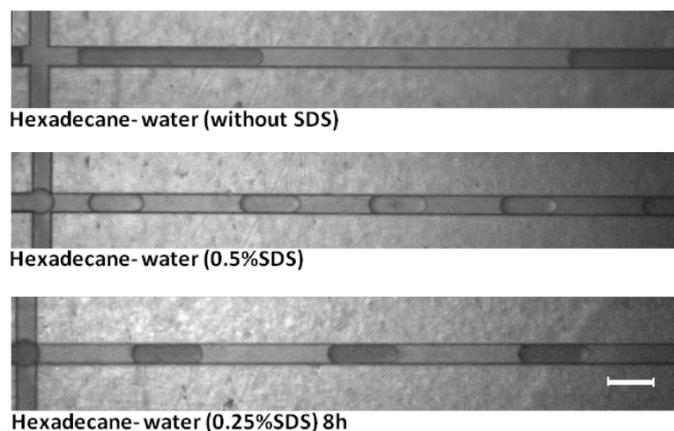


Fig.3 Generation of organic droplets in modified PC microchannels: hexadecane without surfactant and hexadecane with 0.5 and 0.25% of SDS in aqueous continuous phase. The pure oil phase slightly wets the channel walls, a small addition of surfactant solves the problem. The scale bar is 1 mm, rates of flow are 1 mL/h and 2.5 mL/h for the oil phase and for the continuous aqueous phase respectively.

The modified surface was tested with the use of the following oils: hexadecane, silicone oil, mineral oil and fluorinert FC-40. In all cases distilled water (for hexadecane water with 0.25% SDS) was used as a continuous phase. For all tested oils, there was no signs of wetting of the surface and for each type of oils experiment was conducted for at least 8 hours (Fig. 4).

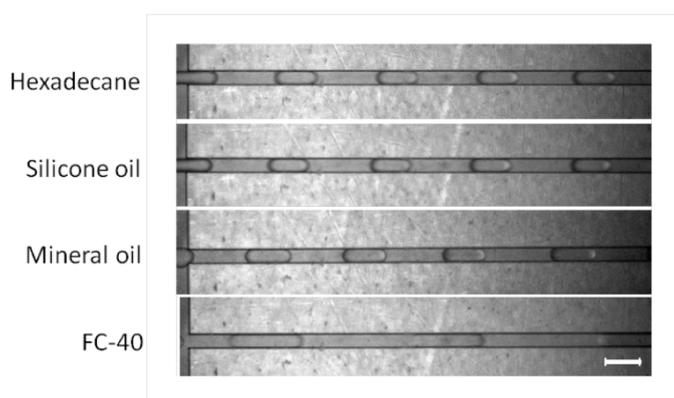


Fig.4 Generation of organic droplets in modified PC microchannels: hexadecane, 20 cSt PDMS oil, mineral oil and Fluorinert FC 40 in aqueous continuous phase. Surfactant is used only for hexadecane (0.25% SDS). All oils form perfect droplets that do not wet the walls of the microchannel. The scale bar is 1 mm, rates of flow are 1 mL/h and 2.5 mL/h for the oil phase and for the continuous aqueous phase respectively.

We also checked whether we can use other polar liquids as the continuous phase. We found that the modification allows formation of oil droplets (hexadecane) using methanol as the continuous phase (Fig. 5).

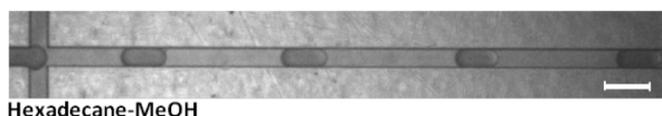


Fig.5 Generation of hexadecane droplets in methanol continuous phase in modified PC microchannels. The scale bar is 1 mm, rates of flow are 1 mL/h and 2.5 mL/h for the oil phase and for the continuous phase respectively.

3.3 Stability of the modification

We tested the system for several hours a day for the next 5 days. The experiment was repeated a month later and we did not observe any differences in wetting during the experiment. Finally, the experiment was repeated after one year with the same result (Fig.6).

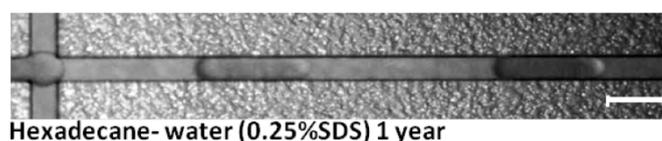


Fig. 6 The stability of modified surface of PC microdevice was tested one year after modification. Hexadecane with 0.25% of SDS in aqueous continuous phase was used. The scale bar is 1 mm, rates of flow are 1 mL/h and 2.5 mL/h for the oil phase and for the continuous phase respectively.

It is important that during all this time the chip was stored on a laboratory table at room temperature in an open box.

4. Conclusions

In this report, we have detailed a new method for modification of polycarbonate. The new technique is based on the chemical modification of the PC surface with branched polyethyleneimine (BPEI) and poly(ethylene-alt-maleic anhydride) (PEMA) as the reagents. As a result of modification we obtained surfaces characterized by exceptional durability and stability. To the best of our knowledge, this is the first surface modification of PC that renders a durable hydrophilic character that does not require any special conditions for its stability over months of storage.

Acknowledgments

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