Hydrophilic polycarbonate for generation of oil in water emulsions in microfluidic devices

Ladislav Derzsi, Paweł Jankowski, Wojciech Lisowski and Piotr Garstecki*

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

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Supplemental Information

This supplemental information contains details of optimization of the coating prosess including graphs and results of additional experiments (UV and plasma pre-treatment of the surface). We also list the results of XPS analysis of elemental composition of the modified surfaces. Finally, we provide detailed description of materials and methods used in our
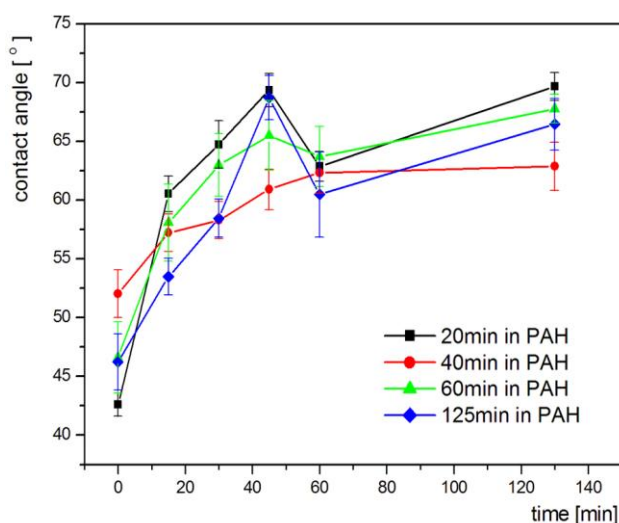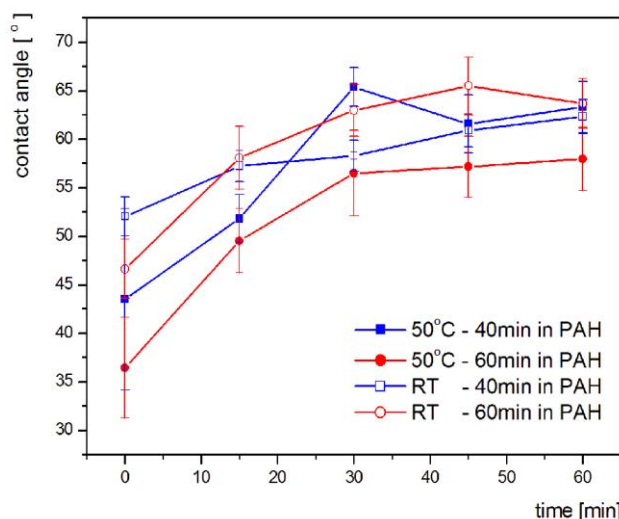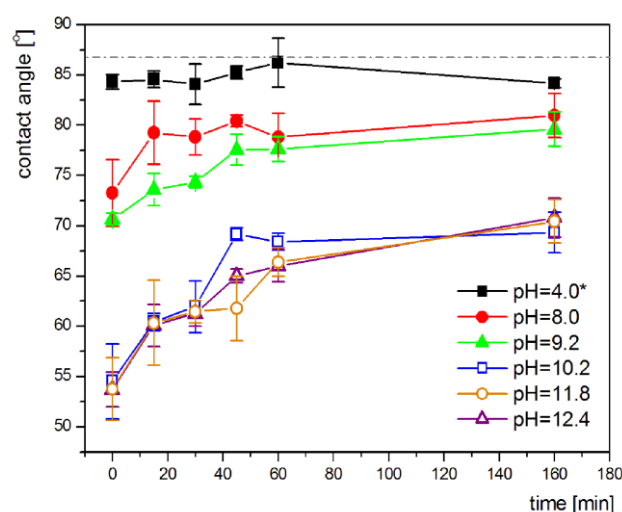10 experiments.

Fig. S1 Optimization of the time of adsorption of PAH*. No significant differences were observed between the various times of the treatment.

15 **Fig. S2** Optimization of the temperature of the PAH* treatment. Only small changes of CA were noticed.

20 **Fig. S3** Optimization of the pH of modifications with PAH*. Below pH of ca. 10 there are not enough free amine groups on the polymer that could react with the surface of PC. Dash-dot line shows the CA of water on native PC, pH=4.0 represents PAH without any addition of NaOH.

25 **Optimization of coating PC with PAH*.**

In order to optimize the procedure of coating PC with PAH* we prepared the coatings at a range of parameters, including the temperature of solution of PAH*, its pH, and the time of immersion. As the experimental error of the measurement of
30 the CA is significant, we used the curves depicting the evolution of CA with time as a more reliable indicator of the hydrophilicity of the surface

We first exposed PC substrates (previously treated with vaporous of dichloromethane (DCM)) to a 0.58% (w/w)
35 solution of PAH* (pH = 11.2) for 20, 40, 60 and 125 minutes at room temperature (T = 22 °C). We washed and dried the plates, left them in air and recorded the evolution of the CA of water in air (Fig S1). We did not observe any significant influence of the time of exposure of PC to the solution of
40 PAH* on the values and evolution of CAs. 40-60 minutes of treatment at room temperature is sufficient to obtain the maximum attainable hydrophilicity of the surface. Higher temperature of the coating results in slightly smaller values of CAs. In accordance with our other experiments on binding

amines[1] suggested that increased temperature may increase the rate of adsorption of the polyamine. We exposed PC plates to PAH* analogously as in the previous experiment but at two different temperatures (T = 22 °C and T = 50 °C) for 40 and 60 min respectively. Higher temperature of the coating results in slightly smaller values of CAs (Fig. S2). We observed that coating conducted at T = 50 °C yields CAs ~5° smaller than in the case of room temperature (RT) (T = 22 °C) regardless of the time of exposure to the solution of PAH*. At temprature T = 50°C 40 minutes and 60 minutes of exposure to PAH* the CAs were measured as 46.9° and 36.1° respectively. At T = 22 °C this values were 52° and 44.6° respectively. These results confirms also the minor decrese of the CA with increasing time of exposition. 60 minutes of exposure to PAH* decreases the CA by 7-9° with respect to 40 minutes of exposure.

Studies[2, 3] of deposition of PAH on other substrates than PC showed the importance of the value of pH of the solution on the efficiency of coating. We found that at low values of pH there are no free amine group to react with the carbonate bonds on PC. In order for the reaction to occur the pH has to be higher than a threshold that we identify as pH=10.15 (Fig. S3).

Additional experiments

To achieve higher efficiency of coating the first layer of polymer we pre-exposed the surface of polycarbonate to O2-plasma and to UV prior to the treatment with a soulution of PAH*.

PC pre-treated with O$_2$-plasma. We exposed the PC plates to high radio frequency O2-plasma (O2 content: 0.5 cubic feet per hour of air; exposure time: 15 and 30 min). After the plasma treatment we applied the PAH* treatment as described above. We measured the CA and the tested its recovery in air. We found that the CA and rate of the recovery was practically the same as in the case of PAH*-PC without plasma treatment.

PC pre-treated with UV. In this experiment we exposed the PC plates to UV light for 180 minutes before the PAH* treatment. We found that the UV treatment yields highly hydrophilic surface of PC with CA of water less than 10°. This hydrophilic character is stable in air but recovers to ~50° in few minutes of immersion in water or alcohols. After illumination with UV we treated the PC with PAH*. This resulted in deposition of an irregular and thick (several micrometers in thickness) layer of polymeric material on the surface of PC (Fig. S4). This layer formed irregular patterns and significantly decreased the transparency of the PC. We have not analyzed the composition of the layer. Exposure of the PC to UV creates –OH and –COOH (both the –C-O-O-H and O=C-O) groups and breaks polymer chains of PC. Such formed chemical entities could possibly react with PAH* creating the thick deposit on the surface of the plate. For these reasons it was not possible to use this method for modification of the microchannels.

In summary neither the O2-plasma nor the UV pre-treatment of the PC increased the efficiency of the application of PAH.
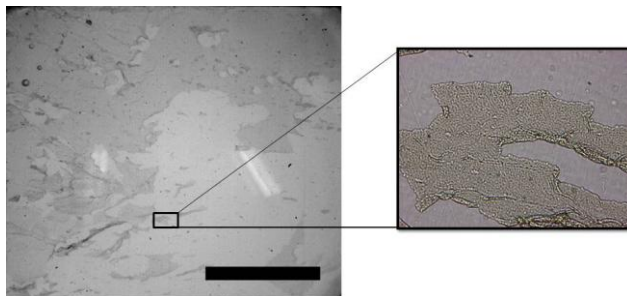

Fig. S4 Surface of UV pre-treated PC surface after exposure to a solution of PAH*. One can clearly see the macroscopic and irregular pattern of thick deposits on the surface of polycarbonate. The scale bar is 10 mm.

Results of XPS analyses.

substrate	PC	PC/DCM	PC/DCM	PC/DCM	PC/DCM	PC/DCM	PC/DCM
coating	none	none	PAH	PAH	PAH	PAH	PAH
exposure	none	none	none	AIR	H$_2$O	HEX	HEX/ISP
C1s	76.72	67.9	73.2	69.1	63.9	82	81.2
O1s	19	22.3	13.5	16.2	19.1	9.1	9.1
N1s	0.63		9.2	8	8.6	8.6	9.3
Si2p	3.7	9.7	4.1	6.7	8.5		0.4
S2p		0.1				0.3	

Table S1 Surface composition of substrates (in atomic %) determined by XPS analysis. The data shows significant increase of the Nitrogen-content in the PC samples coated with PAH*. Exposure of PC-PAH* substrates to air (AIR), water (H$_2$O) and hexadecane (HEX) for 48 hours does not alter the content of Nitrogen This indicates that the PAH* remains on the surface of the PC. Exposure to hexadecane is likely to leave traces of that oil on the substrate as the content of carbon is increased. The data shown for a combined exposure to hexadecane for 24h and subsequent immersion in isopropanol for 48h (HEX/ISP) indicate that the composition of the substrate does not change supporting the hypothesis that partial recovery of the hydrophilic character is associated with reorientation of the amine groups.

coating	none	PAH-PSS	PAH-PSS	PAH-PSS
exposure	none	AIR	H$_2$O	HEX
C1s	67.9	64.4	63.9	76.2
O1s	22.3	21	22.3	15.5
N1s		4.1	4.1	3.9
Si2p	9.7	6.5	6.8	0.5
S2p	0.1	4	3	3.8

Table S2 Surface composition of PC-PAH/PSS substrates (in atomic %) determined by XPS analysis. The data shows significant increase of the content of sulfur (S2p) that is not changed upon exposure to air, water or hexadecane. Samples immersed in hexadecane and then thoroughly washed indicate that trace amounts of the hydrocarbon chains are left on the substrate.

Re-activation of the PAH before PSS treatment.

To stabilize the hydrophilicity of the PC surface we laid on the PAH layer a layer of PSS to create PEM. To do so, first we had to convert the modified free amine groups of the PAH* back to their original forms.

Adding hydrogen chloride to a PC-PAH* converts back the

free -NH$_2$ groups to ammonium groups –NH$_3^+$ and that cationic charged surface can be used as a substrate for deposition of an anionic polyelectrolyte (Fig. S5). To do so we immersed the PC plates into HCl solution (pH=2.3) for 1 hour. (Our experiments showed that this time is necessary to convert a large enough fraction of NH$_2$ groups to the -NH$_3^+$ groups. Shorter treatment resulted in irregular patterns of wetting by water on the PC-PAH/PSS substrates.
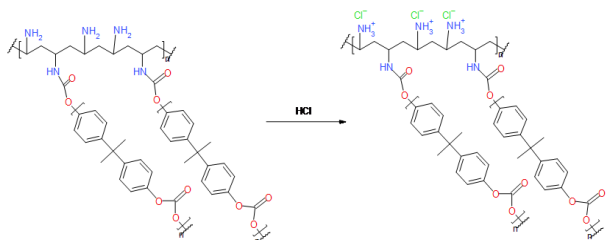

Fig. S5 Adding HCl to the PAH* the free amine groups, which did not react with the PC can be converted back to ammonium groups.

Methods

Chemicals. Hexadecane (n-Hexadecane, 95%) was purchased from Alfa Aesar, Germany; ethanol was purchased from Linegal Chemicals, Poland; isopropanol (2-propanol, pure p.a) was purchased from Chempur, Poland; 20cSt PDMS 200® oil (Poly(dimethylsiloxane), 200® fluid, viscosity 20cSt) was purchased from Sigma-Aldrich, Germany; Fluorinert (Fluorinert™ FC-770) was purchased from 3M, Belgium and Mineral oil was purchased from Sigma-Aldrich, Germany.

Fabrication of microdevice and microfluidic experiments. We milled rectangular microchannels (w=400 μm, h=200 μm) into 20x40 mm polycarbonate plates (Makrolon®, Bayer, Germany) of a thickness of 5 mm using MSG4025 CNG milling machine (ErgWind, Poland). As the covering plate we used PC plates of the same material with the same size but with the thickness of 0.75mm. The pieces were cleaned with detergent and water and dried with pressurized air. We swelled the pieces with DCM (Dichloromethane pure p.a.; Chempur, Poland) in vacuum and sealed as described elsewhere[4].

For generation of organic droples we used syringes (5 ml BD Discardit™ II) and syringe pumps (Harvard Apparatus, PHD 2000) to inject the liquids into the microchannels. For monitoring and recording we used Nikon SMZ1500 stereo microscope and a high speed camera (Photron Fastcam 1024 PCI, model 100K).

Surface treatment. We formed the first PAH* layer using a 0.58% (w/w) aqueous solution of PAH (Poly-(allylamin hydrochloride; Sigma-Aldrich, Germany). We added drop-by-drop 2M NaOH (Sodium hydroxide pure p.a.; Chempur, Poland) to increase the pH and to convert PAH to PAH*. The pH values of the solutions of PAH* used in our experiments were between 10.2 and 11.6. For PAH/PSS treatment first we used the same PAH solution as in PAH* monolayer treatment. Then we rinsed the surface with de-ionized distilled water and immersed the plate in an aqueous solution of HCl (Hydrogen chloride 35-38% pure p.a.; Chempur, Poland) of pH of 2.3. After rinsing we immersed the plate in an aqueous solution of 0.1% (w/w) PSS (poly(sodium 4-styrene sulfonate; Sigma-Aldrich, Germany) and 0.5M NaCl. Then the surface was rinsed again with distilled water than dried with pressurized air. For modification of the microchannels we flushed the solutions through the device with Harvard Apparatus PHD 2000 at low rates of flow (0.5-1 mL/h).

For qualitative analysis of each step of the modification process we used 20x40 mm PC of a thickness of 0.75 mm. The cleaned PC plates were swelled in vacuum with dichloromethane vapour and heated in oven at 130°C prior to use in order to mimic the conditions of the sealing process[13]. After that we coated them with polyelectrolytes as described above and in the text. In the tests against exposure to different fluids, after exposure the plates were rinsed (with water, and in the case of immersion in hexadecane, first with isopropanol and than with water) and dried with pressurized air.

Contact angle measurements were performed using static sessile drop method. We took images of a 2 μL droplet of distilled water on the surface with a CCD camera (uEye; IDS Imaging Development Systems GmbH, Germany; Objective: Pentax TV Zoom Lens 12.5-75 mm 1:1.8) and software (uEye Demo 3.32, IDS Imaging Development Systems GmbH, Germany). The CA was than measured using software (Fiji, ImageJA 1.42e). Each value of a single CA presented in this report is an average of at least 5 independent measurements.

Surface analysis. The chemical nature of the components formed within the surface region were investigated by means of XPS. The XPS spectra were recorded on a PHI 5000 VersaProbe™ scanning ESCA Microprobe using monochromatic Al-K$_\alpha$ radiation (hν = 1486.6 eV) from an X-ray source operating at 200 μm spotsize, 50 W and 15 kV. Elemental quantification was done using PHI_MultiPak ver. 9.0 software.

References and Notes

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