

Video Article

Preparation of Light-responsive Membranes by a Combined Surface Grafting and Postmodification Process

Katrin Schöller¹, Lukas Baumann¹, Dirk Hegemann², Damien De Courten³, Martin Wolf³, René M. Rossi¹, Lukas J. Scherer¹

¹Laboratory for Protection and Physiology, Empa, Swiss Federal Laboratories for Materials Science and Technology

²Laboratory of Advanced Fibers, Empa, Swiss Federal Laboratories for Materials Science and Technology

³Division of Neonatology, University Hospital Zurich

Correspondence to: Lukas J. Scherer at Lukas.Scherer@empa.ch

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Abstract

In order to modify the surface tension of commercial available track-edged polymer membranes, a procedure of surface-initiated polymerization is presented. The polymerization from the membrane surface is induced by plasma treatment of the membrane, followed by reacting the membrane surface with a methanolic solution of 2-hydroxyethyl methacrylate (HEMA). Special attention is given to the process parameters for the plasma treatment prior to the polymerization on the surface. For example, the influence of the plasma-treatment on different types of membranes (e.g. polyester, polycarbonate, polyvinylidene fluoride) is studied. Furthermore, the time-dependent stability of the surface-grafted membranes is shown by contact angle measurements. When grafting poly(2-hydroxyethyl methacrylate) (PHEMA) in this way, the surface can be further modified by esterification of the alcohol moiety of the polymer with a carboxylic acid function of the desired substance. These reactions can therefore be used for the functionalization of the membrane surface. For example, the surface tension of the membrane can be changed or a desired functionality as the presented light-responsiveness can be inserted. This is demonstrated by reacting PHEMA with a carboxylic acid functionalized spiropyrans unit which leads to a light-responsive membrane. The choice of solvent plays a major role in the postmodification step and is discussed in more detail in this paper. The permeability measurements of such functionalized membranes are performed using a Franz cell with an external light source. By changing the wavelength of the light from the visible to the UV-range, a change of permeability of aqueous caffeine solutions is observed.

Video Link

The video component of this article can be found at <https://www.jove.com/video/51680/>

Introduction

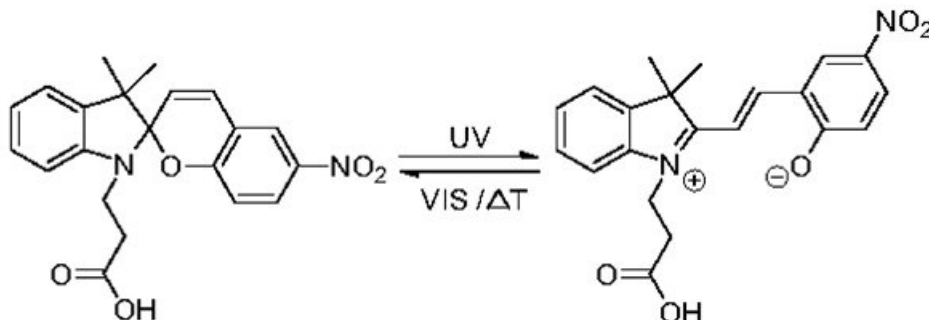
Plasma modification of materials has become an important process in many industrial fields. Cleaning of surfaces and functionalization of surfaces without changing the bulk property of the material has made the plasma treatment an essential process in surface science¹⁻⁸.

Plasma treatment of polymers results in homolytic bond cleavage. This leads to an edging of the polymeric material and to the formation of radical rich surfaces. By using plasma containing oxygen molecules, the surface becomes oxygen rich and thus more hydrophilic⁹⁻¹¹. However, the hydrophilicity of the surfaces is not stable over time¹². In order to enhance the long-term stability, the plasma treated surface can be chemically modified after or during the plasma process¹³⁻¹⁵. This treatment is normally performed by adding a reactive monomer species into the gas phase during the plasma process; these monomers then polymerize from the created radicals of the polymer surface. If the chemical treatment is performed with a nonvolatile monomer, the polymer grafting has to take place after the plasma modification. In order to perform a controlled grafting after the radicals are formed on the surface, a plasma setup is described, which allows the plasma-initiated surface-induced polymerization from the surface in solution under controlled conditions^{12,16}.

The presentation focuses on the modification of track-edged polymer membranes^{12,17}. By modifying the surface tension of these membranes, the permeability rate can be varied¹². This clean and fast process allows the creation of very thin layers (<5 nm), which cover the entire membrane surface without changing the bulk property of the polymer membrane. Due to the edging during the plasma process, the pore diameters of the track-edged membranes augment slightly¹². The edging rate is depending on the polymer and has a linear behavior.

When using monomers with reactive functional groups, the grafted polymers can be further functionalized. This is demonstrated by the postmodification of a PHEMA-grafted membrane with a carboxylic acid functionalized spiropyran. This results in a photochromic surface, since spiropyran is known to transform into a merocyanine species when irradiated with UV-light. The spiropyran form can be reestablished by irradiating the merocyanine form with visible light (**Figure 1**)^{18,19}. Since the merocyanine form is more polar than the spiropyran state, the surface tension of the coating can be triggered with light²⁰. The change in surface tension influences the permeability resistance of the membrane towards aqueous solutions. The set-up how to perform the permeability tests of these light-responsive membranes will be shown and the

significant change in permeability resistance (decrease in permeability resistance by 97%) is demonstrated. Such a membrane can be integrated in a drug delivery setup or in smart sensing systems.



spirobenzopyran 1

Figure 1. Photoisomerization of spirobenzopyran compound 1.

Protocol

1. Plasma-initiated Polymerization

- Preparing of monomer solution.
 - Dissolve HEMA (100 ml; 0.718 mol) in 200 ml water and wash 3x with hexane (100 ml) in a separating funnel. Saturate the aqueous phase with sodium chloride and extract the HEMA with diethyl ether (50 ml). Dry the organic phase over MgSO_4 and remove the solvent *in vacuo* (100 mbar, 40 °C). Distill the HEMA under reduced pressure (15 mbar; 99 °C).
 - Prepare a 0.62 M methanolic solution of the inhibitor-free HEMA produced in Section 1.1.1. Pour 30 ml of the solution into a one-necked flask and eliminate oxygen by bubbling Ar through the solution for 1 hr.
- Surface-induced polymerization.
 - Position two polycarbonate membranes next to each other into the plasma chamber (Figure 2). Place the shiny side of the membrane pointing towards the gas phase.
 - Connect the plasma chamber to a high vacuum (20 mbar) for 5 min. Close the valve to the vacuum and open the other valve, which is connected to argon and oxygen gas and purge the chamber with this mixture for 2 hr with 15 sccm argon and 2.5 sccm oxygen.
 - Initiate the plasma and reduce the power to the desired power (for polycarbonate membrane: 12 W) and treat the membranes for 4 min with the plasma. Connect the monomer solution with the chamber by opening the corresponding valve. Switch off the plasma and evacuate the chamber.
 - Connect the monomer solution with the chamber by opening the corresponding valve and pour the solution into the chamber. Ensure that the membranes are covered with the monomer solution. Open the valve connected to the argon and store the reaction mixture for 12 hr at 20 °C (conditioned room).
 - Remove the monomer solution. Wash the membranes with methanol in an ultrasonic bath for 5 min. Repeat the washing procedure with water.
 - Dry the membrane *in vacuo* over molecular sieves for 2 hr.

2. Postmodification of Coated Membranes

- Prepare a solution of spirobenzopyran 1 (Figure 1) (100 mg; 0.27 mmol), N,N-dicyclohexylcarbodiimide (DCC) (55 mg; 0.27 mmol) and dimethyl aminopyridine (DMAP) (33 mg, 0.27 mmol) in *tert*-butylmethylether (TBME) (12 ml).
- Place a protecting stirrer bar and a protecting grid into a round-bottom flask. Dry the flask and flood the flask with argon.
- Pour the solution into the flask, followed by the coated membrane.
- Stir gently at room temperature for 12 hr.
- Remove the solution and wash the membrane with *tert*-butylmethylether in an ultrasonic bath for 5 min. Repeat the washing procedure with ethanol and water.
- Dry the membrane *in vacuo* over molecular sieves for 2 hr.

3. Surface Tension Measurements

- Fix the membrane with a standard tape on a metal O-ring. Position a drop of nanopure water (3.3 μl) on that part of the membrane surface, which is not in contact with the O-ring. Measure the contact angle (CA) at 5 different spots of the membrane.
- For testing the long term stability of the samples, measure the contact angles at three different spots of the membranes after 0, 1, 2, 3, 7, 14, and 21 days.

4. Permeability Tests of the Photochromic Membranes

1. Fill the receptor chamber of the Franz diffusion cell with water (12 ml).
2. Fix the membrane in a Franz diffusion cell. Ensure that the membrane is in contact with the water of the receptor chamber. Fill the donor chamber (the chamber on top of the membrane) with an aqueous caffeine solution (20 mM; 3.0 ml). Irradiate the membrane from the top of the donor chamber with white-light (**Figure 3**). Collect samples (200 μ l) from the receptor cell; for track-edged polycarbonate membranes with a pore diameter of 200 nm, collect samples every 10 min.
3. Repeat the experiment as described in step 4.2. but irradiate the membrane with UV-light (366 nm, 80 W/m²) during the entire permeability test.
4. Determination of the caffeine concentrations of the collected samples.
 1. Plot a calibration curve with 15 different caffeine concentrations (between 0.05 mg/ml and 1.5 mM/L) using a UV/Vis spectrometer. Calibrate at 293 nm.
 2. Determine the concentration of each of the collected samples using the calibration curve.
 3. Plot the determined concentration vs. the time of the collected samples. Make a linear fit through the points and determine Δc from the slope.

Representative Results

The etch rate can be followed by weighing the membrane after different periods of time. As can be seen from **Figure 4**, the etch rate follows for polyester, polyvinylidene fluoride, and polycarbonate membranes a linear etch rate, which can be determined from the slope of the linear correlation of the etch time *versus* mass loss. As shown in **Figure 4**, the polycarbonate membranes show the lowest etch rate of all the three polymer membranes. One consequence of the etching is the change in pore diameter. The diameter of the pores after plasma treatment increases by about 20%^{12,17}. The subsequent polymer grafting has on the other hand no significant influence on the pore diameter, which is due to the very thin polymer layer of 1–4 nm¹². Most importantly, the whole process does not influence the pore structure of the membrane.

The whole coating process can easily be followed measuring the contact angle. The original polycarbonate membrane has a low contact angle of about 60°, which is due to the polyvinylpyrrolidone (PVP) coating of commercial available polycarbonate membranes. The edging during the plasma treatment destroys the PVP coating and the resulting contact angle before grafting the polymer becomes more hydrophilic (25°) due to the oxygen containing plasma. The unstable surface becomes more and more hydrophobic with time (80° after 21 days)¹². Subsequent PHEMA grafting leads to a coating with a contact angle of about 90°, depending also on the pore size of the membranes. In **Figure 5** the difference in contact angle between the uncoated membranes and PHEMA grafted membranes (with pore diameter of 0.2 μ m and 1 μ m) is shown. **Figure 6** shows additionally the contact angle of a PHEMA coated polycarbonate membrane *versus* time. It is clearly visible that the contact angle does not change over time, which is an indication for a long-term stable coating. The postmodification with compound **1** increases the contact angle to 100°. However, spirobenzopyran can be transferred into the more polar merocyanine species by illuminating with UV-light (**Figure 1**), and this transformation reduces the contact angle of the membrane surface again to 90°.

The permeability of the membranes is measured using a Franz diffusion cell (**Figure 3**). The samples are taken from the receptor chamber to determine the permeability resistance of the membranes. The membrane permeability of the spirobenzopyran modified membrane is studied under UV-light irradiation and under white light irradiation. As can be seen from **Figure 7**, the resistance of the permeability change decreases by 97% when the membrane is illuminated with white light. This demonstrates the presence of a light-responsive membrane.

In addition, it is possible to attach an additional light source to the Franz diffusion cell (**Figure 3**). In this device optical fiber bundles are connected to a white light and UV light (366 nm) source, which allows a faster switching from one wavelength to another. Since optical fibers maintain the temperature during the irradiation, no increase in temperature is observed by either white light illumination or by UV-light illumination.

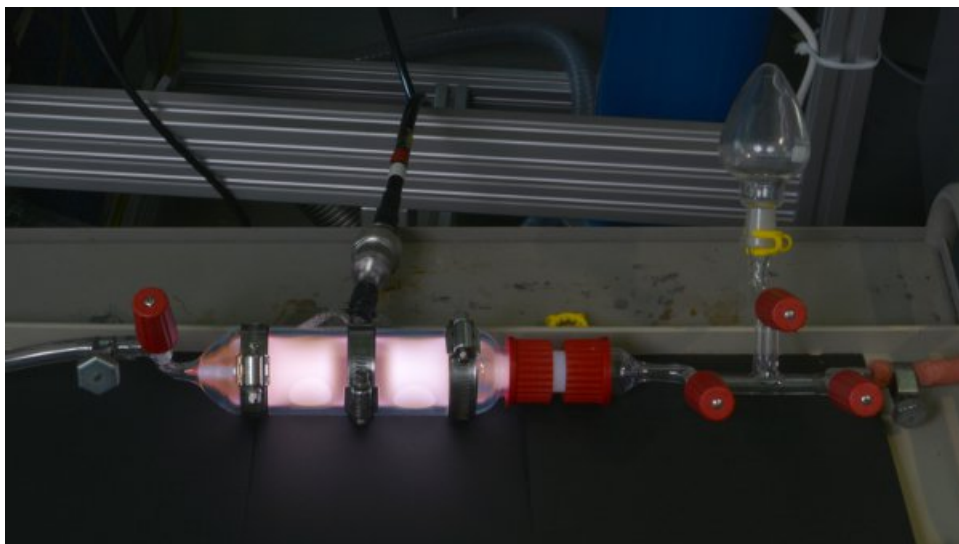


Figure 2. The plasma chamber with the two positioned membranes inside the chamber and the two valves to the *vacuum* and the gas mixture, respectively.



Figure 3. The Franz diffusion cell with the fixed membrane between the receptor chamber (bottom) and the donor chamber (top). The light source is fixed on top of the Franz diffusion cell (here: UV light).

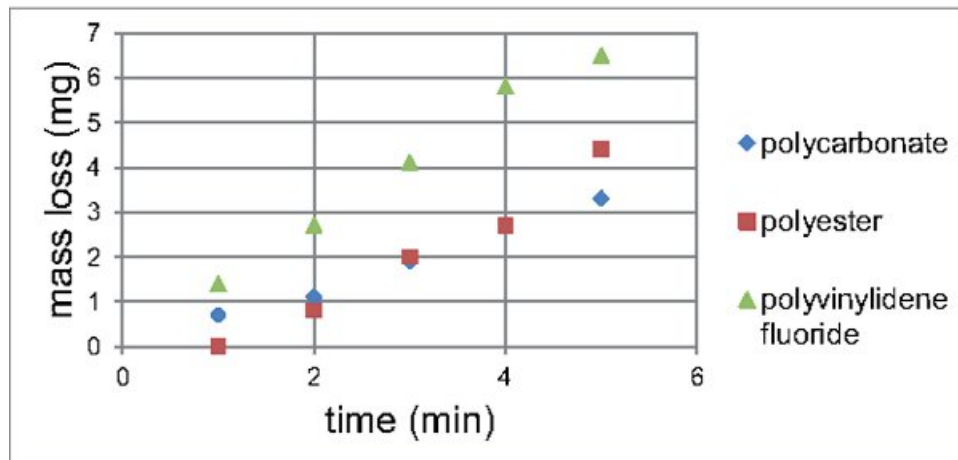
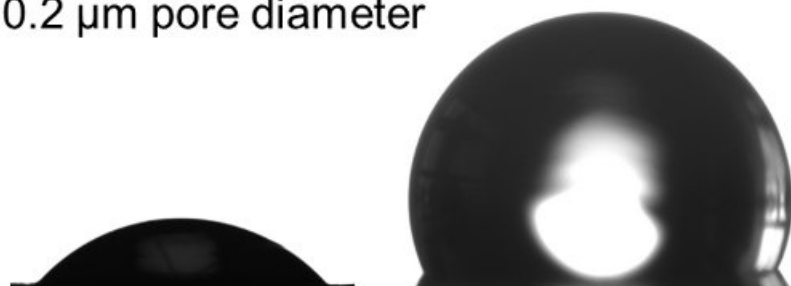


Figure 4. Etch rate at 10 W of membranes consisting of different polymers.

0.2 μm pore diameter



1 μm pore diameter

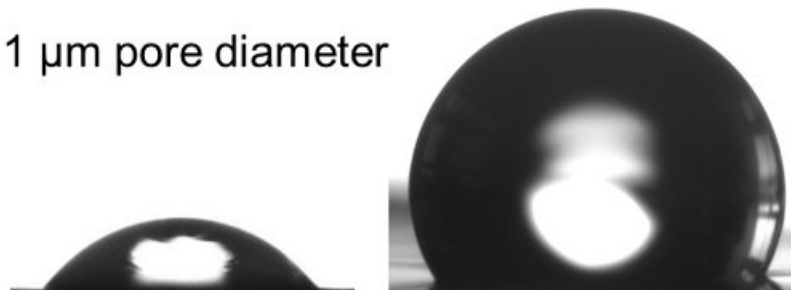


Figure 5. The contact angle of a water droplet changes when the porous polycarbonate membranes (upper row: 0.2 μm pore diameter, lower row: 1 μm pore diameter) are coated with PHEMA via plasma-induced polymerization (left side: before polymerization, right side: after polymerization).

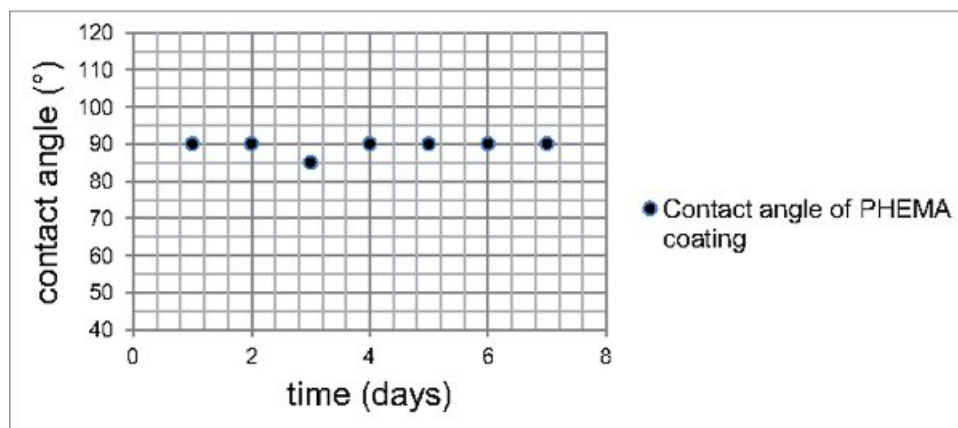


Figure 6. Contact angle measurement of PHEMA grafted membrane showing the long-time stability of the coating.

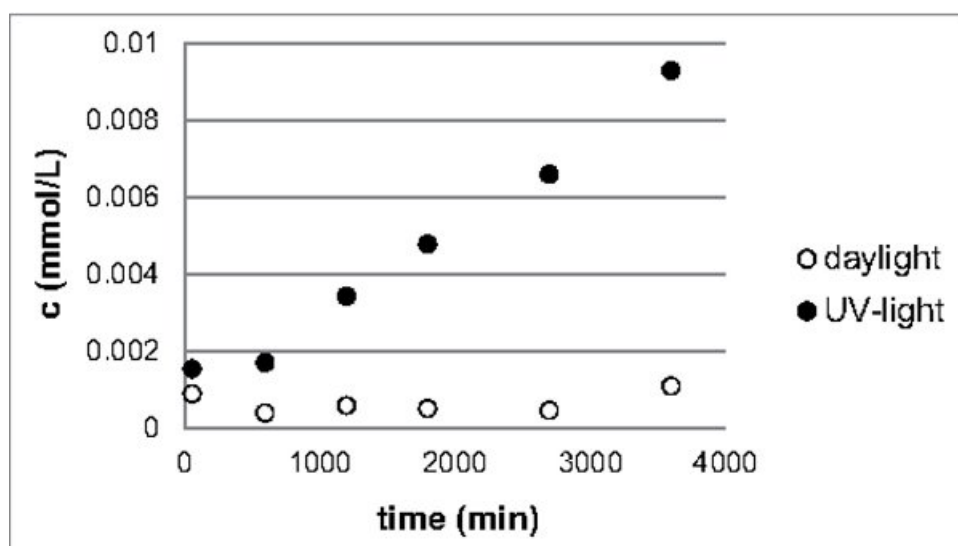


Figure 7. Permeability measurements of aqueous caffeine solution (20 mM) through a white-light irradiated membrane and through an UV-light irradiated membrane.

Discussion

The plasma process produces a purple gas, which is caused by ionized argon. An orange color would indicate the presence of undesired nitrogen from a leak. The plasma process does not only form radicals on the surface but also etches the membrane^{7,12}. Too much etching can change the pore diameter significantly, which would influence the permeability of the membrane. The controlled reaction conditions of the presented setup allow enhancing the reproducibility of the plasma-initiated grafting process. Nevertheless, the exact position of the membranes in the plasma chamber can still influence the density of the formed radicals on the surface due to inhomogeneity of the plasma. The edge rate is also dependent on the applied power and on the exact gas composition.

The characterization of such thin coatings is not trivial due to the comparably rough surface of the commercial membrane. As described before^{12,21}, the layer thickness was determined using ellipsometry and XPS experiments. In order to analyze a flat surface, polycarbonate was spin-coated on Si-wafers as model polycarbonate surfaces. These polycarbonate coatings were then treated as the polycarbonate membranes in the described procedure. In addition, multiphoton microscopy studies revealed to be a very valuable measurement technique to evaluate if only the outer surface of the membrane is coated or if the coating took place in the pores as well²¹.

Due to high compatibility of the random polymerization with functional groups, a broad variety of acrylates can be used as monomers. This allows the use of monomers with functional groups. In the present example, the alcohol group can be esterified with a carboxylic acid group. The limitation of the grafting process is the solvent that can be used. Since the polycarbonate membrane dissolves in many organic solvents such as ethyl acetate, tetrahydrofuran, chloroform, or acetone, these solvents should be avoided for the polymerization as well as later for the postmodification process. Suited solvents are water, alcohols such as methanol, ethanol, propanol, aliphatic and aromatic solvents such as hexane, xylene, and some ethers. The concentration of the monomer solution does not significantly change the coating thickness. Therefore this process is not suited for the formation of thick coatings. However, the thin coating allows the use of brittle and rigid polymers (e.g. PMMA) as coating material without influencing the flexibility of the bulk flexible membrane. As previously shown, the polymer can also consist of different monomers to form copolymers¹⁷.

Since the polycarbonate membrane slightly swells in diethyl ether, TBME is used in the present case for the postmodification procedure. The postmodification takes place at room temperature using TBME as solvent and DCC as coupling agent for the esterification of the alcohol with the carboxylic acid moiety of the spirobenzopyran compound **1**¹⁷. Since TBME as nonpolar solvent does not wet the pore walls, only the outer membrane surface is functionalized with spirobenzopyran. The postmodification process can also be used to change the surface tension of the surface or to bring other functionalities onto the surface¹². The demonstrated example modifies the membrane into a light-responsive membrane. Responsiveness to other stimuli like pH, temperature, chemical compounds or electricity is supposable.

With the demonstrated method, a light-responsive membrane is prepared with a remarkable response concerning the permeability rate of caffeine. Interestingly, when the spirobenzopyran unit is copolymerized with the HEMA in one step, the response is much lower¹⁷. Since the coating is much thinner than the pore diameter (even when swollen in water), the change of pore diameter can be excluded as reason for the change in permeability. Anyway, since the more polar merocyanine would swell the grafted polymer better in water than in its less polar spiropyran state, a reversed photo-switch would then be expected. The reason for the change in permeability is the change in surface tension, which defines the permeability rate of aqueous systems as previously shown¹².

This kind of stimuli-responsive membranes can find applications in switchable drug delivery system or in smart sensor systems. Such a smart drug delivery system can be used to prevent apnea of preterm neonates²¹. Other areas, in which light-responsive membranes can be used are biotechnology, microfluidics or for light-powered molecular shuttles²².

Disclosures

The authors have nothing to disclose.

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