

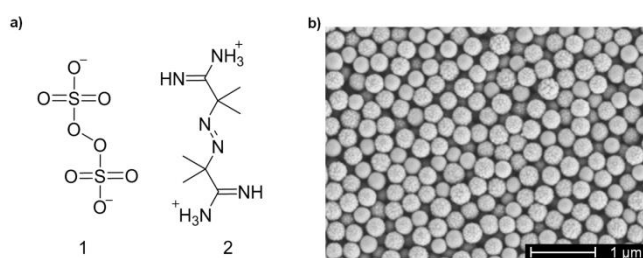
## SUPPLEMENTARY MATERIAL TO ARTICLE

### Particle Adsorption on a Polyether Sulfone Membrane: How Electrostatic Interactions Dominate Membrane Fouling

D. Breite<sup>a</sup>, M. Went<sup>a</sup>, I. Thomas<sup>a</sup> and A. Schulze<sup>a†</sup>

#### Supplementary Material to Section 3.1 Characteristics of PS Beads

The synthesis of PS particles as described in section 2.2 enables the tuning of the surface charge of the beads. According to the reaction mechanism of the radical emulsion polymerization the initiator molecules form radical species which react with small amount of styrene monomer dissolved in water. Oligomers are formed due to chain propagation reaction and finally start to precipitate. Then, the precipitated hydrophobic polymer chains form a spherical shape to minimize their interface with the surrounding aqueous media. The charged and hydrophilic groups of every polymer chain which originate from the initiator molecule (figure **S1a**) assemble at the outer surface of the polystyrene bead. This results in a highly charged particle surface. After this first nucleation process particle growth continues by addition of more precipitating oligomer and polymer chains.



**Figure S1** (a) Initiator molecules (1) KPS and (2) AIBA; (b) SEM picture of cationic PS beads.

The particle growth depends on many different parameters: choice of initiator and surfactant, reaction time, concentration of styrene, initiator and surfactant, impeller shape and speed, temperature and delay time before addition of surfactant. In this study the focus was to present a new method using differently charged polystyrene beads to determine electrostatic interactions while membrane fouling. Therefore,

the particle size was adjusted to a value of around 0.2 µm, which is smaller than the pore size of the PES membranes (~ 0.8 µm). This way, particles can pass through the membrane when no interactions between membrane and particles occur, and fouling due to size exclusion is prevented. The polydispersity index (PDI) characterizes the degree of polydispersity of the particle sizes. Particle suspensions with a PDI below 0.05 can be assumed to be monodisperse, which applies to all synthesized particle suspensions (table **S1**). The particle diameters (table **S1**) were determined with dynamic light scattering and have been confirmed by SEM pictures taken from particles, which were spincoated on silica wafers as shown in figure **S1b**.

**Table S1** Particle size and PDI of PS beads.

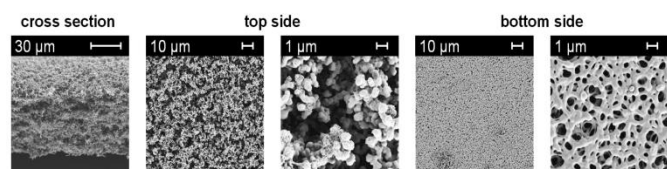
bead species	particle diameter [nm]	PDI
anionic	183	0.015
cationic	220	0.018

#### Supplementary Material to Section 3.2 Characteristics of PES Membranes

The PES membranes used in this work were prepared using a NIPS process. As described in section 2.3 the polymer solution, consisting of PES, NMP, and PEG was casted on a glass plate, followed by humidification, and precipitation in cooled water. The membranes were then washed. After drying, the thickness of the resulting membrane was determined to be  $72 \pm 3$  µm. The structure of the gained membrane was investigated using SEM. SEM images of the cross section, top and bottom side are presented in figure **S2**. The structure was found to be open on top as well as on the bottom side, while the cross section shows a sponge like structure. This way, permeation of differently charged PS beads is preserved.

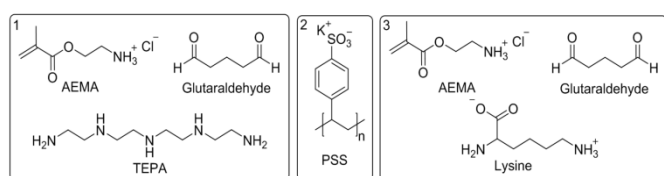
<sup>a</sup> Leibniz Institute of Surface Modification, Permoserstraße 15, Leipzig, D-04318 (Germany).

† E-mail: agnes.schulze@iom-leipzig.de; Tel.: +49 341 235 2400



**Figure S2** SEM pictures of cross section, top and bottom side of the PES-REF membrane.

The modification of the PES membranes as described in section 2.4 with the reagents shown in figure S3 enables to permanently hydrophilize a membrane's surface. Due to the electron beam irradiation radical species are formed leading to a grafting reaction. This way, chemical bonds between the membrane and the used modification reagent are formed. In the case of the PES-TEPA membrane aminoethyl methacrylate (AEMA, figure S3.1) is grafted on the membrane surface following a grafting-from mechanism. This leads to polymer chain growth which starts at the membrane surface and builds up polymer chains containing amino functions. These functions will then be used to react with glutaraldehyde (figure S3.1) forming a Schiff base. The remaining aldehyde function forms in a subsequent reaction a Schiff base with an amino group of TEPA (figure S3.1) leading to the intermediate structure shown in figure S4.1. To obtain the alkaline structure of the PES-TEPA membrane (figure S4.2) the reactions with GA and TEPA are repeated to further improve the density of functional groups.



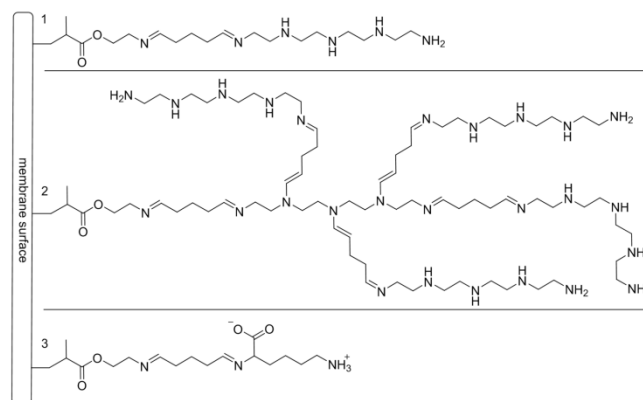
**Figure S3** Reagents for membrane modification (1) PES-TEPA, (2) PES-PSS, (3) PES-Lysine.

The reaction with PSS (figure S3.2) follows a grafting-to mechanism leading to the formation of PES-PSS membrane. Here, no further chemical reactions are needed to gain the final membrane modification.

To obtain the PES-Lysine membrane a grafting-from reaction with AEMA (figure S3.3) and the subsequent reaction with GA (figure S3.3) are conducted as described for the PES-TEPA membrane. Then, the remaining aldehyde function forms a Schiff base with the amino group of lysine (figure S3.3) resulting in the zwitterionic structure of the PES-Lysine membrane (figure S4.3).

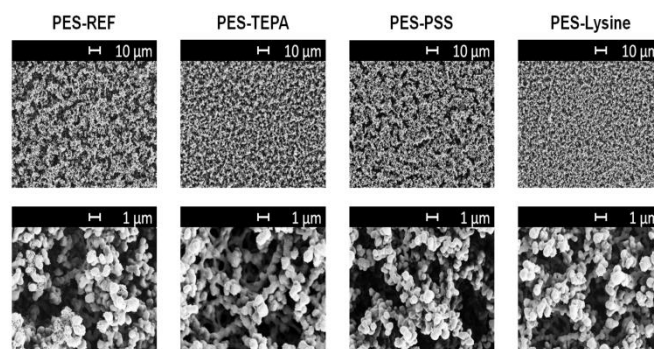
The morphology of the different modified membranes was investigated using SEM and mercury porosimetry. SEM pictures of the untreated and modified membrane's top side are shown in figure S5. The open pore structure remains without unwanted pore blocking independent of the applied modification. This is in agreement with the results obtained from mercury porosimetry, which are shown in table S2. All samples have a porosity of around 70%. The average pore size

of 0.83  $\mu\text{m}$  of the PES-REF membrane slightly decreases for the PES-TEPA (0.74  $\mu\text{m}$ ) and PES-Lysine (0.76  $\mu\text{m}$ ) membrane and the PES-PSS membrane remains with an average pore size of 0.64  $\mu\text{m}$ . This may indicate a narrowing of the membrane pores due to the modifications or results from slight differences during the membrane preparation. Nevertheless, our fouling experiments revealed that in case of electrostatic repulsive interactions, the used PS beads can still permeate through the membrane.



**Figure S4** Structures of modifications (1) PES-TEPA (intermediate), (2) PES-TEPA, (3) PES-Lysine.

The water permeation flux (table S2) also remained the same for all membranes and was determined to be about 32-37 mL/(min $\cdot$ cm $^2$  $\cdot$ bar). The slightly increased values of the PES-TEPA and the PES-Lysine membrane can be explained by the increased hydrophilicity.



**Figure S5** SEM pictures of top side of modified membranes.

XPS elemental composition varies for the differently modified membranes, as shown in table S2. The PES-REF membrane is composed of carbon (74.9%), oxygen (19.8) and sulfur (5.3%). This composition remains nearly unchanged for the PES-PSS membrane (73.3% C, 20.4% O, 6.3% S), because the modification reagent has similar chemical structures. Contrary, the PES-TEPA membrane shows a significant value of nitrogen (3.4%) due to the amino groups of the dendrimeric structures as shown in figure S4.2. The PES-Lysine membrane also shows 1.5% of nitrogen and a slightly increased amount of oxygen (21.6%). This is in accordance with the structure of the surface modification as shown in figure S4.3.

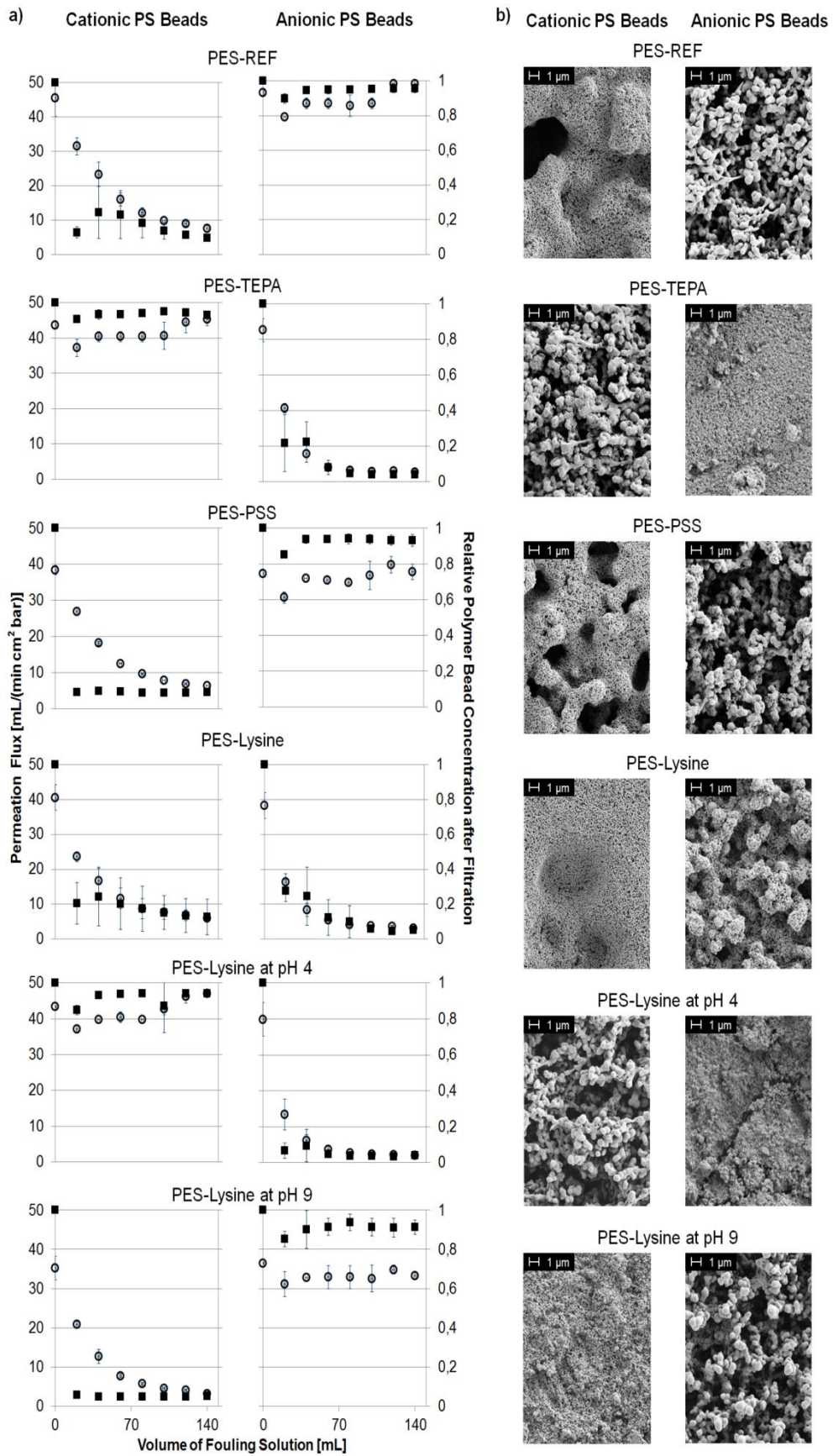
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**Table S2** Characteristics of modified PES membranes.

membrane property	PES-REF	PES-TEPA	PES-PSS	PES-Lysine
water permeation flux [mL/(min cm <sup>2</sup> bar)]	32 ± 6	35 ± 2	32 ± 4	37 ± 1
porosity [%]	73 ± 3	71 ± 7	68 ± 2	75 ± 1
average pore size [μm]	0.83 ± 0.04	0.74 ± 0.05	0.64 ± 0.01	0.76 ± 0.03
elemental composition [%]				
C	74.9	71.3	73.3	72.1
O	19.8	20.6	20.4	21.6
S	5.3	4.7	6.3	4.8
N	-	3.4	-	1.5

**Supplementary Material to Section 3.3 Membrane Fouling with PS Beads**

The following figure **S6a** shows the complete overview of fouling experiments of the different membranes using anionic and cationic PS beads. Permeation flux and the relative concentration of polymer beads in the filtrate are plotted against the volume of PS bead suspension passed through the membrane. If not stated differently, the pH of the filtered solution was 7. All error bars shown represent 95% confidence values. The corresponding SEM pictures of the different membranes after fouling are shown in figure **S6b**.



**Figure S6** (a) Permeation flux of fouling suspension (left axis, open circles) and normalized concentration of PS beads in filtrate (right axis, filled squares) vs. volume of PS bead suspension, and (b) corresponding SEM pictures of all examined membrane after fouling.