Functionalization of Electrospun Membranes with Polyelectrolytes for Separation of Oil-In-Water Emulsions

Yi Min Lin, Chen Song, and Gregory C. Rutledge*

Membrane fouling in microfiltration of oil-in-water emulsions is influenced by electrostatic interaction between the membrane and surfactant-stabilized emulsions. A method to alter the electrostatic properties of electrospun fiber membranes using layer-by-layer (LbL) polyelectrolyte assembly is developed to improve fouling resistance. Plasma pretreatment and successive depositions of polycations and polyanions from solutions are shown to alter the surface charge of electrospun polyamide membranes, while maintaining their interconnected pore structure and high porosity. The LbL composite membranes were challenged by two types of emulsions, stabilized by anionic and cationic surfactants, respectively, in dead-end and cross-flow filtrations. When separating emulsions stabilized by anionic surfactants, the permeate flux of the plasma-treated and polyanion-coated membranes increased ≈3.2-fold and ≈2.5-fold, respectively, compared to that of the as-electrospun membranes, after 4 h of cross-flow filtration. When separating emulsions stabilized by cationic surfactants, the permeate flux of the polycation-coated membrane similarly increased ≈3.3-fold. Electrostatic repulsion strength is proposed as a metric to quantify this behavior. This work demonstrates the versatility of functionalizing electrospun microfiltration membranes using LbL assembly for the separation of oil-in-water emulsions, and suggests a strategy for membrane design to resist fouling based on tuning of the electrostatic interactions.

1. Introduction

Every day, large quantities of oily wastewater are generated from petrochemical, metallurgical, pharmaceutical, food, and beverage industries. The compositions and properties of these effluents differ substantially depending on their sources.\textsuperscript{[1]} Unintentional release of the oily wastewater to the environment without appropriate treatment can cause negative impacts on the aquatic plants and animals. However, the reclamation of industrial oily wastewater faces a number of challenges due to the large volume and the variety of the discharged solutions.\textsuperscript{[2]} Conventional techniques to separate oil and water, such as gravity-based or centrifugal separations, become inefficient when the oil is present as an emulsion, with droplet sizes below 20 μm.\textsuperscript{[3]} In comparison, membrane separations have demonstrated high oil removal efficiency, low energy cost, and compact design; they have therefore received attention for the treatment of oil-in-water emulsions.\textsuperscript{[4,5]}

However, the primary challenge of membrane technology in this application is fouling, which leads to flux decline, inefficient separation, and increased material and energy costs.\textsuperscript{[6]} Hence, developing new strategies and types of membranes to reduce fouling is critically important for separation of oil-in-water emulsions.

It is generally thought that membranes with high hydrophilicity can reduce the adhesion of oil droplets on the membrane surface, thereby limiting the degree of fouling.\textsuperscript{[4]} Therefore, a number of studies have been reported to improve the anti-fouling property, hydrophilicity, and underwater oleophobicity of polymeric membranes by blending with hydrophilic components or surface modification.\textsuperscript{[7–12]} For example, Ochoa et al. blended poly(methyl methacrylate) (PMMA) with polyvinylidene fluoride (PVDF) ultrafiltration membranes, and showed that the addition of PMMA could reduce the deposition of foulants on the membrane surface.\textsuperscript{[9]} Zhao et al. added amphiphilic zwitterionic copolymer brushes into PVDF casting solutions to prepare fouling-resistant ultrafiltration membranes.\textsuperscript{[10]} Moghimifar et al. modified the surface of polyethersulfone phase-inversion membranes by corona plasma-assisted coating of TiO\textsubscript{2} nanoparticles, and enhanced the hydrophilicity and permeate flux.\textsuperscript{[11]} Wang et al. fabricated membranes of electrospun fibers whose surfaces were modified with polydopamine nanoclusters, resulting in high underwater oleophobicity and high permeate flux (≈1600 L m\textsuperscript{-2} h\textsuperscript{-1} (LMH)) when separating oil-in-water emulsions in a gravity-driven process.\textsuperscript{[12]} However, in addition to hydrophobic interaction, several research groups including our own have previously shown that the membrane fouling is also influenced by the electrostatic interaction between the membrane and the emulsified oil drops, due to the presence of stabilizing surfactants.\textsuperscript{[13–19]} Since the compositions and properties of such surfactant-stabilized
oil-in-water emulsions in industrial wastewaters vary widely, we would like to have a membrane design strategy by which the properties of the membrane can be adjusted according to the nature of the emulsion. We propose to take advantage of electrostatic interactions for this purpose to reduce fouling in the filtration process.

One approach to modify the electrostatic properties of membranes is layer-by-layer (LbL) polyelectrolyte assembly. LbL polyelectrolyte assembly is a thin film fabrication technique in which conformal coatings of polyelectrolytes with thickness down to a few nanometers can be formed on the surfaces of various materials. LbL assembly relies on the complementary interactions between two or more oppositely charged polyelectrolytes (i.e., polyanions and polycations) that are adsorbed sequentially onto a surface. The thickness can be tuned by changing the pH or ionic strength of the polyelectrolyte solutions. The surface charge of the substrate is thereby determined predominantly by the outermost layer of the film, being either polyanionic or polycationic. Choi et al. investigated the influence of degree of ionization of poly(allylamine hydrochloride) and poly(acrylic acid) (PAA) on the bilayer thickness by adjusting the pH of solutions. Tripathi et al. enhanced the hydrophilicity of poly(ethylene terephthalate) track-etched membranes by applying multilayer assemblies of poly(sodium styrene sulfonate) and poly(diallyldimethylammonium chloride). LbL depositions of polyelectrolytes have been used to render membranes resistant to proteins, cells, or bacteria.

Also, polyelectrolyte multilayers can act as selective barriers for nanofiltration, reverse osmosis or forward osmosis membranes to separate monovalent or divalent cations and anions in aqueous solutions. Several works have reported improved under-water oleophobicity and thereby antifouling performance of electrospun membranes for separation of oil-in-water emulsions, two model emulsions of dodecane in water were prepared, stabilized by either anionic or cationic surfactants, to simulate the breadth of oily industrial wastewaters. Electrospun polyamide membranes were modified by plasma pretreatment and by LbL deposition of polyelectrolytes for different deposition times and with either polyanion or polycation outermost layers. The as-spun and modified membranes were then challenged by the emulsions in both dead-end and cross-flow systems at constant pressure.

2. Results

2.1. Characterization of Emulsions

Figure 1 shows the distributions of droplet diameter for representative emulsions of dodecane in water (250 ppm) stabilized by sodium dodecyl sulfate (SDS) and myristyltrimethylammonium bromide (MTAB), respectively, along with the best fit Gaussian distributions. These surfactants were chosen for the difference in charge on their head groups and similarity of their linear hydrocarbon tails. The volume-weighted average diameter and standard deviation were 480 ± 33 and 485 ± 36 nm, for SDS and MTAB, respectively. The distributions of drop size in the feed emulsions remained stable for the duration of the separation tests. The pH and zeta potentials of the dodecane emulsions are shown in Table 1. The zeta potentials were determined mainly by the ion head group of the surfactant, and are shown in Table 1.

A particularly interesting class of membranes for LbL modification is that comprising electrospun fiber mats. Electrospun membranes were originally applied to air filtration because of the high separation efficiency provided by their small fiber diameters (∼0.1–1 µm) and correspondingly small interfiber distances. More recently, they have been considered for liquid separations in particular emulsions. The high porosity and high connectivity between the pores of an electrospun membrane ensure that fluids find alternative pathways to flow through the membrane even when some parts of the membrane are blocked. This robustness to blockage results in retention of permeate flux and better performance in the presence of fouling. Several works have reported improved underwater oleophobicity and thereby antifouling performance of electrospun membranes for separation of oil-in-water emulsions through modification of surface morphology. Here, we demonstrate the antifouling enhancement of electrospun fiber membranes in microfiltration of oil-in-water emulsions through modification of surface charge using LbL deposition.

To demonstrate the versatility of combining LbL polyelectrolyte assembly with electrospun polymeric mats for separation of oil-in-water emulsions, two model emulsions of dodecan in water were prepared, stabilized by either anionic or cationic surfactants, to simulate the breadth of oily industrial wastewaters. Electrospun polyamide membranes were modified by plasma pretreatment and by LbL deposition of polyelectrolytes for different deposition times and with either polyanion or polycation outermost layers. The as-spun and modified membranes were then challenged by the emulsions in both dead-end and cross-flow systems at constant pressure.

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2.2. Membrane Characterization

Fibrous membranes were prepared by electrospinning of poly(trimethyl hexamethylene terephthalamide) (PA6(3)T) from solution as described in the Experimental Section. This polymer was chosen due to its hydrophilicity and the ease with which uniform fibers with narrow diameter distribution can be formed.[39] The electrospun membranes were plasma-treated for 3 min (90 s per side) to make the mats hydrophilic and to impart an initial negative charge to the fibers (henceforth denoted as “plasma-3” membranes).[40,41] The plasma-3 membranes were then surface-functionalized with a branched polyethylenimine (bPEI) for 5 min (denoted as “bPEI-5”) to “flip the charge” on the membrane from negative to positive. To investigate the influence of dipping time, plasma-3 membranes were also surface-functionalized with bPEI for 10 min (denoted as “bPEI-10”). Both plasma-3 and bPEI-5 membranes were challenged by emulsions stabilized with SDS and MTAB; bPEI-10 membranes were challenged with MTAB-stabilized emulsions. The effect of polyanion was studied by treating the bPEI-5 membranes with PAA for 5 min (denoted as “bPEI/PAA-5”). The bPEI/PAA-coated membranes were challenged by SDS-stabilized emulsions in separation experiments.

Table 1. Characteristics of feed emulsions with 250 ppm dodecane.

| Surfactant | Surfactant concentration [× 10^{-3} M] | Critical micelle concentration [× 10^{-3} M] | pH     | Droplet diameter [nm] | Zeta potential [mV] |
|------------|---------------------------------------|---------------------------------------------|--------|-----------------------|---------------------|
| SDS        | 0.25                                  | 8.2[37]                                     | 5.5 ± 0.1 | 480 ± 33             | −50.2 ± 2.6         |
| MTAB       | 0.25                                  | 3.9[38]                                     | 5.8 ± 0.2 | 485 ± 36             | 43.2 ± 2.6          |

Figure 2a shows the scanning electron microscopy (SEM) image of an as-electrospun PA6(3)T fiber membrane. The average fiber diameter was 126 ± 21 nm. The membrane thickness was 47.5 ± 7.5 μm, and the porosity was 87 ± 1%. Figure 2b–e shows the SEM images of membranes after plasma treatment and polyelectrolyte deposition(s). The fibrous structure of the electrospun mats appears to be unchanged by surface modification. The results confirm that PA6(3)T was negatively charged (−14.6 ± 1.6 mV) at pH ≈ 5.6, and the plasma treatment imparted additional negative charge to the PA6(3)T film (−26.4 ± 3.9 mV). After the plasma-treated PA6(3)T films were immersed in bPEI solution, the zeta potential was observed to be positive (2.3 ± 3.3 mV). With longer immersion time, i.e., bPEI-10, the zeta potential was increased to 11.8 ± 8.7 mV, which we attributed to better coverage of bPEI on the film. After the bPEI-5 films were immersed in PAA solution, the zeta potential was again observed to be negative (−33.7 ± 4.7 mV). Therefore, Lbl polyelectrolyte deposition was confirmed to alter the surface charge of PA6(3)T films between negative and positive values.

![Figure 2](image-url)
Figure 4a shows the contact angle in air of the sessile drop of deionized (DI) water and the underwater contact angle of the oil drop on PA6(3)T films as-cast and after surface functionalization. The water contact angle on PA6(3)T film was 72.4° ± 1.4°, while the underwater oil (dodecane) contact angle was 108.3° ± 0.9°, confirming that PA6(3)T is hydrophilic and oleophobic.[13] After plasma treatment, the water contact angle decreased to 25.5° ± 1.6°, and the water contact angles on polyelectrolyte-coated PA6(3)T films were around 45°–52°. The underwater oil contact angle of surface-modified films rose to 140°–153°, indicating that plasma treatment and polyelectrolyte coating increased both hydrophilicity and oleophobicity.

The underwater oil contact angle changed when SDS or MTAB was added to the water at concentrations below the critical micelle concentration, as shown in Figure 4b. This effect is attributed to electrostatic interactions between the polymer and liquids. If the surface charge of the polymer film was opposite to that of the surfactant, e.g., PA6(3)T and plasma-3 films in MTAB solution, or bPEI-5 film in SDS solution, the primary effect was adsorption of the surfactant onto the polymer film with the oleophilic tails facing outward, so the oil contact angle was reduced.[42] On the other hand, when the surface charge of the polymer film was alike to that of the surfactant, e.g., plasma-3 and bPEI/PAA-5 films in SDS solution, or bPEI-5 and bPEI-10 films in MTAB solution, the primary effect of the surfactant was reduction of the oil/water interfacial tension, and the oil contact angle was increased. The underwater oil contact angles of surface-modified membranes were measured both before and after 4 h of exposure to 0.25 × 10⁻³ m solutions of each surfactant, and were found to be essentially unchanged (c.f. the Supporting Information).

2.3. Emulsion Separation Experiment

Figure 5 shows the pure water (“hydraulic”) flux of each membrane at 2 psi transmembrane pressure. The hydraulic flux of as-spun PA6(3)T membrane prewetted by ethylene glycol (EG) was measured to be 3766 ± 751 LMH. The average pure water fluxes of membranes after surface functionalization were improved to 4000–4200 LMH at 2 psi. The plasma-treated and LbL-coated membranes were then applied to microfiltration of SDS- and MTAB-stabilized emulsions in both dead-end and cross-flow configurations, and compared with the as-spun PA6(3)T membranes.

Figure 6 shows the permeate flux of plasma-3, bPEI-5, and bPEI/PAA-5 membranes when separating SDS-stabilized...
emulsions in dead-end and cross-flow systems, with as-spun PA6(3)T membrane prewetted by EG as reference. Although the reduction in flux relative to hydraulic flux due to fouling is still large (97%–98%), both negatively charged membranes (plasma-3 and bPEI/PAA-5) exhibited significantly (230%–320%) higher permeate fluxes (141.2 ± 34.7 LMH and 102.8 ± 10.1 LMH, respectively) than the as-spun PA6(3)T membrane (44.3 ± 2.6 LMH) in cross-flow configuration at 4 h. The positively charged bPEI-5 membranes barely altered the flux (46.0 ± 7.8 LMH) in cross-flow configuration after 4 h. The trends were qualitatively similar in the dead-end configuration, albeit with somewhat lower permeate fluxes. After backflushing with DI water for 1 min, the recovered hydraulic flux varied from 60% to 75% (c.f. the Supporting Information).

Figure 7 shows the permeate flux of plasma-3, bPEI-5, and bPEI-10 membranes when separating MTAB-stabilized emulsions in dead-end and cross-flow cells, with as-spun PA6(3)T membrane prewetted by EG again as reference. Both positively charged membranes (bPEI-5 and bPEI-10) exhibited significantly (250%–340%) higher permeate fluxes (67.5 ± 4.0 LMH and 91.0 ± 39.2 LMH, respectively) than the as-spun PA6(3)T membrane (27.3 ± 3.8 LMH) in cross-flow configuration at 4 h. The negatively charged plasma-3 membranes, on the other hand, resulted in only a modest increase of permeate flux (38.0 ± 11.0 LMH). In dead-end configuration, the plasma treatment actually showed a negative influence on the permeate flux, which was decreased from 22.2 ± 4.1 LMH to 14.5 ± 0.4 LMH at 4 h. Based on the results in Figures 6 and 7, it is apparent that like charged membranes and emulsions generally result in higher ultimate permeate fluxes, whereas oppositely charge membranes and emulsion result in similar or lower permeate fluxes, compared to the as-spun PA6(3)T membrane.

The quality of permeate obtained after 4 h of filtration, expressed as total organic carbon (TOC), is presented in Figure 8. The plasma treatment and polyelectrolyte deposition had no apparent influence on the permeate quality. The average TOC concentrations in the filtrate were mostly lower than 15 ppm, which is the Environmental Protection Agency’s (EPA’s) regulatory limit for daily discharge of oily wastewater; the exception was MTAB-stabilized emulsions using untreated PA6(3)T membranes, where the TOC concentration was slightly above the limit (15.2 ± 5.1 ppm). The membranes immersed in bPEI solution for 5 min exhibited the highest rejection of oil, with values of 93.0 ± 2.0% and 92.1 ± 1.8% for SDS and MTAB-stabilized emulsions, respectively; this corresponds to permeate TOC concentrations of 11.9 ± 3.9 ppm and 12.7 ± 2.3 ppm, respectively.
3. Discussion

3.1. Electrostatic Repulsion Strength

In this work, model emulsions stabilized by SDS and MTAB were used to represent different types of industrial oily wastewaters. Previous works have confirmed that membrane fouling by surfactant-stabilized oil-in-water emulsions is influenced by the electrostatic interactions between membrane and emulsion.[13,15,44] Based on this principle, we envisioned a family of polyelectrolyte-functionalized membranes whose surface charge could be selected according to the electrostatic properties of the emulsion to be separated, in order to reduce the membrane fouling. The principle is that stronger repulsive electrostatic interactions translate to reduced fouling and higher retained permeate flux. To demonstrate this principle, a design metric is proposed based on the product of zeta potentials of emulsion and membrane, which we call the “electrostatic repulsion strength.” As measure of merit, we take the permeate flux at 4 h, which is plotted in Figure 9 versus the electrostatic repulsion strength for both dead-end and cross-flow configurations. Indeed, for both configurations, the measure of merit correlates with the design metric, with coefficients of linear regression...
$R^2 = 0.79$ and 0.61 for dead-end and cross-flow systems, respectively. The permeate flux in the cross-flow configuration is systematically higher than that in the dead-end configuration, because cross-flow enjoys an additional hydraulic cleaning mechanism that is absent in the dead-end configuration.

### 3.2. Comparison of Membrane Performance with Previous Work

To evaluate the efficiency of oil-in-water emulsion separation, the performance of the functionalized electrospun membranes reported here is compared with that of other membranes reported in the literature. Each datum is treated as a “black box” with respect to membrane type, emulsion type, and/or fouling propensity; the purpose is to offer a rough picture of the state of the art in performance (permeance, rejection) over time of membranes in the separation of oil-in-water emulsions. For this purpose, Figure 10 shows a 3D plot with filtration time, oil rejection, and permeance (permeate flux over transmembrane pressure) as the $x$, $y$, and $z$-axes, respectively. In this figure, top performers would be found in the upper-right corner, indicating high permeate flux and high oil rejection maintained at long filtration time. In order to highlight the current membranes relative to the prior art, all of the data from the literature are rendered as black rectangles; the literature data encompass a broad range of membrane chemistries, surfactant chemistries, and oil types; the citation sources are listed in Table 2. The results for plasma-3 and bPEI/PAA-5 membranes against SDS-stabilized emulsion, and for bPEI-10 against MTAB-stabilized emulsion, are shown at filtration times of 0.5, 2, and 4 h. As can be seen, the permeances of functionalized electrospun fiber membranes are as good as or better than those of state-of-the-art membranes even after 4 h of filtration. There is still room for improvement for the oil rejection ($\approx 93\%$), but as shown in Figure 8, the TOC contents in the permeate are already below the EPA’s regulatory limit.

### 3.3. Fiber Diameter

In addition to the primary effect on permeate flux exerted by the electrostatic repulsion strength, minor but systematic deviations can be identified based on fiber diameter. In Figure 9, the membranes with smallest diameters (plasma-3 and bPEI-5) tend to fall above the trendlines (higher permeate flux) while those with largest diameters (as-spun PA6(3)T and bPEI/PAA-5) tend to fall below (with some outliers). When removing emulsified oil stabilized by SDS from water, it was found that the plasma-treated membranes exhibited the highest permeate flux in both filtration configurations, despite the lower zeta potential and oleophobicity compared to those of bPEI/PAA-coated membranes. Since the average fiber diameter of the plasma-3 membranes was reduced by $\approx 9$ nm, we hypothesize that the plasma treatment alters not only the surface charge but also the membrane morphology (specifically, fiber diameter and porosity) of the electrospun mats, which can also affect the permeate flux. To verify that the changes in fiber diameter by $\approx 10$ nm are experimentally significant, electrospun PA6(3)T membranes were plasma-treated for 5 min on each side (denoted as “plasma-10”), and observed by SEM. As shown in Figure 11, some fibers were broken after 5 min of plasma treatment, and the average fiber diameter was further reduced to 95 ± 27 nm. The reduction in fiber diameter and breakage of fibers alters the pore morphology of the membranes, suggesting that it is more “open.” The increase in pore space of plasma-treated mats was confirmed by the pure water flux, which increased from 3766 ± 751 LMH to 5039 ± 617 LMH, as shown in Figure 12. The pure water flux of the plasma-3 membrane...
was also the highest among those of membranes after surface functionalization (c.f. Figure 5). Figure 12 presents the zeta potential of the PA6(3)T films after plasma treatment as well. It shows that longer time of plasma treatment led to more negatively charged surface, which could be an advantage for LbL deposition. The resulting high water permeability and negative surface charge could also be beneficial for separation of emulsions with anionic surfactants.

4. Conclusion

In this work, a strategy to reduce membrane fouling in microfiltration of surfactant-stabilized oil-in-water emulsions was developed, based on the electrostatic repulsion between membrane and emulsion. A family of polyelectrolyte-functionalized membranes and plasma-treated membranes was proposed, in which the surface charge was altered with respect to the as-electrospun polyamide membrane. The membranes were then tested using dodecane emulsions stabilized by anionic and cationic surfactants. The results show that like charged membranes and emulsions result in higher permeate fluxes at 4 h, while oppositely charged membranes and emulsions result in similar or lower permeate fluxes, compared to the as-spun membrane. The higher permeate flux is indicative of greater resistance to fouling. This anti-fouling tendency can be expressed quantitatively as a function of electrostatic repulsion strength. Although the nature of oily emulsions in industrial wastewaters varies greatly according to their sources, they can be sorted according to their electrostatic properties, or zeta potentials. Similarly, polymer compositions can be devised, or the resulting membranes post-processed, to create families of membranes that vary in electrostatic charge, or zeta potential. The electrostatic repulsion strength then offers a design metric by which membranes may be selected for microfiltration of a particular oily emulsion in order to mitigate fouling. This work demonstrates a simple but effective illustration of one such family of fouling-resistant membranes for the separation of surfactant-stabilized oil-in-water emulsions. The functionalized membranes are confirmed to be comparable to or better than the state of the art. Using plasma treatment and LbL polyelectrolyte self-assembly, electrospun fiber membranes are made more fouling-resistant.
The same principles can also be applied to other types of membranes, such as those made by phase inversion.

5. Experimental Section

Emulsions: Representative emulsions comprising cationic and anionic surfactants were prepared using SDS and MTAB, respectively, following methods reported previously.[13] Both surfactants were purchased from Sigma-Aldrich. Briefly, dodecane (5 wt%) and a 50 × 10^{-3} M aqueous solution of each surfactant were mixed using a tip sonicator (Branson Sonifier 450) for 15 min (power 4, 20% duty cycle). The resulting emulsions were then monitored for coalescence at room temperature for a period of the order of days. Coalescence was arrested when the emulsion attained a droplet diameter of about 500 nm by dilution to 250 ppm using DI water. These feed emulsions were stable for at least 4 h after dilution. Table 1 reports the relevant properties of each emulsion. Particle size and zeta potential were measured using a Zeta PALS (Brookhaven Instruments).

**Electrospun Membranes**: The base materials and methods of preparation were similar to those used previously.[11] PA6(3)T (Scientific Polymer Products, Inc. (Ontario, NY)) was used as base filter material in this work due to its hydrophilicity and the ease with which uniform fibers with narrow diameter distribution can be formed.[39] The glass transition temperature of this polyamide was measured to be 151 °C using differential scanning calorimetry (TA Q100). N,N-dimethyl formamide (DMF) and formic acid (FA) were purchased from Sigma-Aldrich, and used without further purification. Two wt% of FA in DMF was used as the solvent for PA6(3)T. The addition of FA served to increase the electrical conductivity of the solution for electrospinning.

The electrospinning apparatus was based on that reported previously by Shin et al.[59] Two metal plates were arranged parallel and 22 cm apart. The high voltage aluminum plate was 15 cm in diameter and maintained at 31–36 kV (Gamma High Voltage Research, ES540P). The low voltage collector plate was a grounded, 15 cm × 15 cm, stainless steel platform. A 20 wt% solution of PA6(3)T in DMF/FA was pumped, through a stainless steel needle (U-138, Upchurch Scientific) 2.1 cm long mounted in the high voltage plate, at a constant flow rate of 0.2 mL h^{-1} using a syringe pump (PHD 2000, Harvard Apparatus). The electrospinning process was performed within an environment chamber maintained at room temperature and relative humidity of 25%–30% (Model S100, Electro-Tech Systems). The fibrous membranes were post-processed by thermal annealing in a benchtop oven (Thermo Scientific, Thermolyne FD1545M) at 145 °C for 1 h, to ensure mechanical integrity.[60]

**Surface Functionalization**: bPEI with M_w ≈ 25 000 g mol^{-1} was purchased from Sigma-Aldrich and used as the polycation. bPEI (0.1 wt%) was dissolved in DI water and the pH was adjusted to 4 by titrating with 1.0 M hydrochloric acid. PAA with M_w = 50 000 g mol^{-1} was purchased from Polysciences, Inc., and used as the polyanion. PAA (0.1 wt%) was dissolved in DI water and the pH was adjusted to 6 by titrating with 1.0 M sodium hydroxide. Electrospun PA6(3)T membranes were first pretreated in the plasma cleaner (Harrick, PDC-32G) with room air for 3 min (90 s per side) to make the mats hydrophilic and to impart an initial negative charge to the fibers (henceforth denoted as “plasma-3” membranes).[40,41] The power applied to the induction coil was 6.8 W at radio frequency of 8–12 MHz. The plasma-3 membranes were then immersed in bPEI solution for 5 min, followed by rinsing in two DI water baths (pH ≈ 5.6) for 1 min each (denoted as “bPEI-S”), to “flip the charge” on the membrane from negative to positive. Both plasma-3 and bPEI-S membranes were then challenged by emulsions stabilized with SDS and MTAB. To further investigate the influence of dipping time, plasma-3 membranes were also immersed in bPEI solution for 10 min (denoted as “bPEI-10”) and challenged with MTAB-stabilized emulsions. The effect of polyanion was also studied by dipping the bPEI-S membranes into PAA solutions for 5 min, followed by rinsing in two DI water baths for 1 min each (denoted as bPEI/PAA-S). The bPEI/PAA-coated membranes were challenged by SDS-stabilized emulsions in separation experiments.

**Membrane Characterization**: SEM (JEOL-JSM-6010LA) was used to observe the morphologies of the membranes. All membranes were dried in air at room temperature for 12 h before being characterized by SEM. The diameters of 30–50 fibers were measured from the SEM images to calculate the average and standard deviation of fiber diameter. An adjustable Digimatic Micrometer (CLM 1.6″ QM, Mitutoyo) was used to measure the membrane thickness at a constant applied force of 0.5 N. Combined with basis weight, the apparent density of the membrane could be calculated, and then converted to mat porosity using the bulk density of PA6(3)T (1120 kg m^{-3}).[80]

Surface zeta potentials were measured by the streaming current method using an electrokinetic analyzer (SurPass, Anton Paar). The background electrolyte solution was 10 × 10^{-3} M KCl solution. The zeta potential was measured at pH of ≈5.6, consistent with the model emulsions used for separation experiments. PA6(3)T solution was cast onto polypropylene sheets to form flat films, which were then modified with plasma and LbL deposition using the same protocols as described.
above for the electrospun membranes. An adjustable gap cell was used to measure the zeta potential of the flat films, at a pressure-driven flow of 300 mBar. In practice, this technique measures the charge at the Stern layer, which is 0.3–0.5 nm above the surface, rather than the actual surface charge. Nevertheless, “zeta potential” and “surface charge” are used interchangeably in this paper.

An advanced goniometer (Model 500, Ramé-Hart) was used to measure water contact angles in three replicates[81]; the drop size was 4 µL of DI water. Evaporation was mitigated by creating a humid environment within the quartz cell using water-wetted tissue papers, so that contact angles measurements were stable for at least 30 min. For the underwater oil contact angle, the drop size was 4 µL of dodecane, dispensed using an inverted needle onto a downward-facing sample submersed in DI water surface. The contact angles were determined using Ramé-Hart DROlimage software.

Separation Experiments: Emulsion separation experiments were performed simultaneously in both dead-end (UHP 25, Sterlitech, unstirred, effective filtration area 3.5 cm²) and cross-flow (CF016, performed simultaneously in both dead-end (UHP 25, Sterlitech, using Ramé-Hart DROPimage software.

Prior to measurement, membranes were conditioned with pure water flow at 4 psi for 1 min.[82] For reference purposes, unmodified PA6(3)T membranes were prewetted with EG and rinsed extensively with DI water; the surface functionalized membranes wetted spontaneously. During measurement, the feed side pressure was lowered to 2 psi to measure the pure water flux of each membrane. Then the feed was switched to the emulsion, and separation was conducted for 4 h. During the first 10 min, the mass was recorded every 30 s using the Logger Lite software; thereafter the mass was recorded every 2 min. Flux was determined from the effective area of the membrane and the accumulated mass of liquid permeated, after correction for the density of water, since the concentration of dodecane in the permeate was always low. Three replicates were performed for each case.

A TOC analyzer (Shimadzu TOC-L) was used to measure the oil content of feed, permeate, and retentate streams (where relevant), from which the oil rejection was calculated according to Equation (1)

\[
R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100
\]

where \(C_p\) and \(C_f\) represent TOC concentrations of the permeate and feed solutions, respectively. For each measurement, 0.2 mL aliquots were diluted with DI water to a final volume of 5 mL. The TOC analyzer was calibrated with 10 ppm potassium hydrogen phthalate standard solution.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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