Reactive Amphiphilic Graft Copolymer Coatings Applied to Poly(vinylidene fluoride) Ultrafiltration Membranes

Ravindra Revanur,[†] Bryan McCloskey,[‡] Kurt Breitenkamp,[†] Benny D. Freeman,*,[‡] and Todd Emrick*,[†]

Polymer Science & Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003, and Department of Chemical Engineering, University of Texas, Austin, Texas 78758

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ABSTRACT: Amphiphilic graft copolymers, composed of a poly(cyclooctene) backbone with poly(ethylene oxide) (PEO) and phenyl azide grafts and pendant groups, were synthesized and applied as coatings to commercially available poly(vinylidene fluoride) ultrafiltration (PVDF-UF) membranes. The structure and tunable nature of this type of graft copolymer, in terms of graft density and functionality, make it appealing for enhancing the properties of existing polymer membranes with regards to membrane fouling. Photoinduced cross-linking of the graft copolymer coating provides a means by which the coating resists delamination from the underlying membrane, which in turn provides a mechanism for preventing fouling of the membrane when exposed to oil-in-water emulsions. Significant differences in fouling between the coated and uncoated PVDF-UF membranes are shown.

Introduction

Fouling represents a critically important barrier against wider adoption of microporous polymer membranes for many applications, including water purification.[1−3] Surface and internal membrane fouling by proteins, emulsified oil droplets, and various types of particles leads to considerable loss in flux and selectivity over time.[4] While a number of commodity polymers have been fabricated into useful and commercially viable membranes, new synthetic polymers designed to improve existing membranes are needed to prevent fouling and/or improve separation efficiency and enhance the performance of commercial membranes beyond their current state.

The known antifouling and surface-active properties of poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO) are appealing for integration into polymer membranes.[5,6] However, the water solubility and crystallinity of PEG make it unsuitable for fabrication into robust membranes for aqueous applications. Thus, covalent attachment of PEG to hydrophobic polymers provides a means by which PEG-based polymers can be integrated into membranes with antifouling properties, yet maintain the integrity of the membrane in an aqueous environment. PEG has been attached covalently to a variety of membrane materials, including cellulose,[7] poly(acrylonitrile),[8] poly(acrylonitrile-*co*-vinyl chloride),[9] polysulfone,[10,11] and polypropylene and cellulose acetate.[12] Such PEGylated membranes typically show considerably different properties from the non-PEGylated versions, especially with regards to reduced fouling and permeability/selectivity characteristics.[10,13−15] For polysulfone UF membranes, UV-induced reactions of PEG derivatives have been used for membrane surface modification.[10,11] In these examples, the ester linkage chosen to connect PEG to the underlying membrane is convenient synthetically but ultimately not suited ideally for water purification applications due to the inherent hydrolytic instability of esters. Membranes prepared from polymer blends, such as polyether sulfone/poly(vinylpyrrolidone)[16] and poly(vinylidene fluoride) (PVDF)/PVDF−PEGylated PMMA,[13,14] also provide examples of materials that exhibit reduced fouling relative to conventional commercial membranes. Alternatively, polyamide-*b*-poly(ethylene oxide) (Pebax) can be applied as a coating on membranes such as porous PVDF supports to address the fouling problem associated with uncoated PVDF membranes.[15]

In this study, polyolefin-*graft*-PEG amphiphilic graft copolymers were prepared and used as antifouling coatings on commercial poly(vinylidene fluoride) ultrafiltration (PVDF-UF) membranes. Ring-opening metathesis copolymerization of cyclooctene with functionalized cyclooctene derivatives was performed to generate the desired graft copolymers. These graft copolymers were fabricated into dense film membranes and characterized in this form to evaluate their water uptake and ability to resist protein adsorption. Then, phenylazide functionalized variants of the graft copolymers were prepared and applied as thin-film coatings to PVDF-UF membranes. These composite membranes were subjected to oil-in-water emulsions under cross-flow conditions at 10 atm. The presence of this reactive functionality on the PEGylated polyolefin backbone proved critically important for the successful application of these coated UF membranes, as physical adsorption of the graft copolymers on the PVDF-UF membranes proved ineffective. However, photoinduced cross-linking of the graft copolymers coatings stabilized the coatings under cross-flow conditions and provided a means by which membrane fouling from oil-in-water emulsions was reduced markedly relative to the uncoated membranes.

Poly(cyclooctene)-*graft*-PEG Amphiphilic Graft Copolymer Synthesis. Amphiphilic graft copolymers containing poly(cyclooctene) backbones, and various length and density of PEG grafts, were prepared by ruthenium benzylidene catalyzed ring-opening metathesis polymerization (ROMP) of cyclooctene with PEGylated cyclooctene and phenylazide-functionalized cyclooctene. For example, as shown in Scheme 1, graft copolymers **1**−**5** were prepared by polymerization of different ratios of cyclooctene (**6**) and PEGylated cyclooctene macromonomers **7** and **8**. These macromonomers were prepared by the 5-hydroxycyclooctene-initiated anionic polymerization of ethylene oxide (Scheme 2). This macromonomer synthesis enables integration of PEG into the copolymer structure in the absence of post-

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[†] University of Massachusetts.
[‡] University of Texas.

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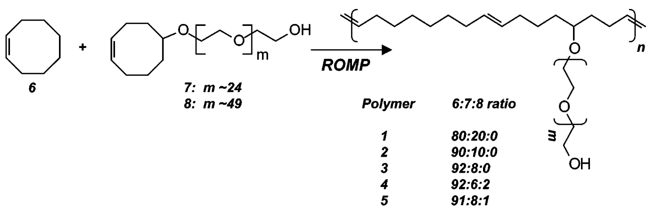
Scheme 1



Scheme 2

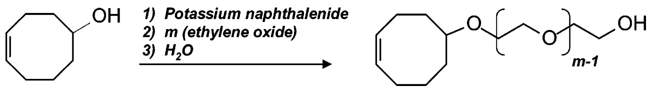


Table 1. Data for Polymers 1−5, Using Different Mole Percentages of Monomers 6, 7, and 8[a]

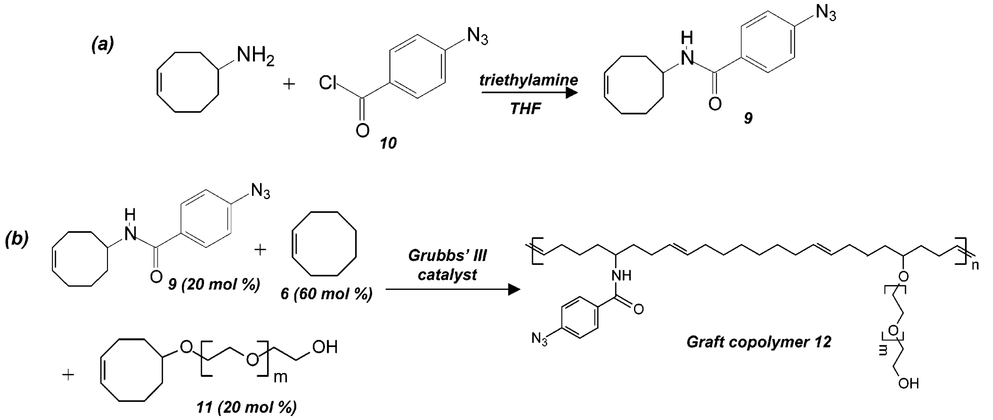
polymer[b]	molar ratio **6**:**7**:**8**	PEG (wt %)	M_n (GPC)[c]	PDI (M_w/M_n)	water uptake (wt %)
1	80:20:0	73	42 800	1.9	220−240
2	80:10:0	55	34 400	2.0	60−70
3	92:8:0	49	15 800	1.6	50−60
4	92:6:2	53	22 700	1.8	45−50
5	91:8:1	54	27 800	2.1	40−45

[a] **6** = cyclooctene; **7** = PEG-1100 cyclooctene macromonomer; **8** = PEG-2200 cyclooctene macromonomer. Water uptake performed on membranes of these polymers prepared using ~7 wt % of the bis-cyclooctene PEG. Membrane thickness in each case was ~50 μm. [b] [M] = 2.0 mol/L, [M]/[Cat.] = 500, [M]/[1-hexene] = 100, 40 °C in CH_2Cl_2. [c] GPC in $CHCl_3$ vs polystyrene standards.

polymerization grafting chemistry. Moreover, this approach connects the PEG grafts to the macromonomer, and subsequently to the polymer backbone, by ether bonds, which are advantageous from the standpoint of hydrolytic and chemical stability. Graft copolymers **1**−**5** were prepared by ROMP of the appropriate monomers/macromonomers in dichloromethane, using Grubbs' generation II catalyst,[17] with a 250:1 monomer-to-catalyst ratio, and 1-hexene as the chain transfer agent (50:1 monomer-to-chain transfer agent ratio). The polymerization was terminated by addition of ethyl vinyl ether, and the polymer was isolated as a powder following precipitation into cold hexane. Gel permeation chromatography (against linear polystyrene standards), run using $CHCl_3$ as eluent, was used to estimate the molecular weights and polydispersities of the graft copolymers, as presented in Table 1. As expected for ROMP polymers, the polydispersity of these samples was estimated (by GPC) to be ~2. Importantly, the copolymers obtained by this process, as characterized by NMR spectroscopy, show comonomer incorporation into the graft copolymer in accord with the feed ratios employed.

Phenylazide-functionalized cyclooctene **9** was prepared as shown in Scheme 3a and used in ROMP copolymerizations with cyclooctene and PEGylated cyclooctene macromonomer **11** (PEG MW 4400 g/mol). Monomer **9** was prepared by reaction of acid chloride **10** with 5-aminocyclooctene in 73% yield after purification by crystallization in diethyl ether/hexane and characterized by ^{1}H and ^{13}C NMR, as well as FT-IR, spectroscopy. The ^{13}C NMR spectrum of compound **10** showed the amide carbonyl at 165.1 ppm and a characteristic azide signal in the IR spectrum at 2120 cm^{-1}. Monomer **9** was integrated into poly(cyclooctene-*graft*-PEG) copolymers by the ROMP copolymerization shown in Scheme 3b to give graft copolymer **12**, using Grubbs' generation III catalyst.[18] For the membrane coatings prepared in this work, graft copolymer **12** was prepared from 20 mol % cyclooctene azide **9**, 60 mol % cyclooctene, and 20 mol % PEGylated cyclooctene **11**. This composition of amphiphilic graft copolymer **12** proved convenient for the PVDF-UF coating experiments, as its solubility in ethanol is well-suited to solution-based coating of PVDF-UF membranes (and in principle other commercial membranes) and also provides sufficient phenyl azide functionality for effective cross-linking of the coating. Typical preparations of graft copolymer **12** gave materials that by GPC in THF had number-average molecular weights of ~35 000 g/mol and PDI values of ~1.7. ^{1}H NMR spectroscopy performed on $CDCl_3$ solutions of **12** showed backbone olefin resonances at ~5.4 ppm, in the typical region for poly(cyclooctene)-based polymers, and no evidence of residual cyclic olefin monomers (otherwise seen at ~5.7 ppm for the double bond). In the ^{1}H NMR spectra, aromatic resonances of the phenyl azide group were observed at 7.04 and 8.00 ppm, and integrated against proton resonances from the polymer backbone, which confirmed the expected mole percent incorporation. FTIR spectroscopy on **12** showed a diagnostic azide stretch at ~2120 cm^{-1}. This synthetic strategy connects the reactive azide functionality to the polymer backbone through an amide bond which, like the ether connectivity of the PEG chains, is stable hydrolytically and thus well-suited for aqueous-based membrane applications. We also prepared other polymers of type **12** by fixing macromonomer **11** at 20 mol % and varying **9** from 5 to 15 mol % and **6** from 65 to 75 mol %. However, solubility proved problematic in these cases, as ethanol no longer dissolved the polymer, and good solvents for the polymer such as chloroform and toluene are not well-suited for coating procedures due to interaction with many underlying membrane supports. Thus, the composite membrane experiments described below were performed with polymer **12** having a 60:20:20 mole ratio of **6**, **9**, and **11**.

Scheme 3



Polycyclooctene-*graft*-PEG Copolymers as Dense Films. Before applying polyolefin-*graft*-PEG copolymers as coatings to PVDF-UF membranes, dense films of the copolymers were prepared and characterized for pure water uptake and pure water flux under dead-end flow conditions. Such characterization is important for determining coating compositions that possess sufficient hydrophilicity for water purification applications. Dense film membranes of polyolefin-*graft*-PEG copolymers **1**−**5** were prepared by casting films from 20 wt % toluene solutions of copolymer onto glass plates and then drawing the film to the desired thickness with a Gardco film applicator. Residual solvent was removed from the films by allowing them stand at room temperature and then by placing them in vacuum (∼100 mTorr) for 12 h. For the preparation of these cross-linked polymer films, ring-opening cross-metathesis was employed,[19] by addition of a toluene solution of 20 wt % graft copolymer and 7 wt % bis-cyclooctene PEG[20] to Grubbs' generation II catalyst (∼3 mg) under constant agitation. As cross-linking occurs quickly using this method, the mixture was cast immediately onto a glass slide to give the desired membrane as a cross-linked dense film of ∼50 μm thickness. This cross-linking gave dense films with far more robust properties than non-cross-linked films; moreover, the degree of cross-linking provides a variable by which water uptake can be controlled, as shown in Table 1, for a variety of cross-linked poly(cyclooctene)-*graft*-PEG membranes. In copolymers containing lower PEG-grafting density (i.e., from 1 to 10 mol % PEG 1100 g/mol and/or PEG 2200 g/mol), water uptake values in the 40−70% range were observed. Equilibrium water uptake values were obtained by dividing the weight difference between the water-soaked and dry membranes by that of the dry membrane. These membranes exhibited, qualitatively, appreciable mechanical properties, such that they could be removed from the glass plate onto which they were cast and handled without tearing. Poly(cyclooctene)-*graft*-PEG copolymer membranes with higher PEG densities, for example 20 mol % of PEG 1100 g/mol, possessed very high water uptake values (200% or more). However, the highly PEGylated copolymer films were not mechanically robust and thus required cross-linking and/or an underlying substrate to study their utility. Increasing PEG grafting density in the poly(cyclooctene)-*graft*-PEG copolymer dense films was seen, as expected, to result in enhanced pure water flux, using an Amicon stirred cell in a dead-end flow setup. Films from polymers **4** and **5**, with similar weight percent PEG, possess appreciable differences in water sorption and flux. However, this is not necessarily an intrinsic property of the polymer composition but rather is likely due to sample-to-sample variation in cross-linking efficiency. Membranes prepared from graft copolymer **5** in the absence of cross-linking exhibit high water sorption and flux. Water sorption and flux drop to about 50% their initial value in the case of 2 wt % cross-linker. Up to about 7 wt % cross-linker, water sorption and permeance decrease with increasing cross-linker content. Experiments with these dense films were conducted to analyze the effect of cross-linker content on water flux at various feed pressures in a dead-end flow setup (Figure 1). In a membrane without any cross-linker, measurable permeate was collected at a feed pressure of only 0.7 atm. A control over flux in these films; even cross-linked films exhibit appreciable water flux, such that application of these materials as coatings appeared feasible.

While poly(cyclooctene)-*graft*-PEG copolymer films tested against bovine serum albumin (BSA) solutions in the Bradford titration method[21] showed very low levels (∼1 μg/cm^2) of protein adsorption, the appreciable antifouling properties of these films made protein adsorption somewhat difficult to quantify by this method. This contrasts the situation for many commercial membranes, such as polysulfone and polyamide, in which protein adsorption is appreciable and readily quantified.[22] Fluorescence confocal laser scanning microscopy provides a method to visualize membrane fouling.[23] Figure 2 shows fluorescence confocal microscope images of several membranes following exposure to aqueous solutions of fluorescent BSA. These membranes were cut as ∼2 cm^2 sections from polyamide reverse osmosis (RO) thin film composite membranes, cellulose acetate asymmetric RO membranes, polysulfone UF membranes, and poly(cyclooctene)-*graft*-PEG dense films. The membranes were immersed in a phosphate buffered saline (PBS, pH 7.4) solution of fluorescein-conjugated BSA (0.02 mg/mL) for 24 h, followed by rinsing with PBS. As shown in Figure 2, confocal fluorescence images of these membranes (excitation at 488 nm) reveal striking differences in protein adsorption on the commercial membranes relative to the PEGylated graft copolymer film. The polyolefin-*graft*-PEG membrane sample used in these experiments contained 54 wt % PEG (polymer **5**), a modest level of PEGylation, yet clearly sufficient to resist fouling. These data indicate that the PEGylated graft copolymers are well-suited to prevent protein fouling, which was expected to translate to reduced fouling against oil-in-water feed emulsions, and led to the experiments described below.

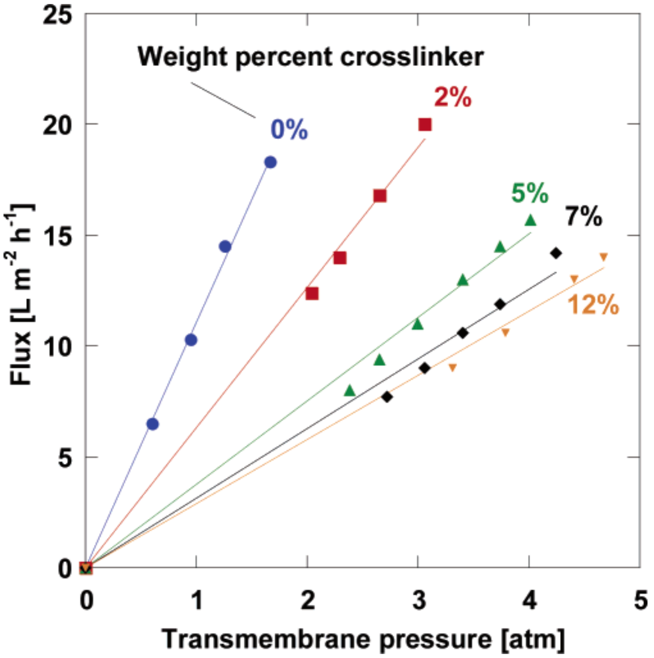


Figure 1. Effect of bis-cyclooctene PEG cross-linker concentration on water flux through dense films (∼50 μm in thickness) prepared from polymer **5**. Experiments employed Amicon stirred cells and dead-end flow. Data points were extrapolated to pass through origin. For each membrane with varying weight percent added cross-linker, the (water sorption in weight percent, average water permeance in LHM/atm) values are as follows: 0% (108, 11), 2% (65, 6.2), 5% (50, 3.7), 7% (42, 3.0), and 12% (40, 2.8). The average water permeance was calculated as the average of the permeance at each of the data points shown.

Poly(cyclooctene)-*graft*-PEG copolymer coated PVDF-UF membranes were prepared initially by casting a 20 wt % toluene solution of graft copolymer with a known amount of cross-linker (0−15 wt %) and catalyst onto the PVDF-UF support and then spread to a desired thickness with a Gardco film applicator. The coated membrane was dried at room temperature and then in a vacuum to remove solvent. Membranes coated in this fashion were placed in a cross-flow unit at 10 atm. However,

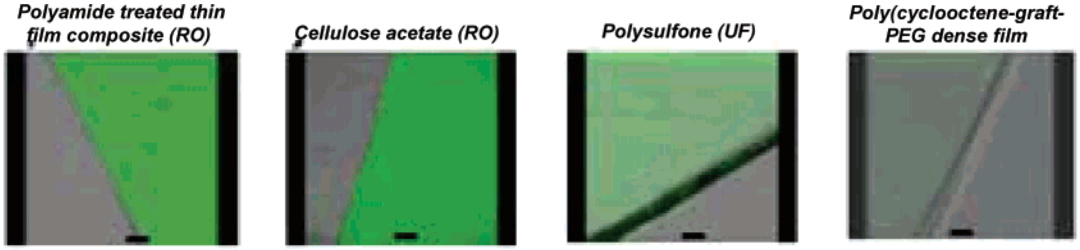


Figure 2. Fluorescence confocal microscopy images of protein (fluorescein−BSA) adsorption on a dense film of polyolefin-*graft*-PEG (far right) and on commercial samples of polyamide, cellulose acetate, and polysulfone membranes. The green color arises from the fluorescence of the dye-labeled protein. The polyolefin-*graft*-PEG copolymer exhibits very little fouling relative to the commercial membranes. The black bar in each image is 50 μm.

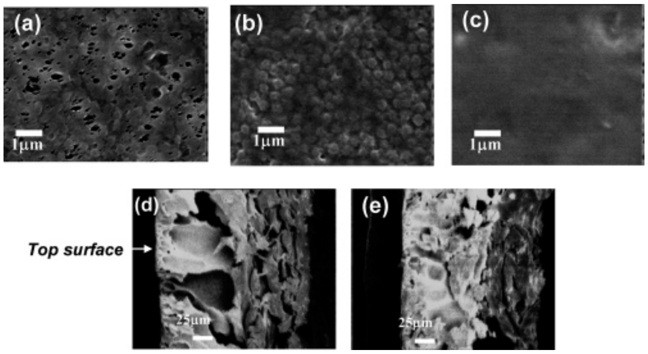


Figure 3. SEM images of PVDF-UF membranes: (a) top view before coating; (b) top view after coating and UV irradiation with graft copolymer **12**; (c) top view after cross-flow experiments; (d) cross-section before coating with **12**; (e) cross-section after coating with graft copolymer **12**.

in the early stages of cross-flow experiments, delamination of the graft copolymer coating was observed due to the substantial swelling of the polymer in water that overcomes its adhesion to the underlying PVDF support. In general, the bis-cyclooctene cross-linking strategies were not applied easily to coating procedures, due in part to formation of defects (e.g., bubbles) within the coatings. Thus, a different method was employed to generate the desired coated membranes, in which the coating and cross-linking steps were conducted separately, by embedding UV-reactive arylazide groups into the graft copolymer structure. For this, poly(cyclooctene)-*graft*-PEG copolymers containing pendant phenyl azide groups were prepared, with the expectation that UV irradiation of these coatings would provide enhanced stability due to the cross-linking reactions from the photogenerated nitrenes.

Phenyl Azide Functionalized Graft Copolymer Coatings on PVDF-UF Membranes. The PVDF-UF membranes used in this study were purchased from Sterlitech, Inc. Scanning electron micrograph (SEM) images of the top surface of the commercial membrane are shown in Figure 3; the porous structure of the top surface of the membrane is evident. For the coating procedure, an ethanol solution of graft copolymer **12** (~50 mg/mL, M_n ~35 000 g/mol, PDI 1.7) was applied by spin-coating onto the PVDF membrane. The coated membrane was then irradiated in a UV-light source box at 302 nm for 6 min. Irradiation converts the phenyl azide ($Ph-N_3$) groups into phenyl nitrenes (Ph−N:) by loss of nitrogen gas. The highly reactive nitrenes[24,25] can insert into olefins in the polymer backbone to give aziridines, C−H bonds in the polymer backbone and grafts, and possibly in the underlying PVDF-UF support, to give amines. This UV-induced cross-linking proved successful for stabilizing the graft copolymer coating on the PVDF-UF membrane surface and eliminated problems associated with rapid delamination of the coating during cross-flow. FTIR spectroscopy performed on the coated membrane following irradiation confirmed the disappearance of the diagnostic azide stretch at ~2120 cm^{-1} in the graft copolymer structure. Characterizing nitrene insertion into the underlying substrate remains under investigation.

Cross-Flow Experiments on Graft Copolymer-Coated PVDF-UF Composite Membrane. Cross-flow experiments on both uncoated and graft copolymer-coated PVDF-UF membranes were conducted at a feed pressure of 10 atm and a cross-flow velocity of 40 cm/s. The feed solution consisted of a 1500 ppm oil-in-water emulsion (9:1 ratio of soybean oil:DC 193 surfactant obtained from Dow-Corning), prepared by blending the oil, water, and surfactant at 20 000 rpm for ~3 min. Periodic evaluation of the oil concentration was carried out using a total organic carbon (TOC) analyzer (Shimadzu TOC-5050A). The delamination problem observed for graft copolymers **1**−**5** during the cross-flow operation was not seen for the coated membranes prepared by irradiation of phenyl azide functionalized graft copolymer **12**, despite the very high (>80 wt %) weight percent of PEG in the polymer coating. Control experiments confirmed the importance of the azide groups. A PVDF-UF membrane was coated with a graft copolymer containing an 80:20 molar ratio of cyclooctene and PEG-4400 cyclooctene macromonomer **11**, followed by an irradiation step identical to that used for the azide-containing coating. Cross-flow experiments with oil−water emulsion feed solutions carried out with these un-cross-linked copolymer coatings led to rapid membrane fouling, with little influence of the coating. This is shown in Figure 4, in which the uncoated and coated PVDF supports follow essentially the same trend of decreasing flux as a function of time due to membrane fouling. Water contact angle measurements taken on the membrane surface after cross-flow (~60−65°) were quite close to those of the uncoated membrane (64−67°), confirming the expected loss of graft copolymer from the surface, and much higher than those of membranes with stable cross-linked graft copolymer coatings.

Cross-flow experiments were then performed to compare the uncoated PVDF-UF membranes to those coated with a cross-linked film of graft copolymer **12**, again using oil-in-water emulsions at 10 atm feed pressure and 40 cm/s cross-flow velocity. The ability of the coated PVDF-UF membranes to resist fouling relative to the uncoated membranes is seen in Figure 5. In Figure 5a, four different graft copolymer coated membranes are shown, and their performance is compared to an uncoated PVDF-UF membrane over a period of 3 days. While the coated membranes exhibit, as expected, a drop in initial flux as a consequence of the coating, all of the coated membranes maintain a relatively stable flux from about 2 h through the end of the experiment. On the other hand, the uncoated PVDF membrane shows a considerable decline in flux during the same period, from ~14 to ~6−7 LMH/atm. When

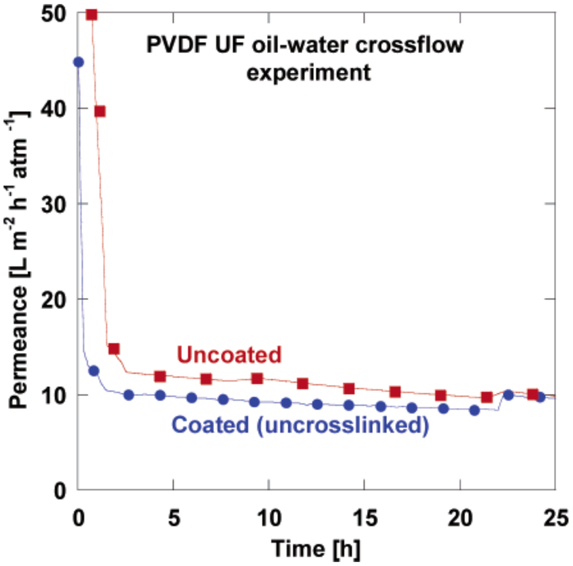


Figure 4. Cross-flow experimental results with uncoated PVDF-UF membrane (red line with square symbols) and graft copolymer **12** coated membrane (without aryl azide, control experiment, blue line with circle symbols).

this coated vs uncoated membrane experiment is extended to longer time periods, as shown in Figure 5b, a crossover is seen in which the water flux through the coated membrane equals, then slightly exceeds, that of the uncoated membrane. Ultimately, the uncoated membrane is expected to approach zero flux at some time period due to complete fouling.[26] This result is significant given the long desired lifetime of membranes of this type and the stability against oil droplet fouling provided by the graft copolymer coating. Interestingly, in some cases the observed flux of the graft copolymer-coated membrane was seen to increase slightly over the measured period. This may be due to some attrition of the coating in areas of the membrane where cross-linking was inefficient, either on the membrane surface or perhaps in areas where the polymer had penetrated the membrane pores. However, rapid fouling was not observed even for these samples. Finally, as shown in Figure 5c, the graft copolymer coating was seen to improve the oil rejection values, as determined by TOC analysis of the permeate. For the uncoated PVDF-UF membranes, the initial organic rejection was low due to the relatively unconstricted porous structure of the membrane, which allowed passage to a larger amount of organics.[27] As the degree of fouling increased over time (as indicated by a dramatic drop in flux), the resistance to organic transport through the membrane also increased, which consequently decreases organic content in the permeate. The graft copolymer-coated membranes maintained 98.5−99% organic rejection during the course of the experiment.

Figure 3 shows SEM images of the top surface of the commercial (Figure 3a) and coated (Figure 3b) PVDF-UF membranes used in this study. SEM shows that the graft copolymer coating covers the membrane pore structure. In cross-sectional SEM of the coated membranes, there appears to be a filling of the pores in going from the uncoated to the coated samples (Figure 3d,e). While the presence of the graft copolymer on the membrane surface, and in the inner-pore structure, will lower the initial flux of the membranes, the substantial hydrophilicity of the graft copolymer leads to only modest flux decline. An ideal coating process would minimize such pore penetration, and efforts along these lines are in progress. Importantly, the graft copolymer coating remains intact on the support throughout the cross-flow experiments. This is confirmed in the SEM image of Figure 3c, taken on the composite membrane following removal from the cross-flow unit. In addition, a smoother membrane surface in the coated membrane is present following cross-flow experiments. This may be associated with some loss of the coating during the cross-flow operation or more likely reorganization of the graft polymer during exposure to an aqueous environment. Nevertheless, after cross-flow, the water contact angle of the coated membrane (44−46°) is identical to that before the cross-flow experiment and considerably lower than that of the uncoated membrane (64−67°). Finally, while fouling prevention can be attributed to the PEGylation,[15,28] it should also be noted that the smoother surface of the coated membranes may augment the effect.[29]

In summary, a novel poly(cyclooctene)-*graft*-PEG copolymer has been synthesized and applied as an antifouling coating for PVDF-UF membranes. Problems associated with delamination of such graft copolymers from the underlying membrane were overcome using phenylazide-functionalized graft copolymers for UV irradiation and cross-linking following spin-coating onto the PVDF-UF support. Cross-flow experiments conducted with oil-in-water emulsions confirmed that the graft copolymer coating prevents fouling and leads to an eventual crossover in flux with the uncoated commercial membranes. Future studies will include an optimization of both the graft copolymer as well as the coating process, exploiting the tunable nature of the graft copolymer itself, as well as processing conditions associated with coating. Moreover, the ability of these copolymer coatings to prevent fouling in other membranes, including those used in reverse osmosis for desalination, will be studied.

Experimental Section

cis-Cyclooctene and lithium aluminum hydride (95%) were purchased from Alfa Aesar. 1,5-Cyclooctadiene (99%), *m*-chloroperoxybenzoic acid (77%), 1-hexene (97%), ethyl vinyl ether (99%), ethylene oxide (99.5%), 3-bromopyridine (99%), triethylamine (99.5%), sodium azide (99.5%), triphenylphosphine (99%), and Grubbs' generation II catalyst were purchased from Aldrich. Grubbs' generation III catalyst was prepared according to literature procedures.[18] Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl, and dichloromethane was distilled from calcium hydride.

Molecular weights and PDIs of copolymers **1**−**5** were determined by gel permeation chromatography (GPC) performed in chloroform (1.0 mL/min) at 25 °C on a Polymer Laboratories (PL) GPC 50 equipped with two PL Mixed D columns (5 μm, 300 × 7.5 mm), referenced against linear polystyrene standards. GPC of copolymer **12** was performed in THF (1.0 mL/min) and referenced against linear polystyrene standards. The system utilizes three columns (PL Mixed-D columns, 5 μm, 300 × 7.5 mm), a dual-wavelength UV detector (Knauer K-2600, analysis at 260 nm), and a refractive index detector (Knauer K-2301). NMR spectroscopy was performed on a Brüker Avance 400 (referenced to $CDCl_3$): ^{1}H at 400 MHz and ^{13}C at 100 MHz. Infrared spectroscopy (IR) was performed on a Perkin-Elmer Spectrum One equipped with a Universal Diamond ATR sampling accessory. Fluorescence confocal micrographs were obtained using TCS SP2 confocal microscope (Leica). Scanning electron microscopy (SEM) images were obtained on a JEOL 6320FXV. A Rame-hart model 1000 goniometer was employed for contact angle measurements, by placement of a drop of water on the membrane surface, using a microsyringe attached to the goniometer.

PVDF-UF membranes (30 000 g/mol MWCO) were purchased from Sterlitech, Inc.. The graft copolymer coating was performed from ethanol solutions by spin-coating onto the membranes at 800 rpm for 1 min. The coated membrane was then placed in a UV-light source box (CL-1000 ultraviolet cross-linker, UVP, Inc.) and irradiated at 302 nm (intensity 3800 μW/cm^2) for 6 min. Pure water

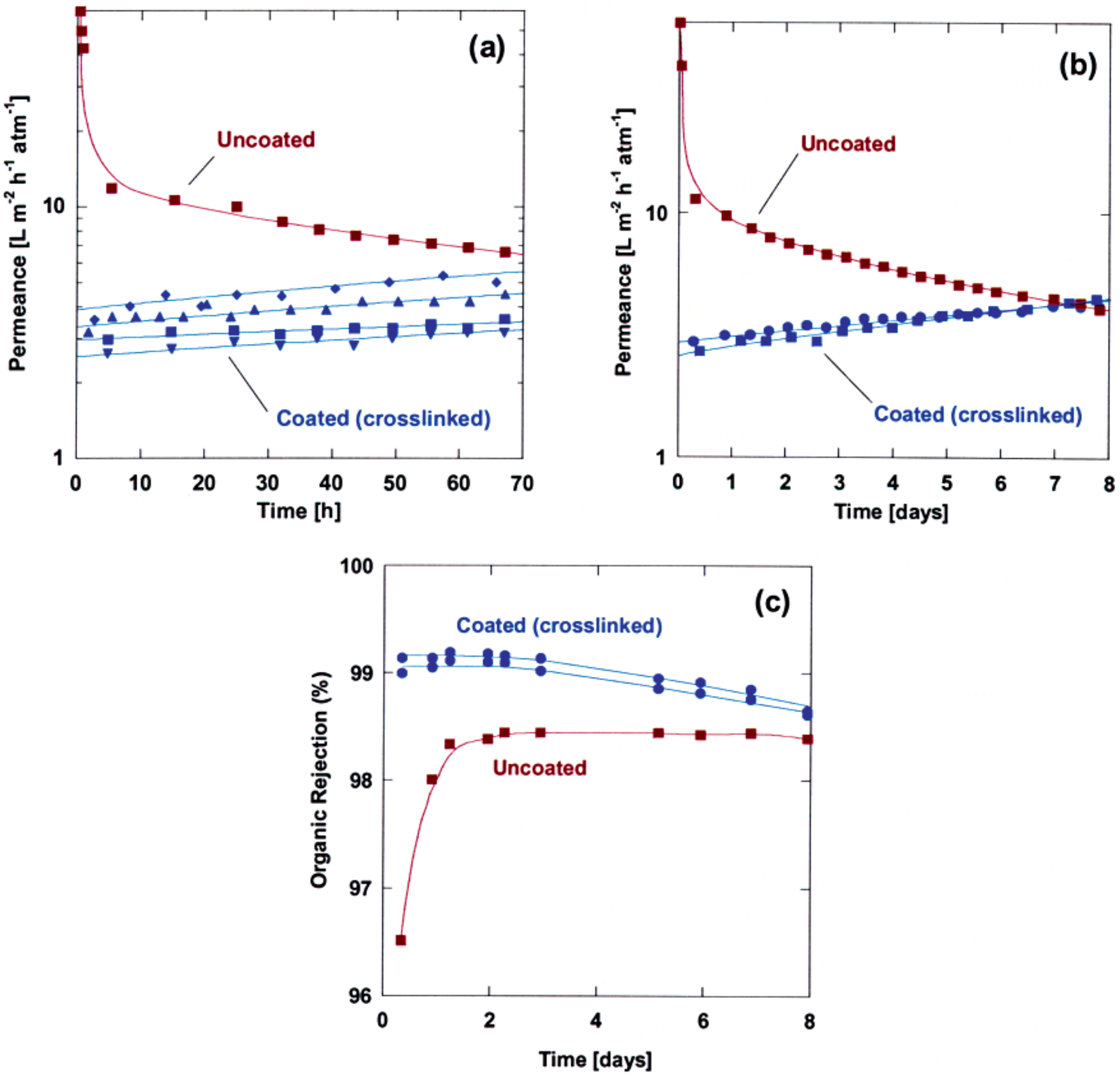


Figure 5. Cross-flow experimental results with coated and uncoated PVDF-UF membranes: (a) plot of permeance vs time using membranes with a cross-linked coating of graft copolymer **12**; (b) continuation of cross-flow experiment to 8 days; (c) oil rejection values (lines are added to guide the eye).

flux through dense films of the graft copolymers was performed using Amicon 8200 stirred ultrafiltration cells.

Representative Synthesis of PEG−Cyclooctene Macromonomer. Into a flame-dried air-free flask under N_2 atmosphere was introduced a THF solution of 5-hydroxycyclooctene (1.0 M, 3.5 mL), followed by dry THF (150 mL). The solution was titrated with a THF solution of potassium napthalenide (0.2 M), until a slight green end-point was observed (35.0 mL). The green solution was stirred for 30 min at room temperature and then cooled to ∼0 °C (ice water bath). Ethylene oxide (15.0 mL, 340 mmol) was condensed at −78 °C using a stainless steel gas transfer manifold and then slowly warmed to room temperature as the ethylene oxide transferred into the cyclooctene alkoxide solution under static vacuum. The reaction mixture was pressurized with argon, sealed, and allowed to stir at room temperature for 16 h. The solution was concentrated, and the macromonomer was purified by column chromatography over silica gel, eluting with chloroform/methanol mixtures. The macromonomer was purified further by precipitation into diethyl ether from a concentrated chloroform solution and isolated by filtration to give 11.3 g (75% yield) of the macromonomer as a white powder: ^{1}H NMR ($CDCl_3$): δ 5.62 (m, 2H), 3.28−3.84 (complex, br m, 228 H), 2.54 (br s, 1H), 1.28−2.36 (complex br m, 11H). ^{13}C NMR ($CDCl_3$): δ 130.2, 129.6, 81.1, 72.7, 71.0, 70.7, 70.4, 67.8, 61.8, 34.2, 33.5, 25.9, 25.8, 22.8. ATR-FTIR: 3491, 2882, 1467, 1359, 1341, 1280, 1242, 1100, 1060, 959, 841, 725 cm^{-1}. GPC (THF, relative to PEG standards): M_n 2300 Da, M_w 2350 Da, PDI 1.1.

Representative Synthesis of PCOE-*g*-PEG Copolymer. PEG 1200 macromonomer (m ∼24, 0.2 g, 0.2 mmol), PEG 2200 macromonomer (m ∼49, 0.10 g, 0.06 mmol), and cyclooctene (0.30 g, 2.7 mmol) were combined in a dry reaction tube. 0.6 mL of a 0.05 M 1-hexene solution in dichloromethane was added to the reaction under N_2, followed by dry dichloromethane (0.5 mL). In a separate vial, Grubbs' generation II catalyst (4.9 mg, 5.7 μmol) was diluted with dry dichloromethane (0.4 mL). Both the monomer mixture and catalyst solution were subjected to two freeze/pump/thaw cycles and then warmed to 40 °C. The catalyst solution was added rapidly to the monomer solution and stirred until vitrification was seen (∼5 min). Ethyl vinyl ether (1 mL) was added to terminate the polymerization, and dichloromethane was added to dilute the polymer solution. The product was precipitated into cold hexane containing 0.01 wt % butylated hydroxytoluene (BHT), isolated by filtration, and dried under vacuum to yield 0.58 g (93.5% yield) of an off-white solid. ^{1}H NMR ($CDCl_3$): δ 5.36 (m), 3.37−3.97 (br m), 3.24 (br m), 2.43 (br s), 1.94, (br m), 1.27−1.53 (br m). ^{13}C NMR ($CDCl_3$): δ 130.2, 72.6, 70.6, 70.3, 61.7, 32.6, 29.6, 29.1. ATR-FTIR: 2921, 2852, 1468, 1344, 1281, 1242, 1104, 963, 842 cm^{-1}. GPC ($CHCl_3$, relative to PS standards): M_n 22 700 g/mol, M_w 39 800 g/mol, PDI 1.76.

Synthesis of Phenyl Azide Cyclooctene 9. 4-Azidobenzoic acid[30] (2.00 g, 12.2 mmol) was added to a dry round-bottom flask and diluted with anhydrous THF (100 mL) under N_2(g). The solution was cooled to 0 °C, and thionyl chloride (0.90 mL, 12.8 mmol) was added by syringe over ∼5 min. The reaction mixture was allowed to stir for 1 h while warming to room temperature. The reaction was again cooled to 0 °C, and triethylamine (4.20 mL, 24.4 mmol) was added by syringe. A white precipitate formed, and the mixture was allowed to stir for an additional 15 min at 0 °C. A solution of 5-aminocyclooctene[31] (1.70 g, 13.4 mmol) in anyhydrous THF (10 mL) was then added by syringe, and the reaction was warmed to room temperature and stirred for 16 h. The reaction mixture was filtered over Celite to remove the salt byproducts, and the solution was concentrated to a light yellow solid. The crude product was dissolved in diethyl ether and washed once with DI water and once with 1 M HCl(aq). The organic layer was dried over $MgSO_4$ and concentrated. The resulting solid was purified by recrystallization (diethyl ether/hexane) to afford 2.4 g (73% yield) of a light yellow crystalline solid. ^1H NMR ($CDCl_3$): δ 7.74 (d, 2H), 7.02 (d, 2H), 6.23 (br s, 1H), 5.72 (m, 2H), 4.16 (m, 1H), 2.14−2.40 (complex br m, 4H), 1.80−2.01 (complex br m, 2H), 1.50−1.76 (complex br m, 4H). ^{13}C NMR ($CDCl_3$): δ 165.1, 143.1, 131.5, 130.5, 129.8, 128.7, 128.6, 118.9, 49.9, 35.3, 34.4, 26.0, 25.9, 23.4. ATR-FTIR: 3306, 3058, 3023, 2933, 2855, 2120, 1625, 1601, 1571, 1542, 1498, 1337, 1279, 1187, 1149, 1123, 847, 768, 725 cm^{-1}.

Synthesis of Copolymer 12. PEG 4400 macromonomer (m ∼ 99, 1.7 g, 0.40 mmol), cyclooctene (0.10 g, 1.1 mmol), and phenylazide-substituted cyclooctene **9** (0.1 g, 0.4 mmol) were combined in a dry reaction tube. 0.9 mL of a 0.05 M 1-hexene solution in dichloromethane was added to the reaction mixture under $N_2(g)$, followed by dry THF (0.7 mL). In a separate vial, Grubbs' generation III catalyst (9.2 mg, 10 μmol) was diluted with dry THF (0.2 mL). Both the monomer mixture and catalyst solution were subjected to two freeze/pump/thaw cycles and subsequently warmed to room temperature. The catalyst solution was added rapidly to the monomer mixture, and the resulting mixture was stirred for 30 min. Ethyl vinyl ether (1 mL) was added to terminate the polymerization, and the mixture was diluted with dichloromethane. The product was precipitated into diethyl ether, isolated by filtration, and dried under vacuum to yield 1.75 g (92% yield) of a pale solid. ^1H NMR ($CDCl_3$): δ 7.74 (d), 7.02 (d), 5.35 (m), 4.30 (m), 4.12 (m), 3.37−3.80 (br m), 3.23 (br m), 2.30 (br s), 1.94, (br m), 1.27−1.53 (br m). ATR-FTIR: 3477, 2882, 2121, 1634, 1467, 1360, 1342, 1279, 1241, 1147, 1102, 1061, 962, 842 cm^{-1}. GPC (THF, relative to PS standards): M_n 27 600 g/mol, M_w 54 000 g/mol, PDI 1.9.

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