Fabrication of a Polymeric Coating Layer with Unique Micro-Spherical Structure on Water Treatment Membranes

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The fabrication of stable, non-leachable spherical polymers on solid surfaces, particularly on water treatment membranes, has the advantage of high surface area and high permeability, which is beneficial for anti-fouling coatings of water treatment membranes. We describe a straight, one-step generation of spherical polymeric coatings on nanofiltration membrane surface which was performed by emulsion co-polymerization of styrene and polyethylene glycol methacrylate (PEGMA) in water. The chemical characterization of the membrane surface and its coating layer was done by Fourier transform infrared spectroscopy (FTIR). Microscopic images showed micelles of 30 – 120 µm size. PEGMA with molecular weight of 526 g/mole was found to have a critical micelle concentration (CMC) value of 0.05 M, which is much lower than its concentration in the polymerization mixture. Hence, in the copolymerization reaction PEGMA-526 created stable micelles and also acted as a surfactant in respect to the styrene. The produced poly(PEGMA) may also act as a surfactant due to its amphiphilic nature. A homogeneous surface morphology on the NF membrane was achieved, with spherical polymeric micelles that have a large surface area.

1. Introduction

Membrane-based water treatment technologies play a pivotal role in meeting the challenge of water scarcity and have a high potential of coping with the water shortage due to their low energy demand as compared with other technologies (Elimelech and Phillip, 2011). Reverse osmosis (RO) and nanofiltration (NF) membranes are widely applied for seawater and brackish water desalination, as well as for industrial-wastewater treatment (Stoller et al., 2016). The key problem in all membrane technologies is membrane fouling and biofouling (Ochando-Pulido et al., 2016), which is the accumulation of organic matter and growth of bacterial biofilms on the membrane surface, which lead to flux decline that very often cleaning cannot restore.

A promising approach to the control of fouling on water treatment membranes is based on increasing the hydrophilic character of the membrane surface in order to make it less susceptible to organic- and bio-fouling. Poly(ethylene glycol) (PEG) was shown to resist non-specific binding of proteins to surfaces (Kane et al., 2003) and was successfully incorporated in the design of water treatment membranes by several groups to reduce organic- and bio-fouling; the PEG moiety was either grafted on the membrane surfaces or incorporated in the polymer blend as an additive (Asatekin et al., 2007). PEG-coated surfaces were also found to be favourable in decreasing calcium phosphate scaling in desalination of domestic wastewater (Steiner et al., 2010). Redox-initiated graft polymerization with hydrophilic methacrylate monomers was reported previously by our group as an efficient method of antifouling coatings of RO and NF membranes (Belfer et al., 1998). The swelling properties of the coating layer was shown to have an important role of anti-fouling (Herzberg et al., 2011); an additional contribution to anti-fouling was the chemical nature of coating - where poly(ethylene glycol) moieties reduced fouling and sorption of organic matter (Eshet et al., 2011).

Polymeric coatings with micro-spherical morphology, as opposed to smooth-flat coating, has the advantage of high surface area, which can be beneficial for anti-fouling coatings of membranes (Figure 1). It may also be beneficial for applications in other fields, such as materials with high sorption capacity, nano-reactors, and resins for heterogeneous chemical catalysis.
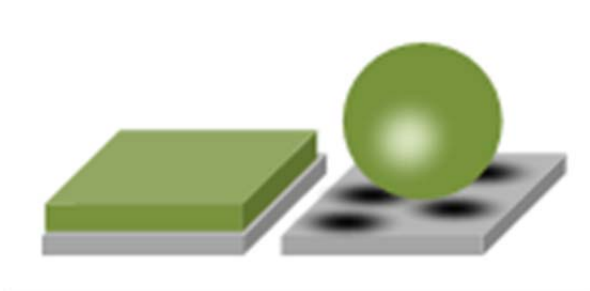
Figure 1: Flat (smooth) vs. spherical coating of membrane surface.

Several strategies were described in the literature for preparing polymeric coatings with spherical architectures. Micelles based on comb-like PEG derivatives were previously reported: Li (2006) performed atom-transfer radical polymerization of poly(ethylene glycol) methacrylate (PEGMA), the produced polymer self-assembled into micelles with critical micelle concentration of 6 mg/L, that were further crosslinked to gain stability (Li et al., 2006). Microscopic analyses showed 200-500 nm wide vesicles, with 50 nm width of the walls. The use of PEG as a coating shell provides the vesicles with anti-adhesive properties (Otsuka et al., 2001). Yang and his group obtained spherical particles of 0.35 - 1.30 µm coating a surface, by UV-initiated co-polymerization of the amphiphilic monomer N-vinylpyrrolidone (NVP) with emulsion of methyl-methacrylate and divinyl-benzene stabilized by surfactants (Wang and Yang, 2004). The spherical particles were either hollow or solid, depending on the exact monomer composition.

In this study a straight, one-step generation of spherical polymeric coating on NF membrane surfaces was performed by emulsion co-polymerization of styrene and polyethylene glycol methacrylate (PEGMA) in water. The coating showed micelles of 30 – 120 µm size; we hypothesize that these micelles were stabilized by PEGMA and poly(PEGMA) in the polymerization emulsion. A homogeneous surface morphology on the NF membrane was achieved, with spherical polymeric micelles that have a large surface area.

2. Experimental section

2.1 Materials

The initiators potassium persulfate ($K_2S_2O_8$) and potassium metabisulfite ($K_2S_2O_5$), poly(ethylene glycol) methacrylate (with number average molecular weight of 360 (n ~ 6) or 526 g/mol (n ~ 10)) and styrene, were all purchased from Sigma-Aldrich (St. Louis, MO, USA). NF270 membranes were provided as a gift from FILMTECH Dow Water Solutions (Midland, MA, USA).

2.2 Redox initiated emulsion copolymerization and NF membrane coating

Polymerization was performed in aqueous solution comprised of 5 mL styrene, 5 mL PEGMA-360 and 40 mL water. Polymerization initiated by adding potassium persulfate and potassium metabisulfite (0.2 g each), and the reaction proceeded for 5 h at 68 °C while thoroughly mixing. The solution was then cooled to room temperature. The NF270 membrane was coated with the micelles by spin coating, where 100 µL of the polymerization mixture was added to the middle point of a membrane rotating at 40 rounds per second for 5 min. The coated NF270 membrane was dried in vacuum overnight at room temperature.

2.3 Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR measurements for NF270 membranes and coated membranes were performed on VERTEX 70/80 (BRUKER Optiks GmbH, Ettlingen, Germany) FTIR spectrometer equipped with an ATR element (45° single reflection diamond-coated KRS-5 internal reflection crystal). The membranes were completely dried overnight in a vacuum desiccator prior to measurements. When pressed tightly against membrane, the KRS-5 element samples a circular disc of ~2 mm in diameter. Five replicate spectra were obtained for every membrane, with each spectrum averaged from 30 scans collected in the spectral range 400 – 4000 cm^{-1} at 4 cm^{-1} resolution. The resulted spectra were subsequently corrected for the wavelength-dependent penetration depth of evanescent IR wave (~1 µm) and background subtraction with the OPUS software (version 6.5, BRUKER).

2.4 Microscopic imaging

Optical microscope was used to visualize the membrane surface and micelles.

2.5 Critical micelle concentration (CMC) measurements

The amphiphilic characteristic of PEGMA-526 was determined in terms of its 2.5 Critical micelle concentration (CMC) by surface tension measurements that were performed by KSV's tensiometer (Model Sigma 70, Finland). Several aqueous solutions with different concentration of the examined monomer were measured with 10-15 repetitions having DI water as a standard reference at temperature of 21±1 °C. Using standard computational program, plotting the relationship between the logarithmic concentration and the tension, the CMC was extrapolated.

3. Results and discussion

3.1 Emulsion copolymerization resulted in micelles formation

The copolymerization of PEGMA with styrene (Figure 2) was performed in aqueous solutions; PEGMA was chosen as monomer for coating membranes due to its PEG chain which enables antifouling properties, and to the amphiphilic nature of its corresponding polymer which stabilized the emulsion of styrene.
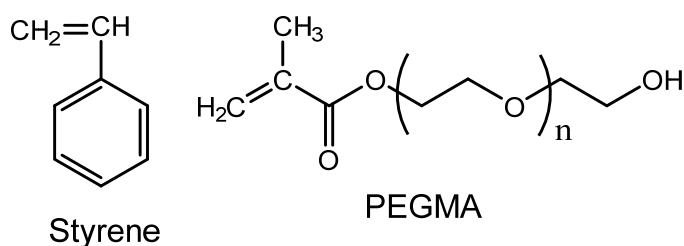

Figure 2: Chemical structures of monomer that were used in emulsion copolymerization.

The formation of micelles and granules in copolymerization of PEGMA with styrene in water was observed by optical microscope; as can be seen in Figure 3, granules and micelles isolated from the copolymerization had 50-120 µm size. FTIR spectroscopic analysis of the micelles was performed (Figure 3): The presence of poly(PEGMA) was evident from the peak at 1,723 cm^{-1} which is assigned to the ester carbonyl (C=O) group, and 1,094 and 948 cm^{-1} that are related to ether (C-O-C) groups of PEG. The polystyrene was observed by peaks at 798 and 1028 cm^{-1} that are assigned to the aryl and aromatic C-C vibrations.
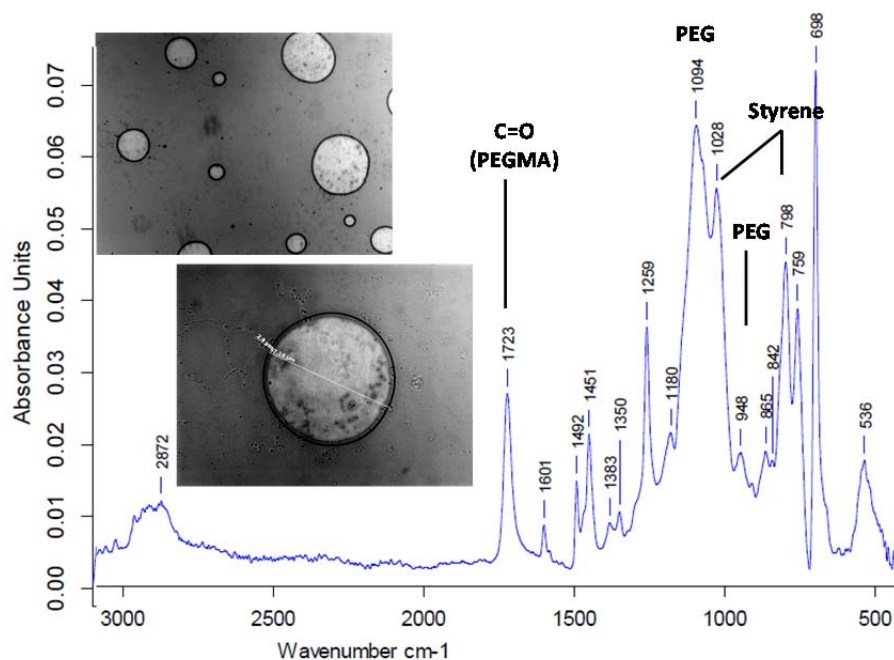

Figure 3. Optical microscope images (x40) of isolated granules and micelles and ATR-FTIR spectrum of copolymerization of PEGMA-360 with styrene.

3.2 NF membrane coated by copolymers

NF270 membranes were spin-coated by copolymers of PEGMA-360 with styrene. FTIR analysis of the coated membrane in comparison to pristine NF270 membrane (Figure 4) confirmed the chemical identification of styrene-PEGMA copolymer coated on polyamide NF membrane: The poly(PEGMA) coating on the membranes is evident from the peak at 1,724 cm^{-1} (ester carbonyl group), and peaks at 1,101 and 948 cm^{-1} of the ether groups of PEG. The poly(styrene) absorbs at 700 cm^{-1}. This coated membrane shows also low-intensity amide peaks (corresponding to Amide-I and Amide-II groups). On the other hand, the pristine membrane has intense two absorption peaks of the amide bond (Amide-I and Amide-II), no absorption peaks in the carbonyl (ester) region, and no absorption in the PEG region. These findings imply that the coating layer of the membrane consists of poly(PEGMA)-copolymer-poly(styrene); furthermore, the copolymer coating masks the IR absorption of the polyamide film of NF membrane, which results in low intensity amide peaks.

The microscopic images of pristine and coated NF membranes (Figure 4) show that the micelles maintained their stability when coated on the membrane surface.
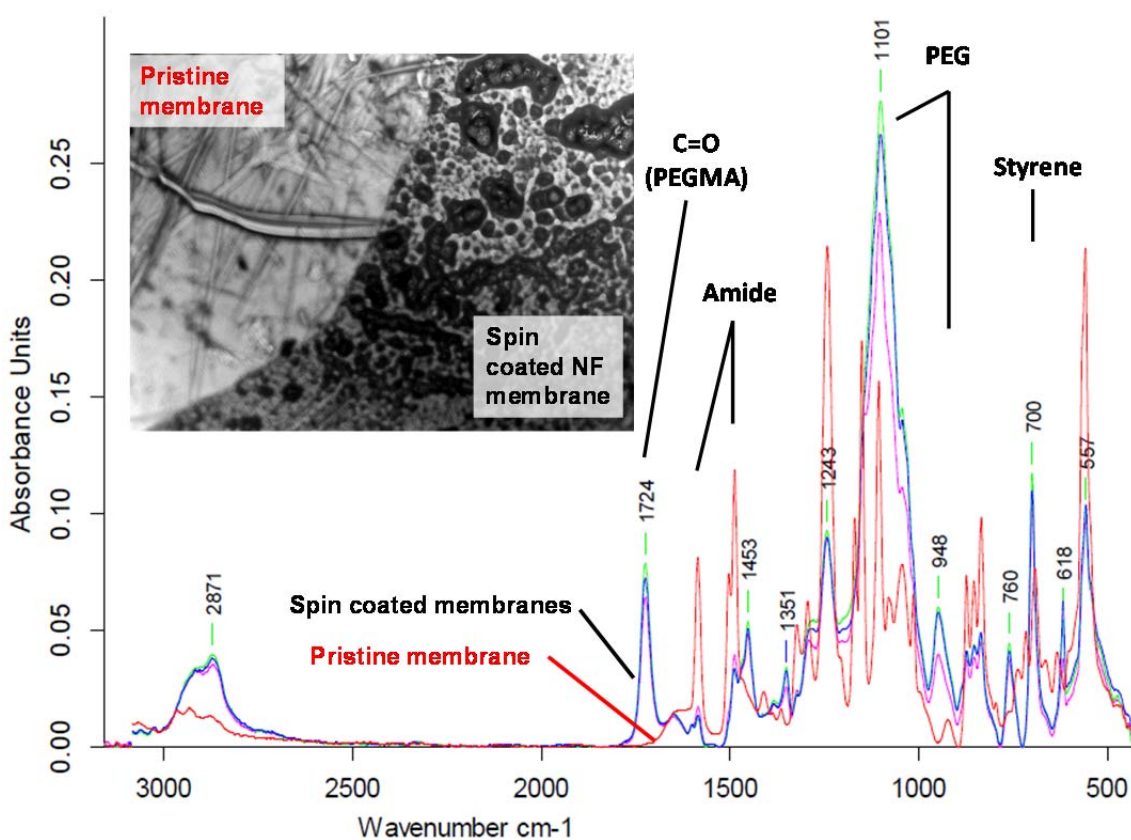

Figure 4. ATR-FTIR spectra of NF270 membranes coated by copolymerization of PEGMA-360 with styrene, in comparison to pristine membrane. The insert shows an optical microscope image (x40) of pristine NF270 membrane (upper left) and coated membrane (lower right).

To evaluate the amphiphilic nature of the monomer PEGMA-526, in order to understand whether it can create micelle in water, we determined the critical micelle concentration (CMC; Figure 5). It was found that PEGMA-526 has CMC of 0.05 M, which is much lower concentration than its concentration in the polymerization mixture (~0.19 M). Hence, in the copolymerization reaction PEGMA-526 was above its CMC value, therefore it created stable micelles and also acted as a surfactant in respect to the styrene.
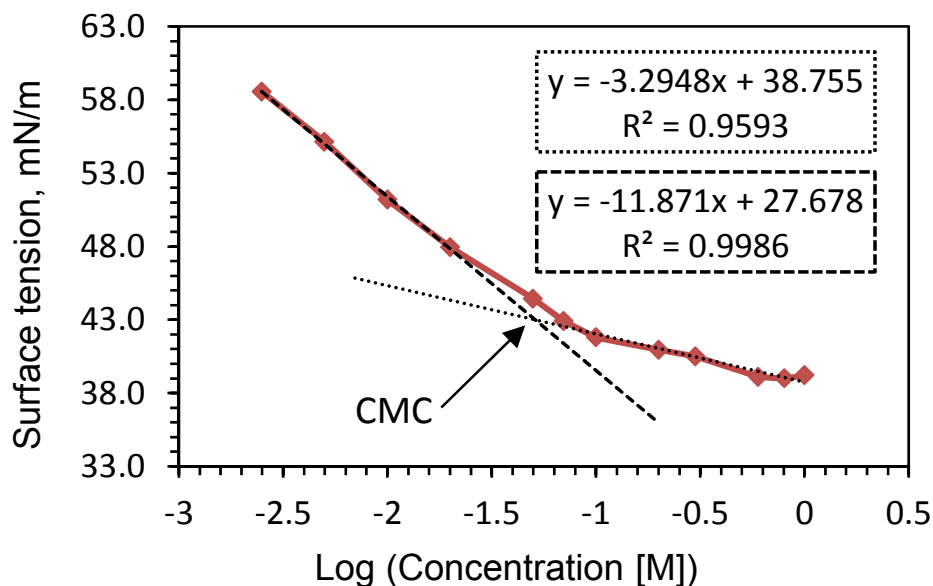
Figure 5. Critical micelle concentration (CMC) measurement of PEGMA with molecular weight of 526 g/mol resulted in CMC of 0.05 M.

4. Conclusions

The fabrication of spherical polymeric particles containing PEG moiety was achieved in one-stage copolymerization. The spherical polymeric particles were coated on NF membranes, and characterized spectroscopically and microscopically. The fact that PEGMA-526 was above its CMC value in the copolymerization reaction resulted in stable micelles and also stabilized the styrene emulsion due to the PEGMA surfactant behaviour. It led to stabilized spherical polymeric particles in the resulted copolymer coating. Copolymers based on PEGMA were reported previously in the literature to have micellar nature (Otsuka et al., 2001); in addition, Li et al. fabricated spherical polymeric particles based on the micellar nature of PEGMA by using atom-transfer radical polymerization (Li et al., 2006). The advantage of the present study is the simplicity of the copolymerization protocol, which uses low cost materials and is performed in aqueous solutions. The simple technique used in this study complies with a strict demand for low-cost and robust materials in industrial applications of water treatment technologies, and therefore it is highly attractive method for further development.

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