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Molecular Weight Cut-off Determination of Organic Solvent Nanofiltration Membranes Using Poly(propylene) Glycols

Christopher John Davey,^{a,b} Ze-Xian Low,^{b,c} Remigius H. Wirawan,^{a,b} Darrell Alec Patterson^{*a,b,c}

^aCentre for Sustainable Chemical Technologies, University of Bath, Claverton Down, Bath, BA2 7AY

^bBath Process Intensification Laboratory, Department of Chemical Engineering, University of Bath, Claverton Down, Bath, BA2 7AY, UK

^cCentre for Advanced Separations Engineering, University of Bath, Claverton Down, Bath, BA2 7AY, UK

Corresponding Author: Darrell Alec Patterson, Email: d.patterson@bath.ac.uk; darrell.patterson@gmail.com, Phone: +44 (0) 1225 386088

Abstract

A new method for determining the molecular weight cut-off (MWCO) of an organic solvent nanofiltration (OSN) membrane has been developed utilising poly(propylene) glycol (PPG) oligomers. This new MWCO method overcomes the limitations of the currently popular methods: namely the high molecule cost in the popular polystyrene method, the Donnan Exclusion effects when using dye molecules and the solvent compatibility and HPLC separation resolution limitations of the lesser used poly(ethylene) glycol (PEG) method. A new reverse phase high-performance liquid chromatography separation with evaporative light scattering detection (ELSD) allows the concentration of each oligomer of PPG to be accurately determined and from this the MWCO curves are constructed. The method has a high resolution (size increment of 58 g mol⁻¹ corresponding to the OCH(CH₃)CH₂ structural unit) and can be used in polar, polar aprotic, and non-polar solvents. The accuracy of the method has been demonstrated in three different solvents (methanol, acetone, and toluene) and 5 different OSN membranes (DuraMem® 150, 200, 500, PuraMem® 280 and StarMem™ 240). Other advantages include; oligomers of PPG are cheap and widely available, can probe a wide range of MWCO and provide high resolution MWCO curves. Consequently, it is proposed that this method be adopted as a new standard MWCO test for OSN membranes.

Keywords: Molecular weight cut-off (MWCO); organic solvent nanofiltration (OSN); Solvent Resistant Nanofiltration (SRNF); Poly(propylene) glycol (PPG); Poly(propylene) oxide (PPO); reverse phase high-performance liquid chromatography (HPLC); evaporative light scattering detection (ELSD); membranes.

1. Introduction

Membrane separation processes are increasingly being adopted throughout industry as they can provide low energy separations for a number of commercially important chemical species.[1, 2] Among these, organic solvent nanofiltration (OSN; also known as solvent resistant nanofiltration, SRNF) is an emerging technology for more efficient separations within the chemical and pharmaceutical industries.[2-5] When applying a particular membrane to a separation it is important to understand its general separation ability before conducting feasibility testing; or if a new membrane material has been developed it is important to be able to generally quantify its separation potential. For nanofiltration (NF) membranes, the molecular weight cut-off (MWCO) is an important characteristic for determining their usefulness in a particular separation. Used as a general guide for the separation ability of a membrane it is defined as the molecular weight (MW) for which 90 % of a solute is rejected.[1, 6] In practice, a range of different MW solutes are filtered in the target solvent and the MWCO value is the real or interpolated MW of the solute molecule that gives a 90 % rejection. Although in many circumstances a key factor, it is important to note that MW is not the only property to affect separation.[7] Despite this, the MWCO of a membrane provides an important general description of a membrane's separation ability.

In aqueous solutions, a number of methods have been developed to determine the MWCO of a NF membrane.[6, 8-10] However, these methods cannot be directly applied for use in organic solvent systems due to various issues such as solute solubility and compatibility in organic solvents, as well as the numerous and complex solute-solvent-membrane interactions present. Suitable techniques for determining the concentration of the probe molecule in the permeate is also problematic when applied across a range of solvents. Thus, several new methods using different solute molecule types have been developed specifically for OSN systems as summarized in Table 1. Researchers also use a range of different MW dye molecules (including methylene blue and rose bengal) – however these have not been included in Table 1, since the rejection is generally due to both charge (Donnan Exclusion) and MW related factors that make them less comparable (and ultimately less accurate and therefore applicable to MWCO determination) than those listed.

Table 1. Comparison of important attributes of common methods of MWCO determination in OSN, (✓ = advantage, ✗ = disadvantage, ~ = neutral).

Important attributes of the MWCO method	Solute used in MWCO method			
	Alkanes Ref:[11]	Polystyrene Ref: [12]	Poly(ethylene) glycols Ref:[13]	Poly(propylene) glycols Ref: this work
Detection method	~ Gas chromatography	✓ Simple detection via UV	~ Use of ELSD	~ Use of ELSD
MWCO attributes	✓ Can investigate influence of MW and structure on rejection	MW of solute only	MW of solute only	MW of solute only
MW of solute repeating unit	Not constant	104 g mol ⁻¹	44 g mol ⁻¹	58 g mol ⁻¹
Solvent applicability	✗ Limited solubility in more polar organic solvents	✗ Solvent swap required for solvents that obscure chromatogram (e.g. toluene, hexane, ethyl acetate)	✗ Insoluble in most non-polar solvents ✗ Poor rejection by commercial membranes in organic solvents	✓/✗ Soluble in non-polar solvents however a solvent swap required for non-polar solvents that obscure the chromatogram
Quantitative solute concentration determination	✓ Can determine exact concentrations of each MW	✗ Difficult to determine absolute concentrations of each oligomer	✗ Difficult to determine absolute concentrations of each oligomer	✗ Difficult to determine absolute concentrations of each oligomer
Solutes cost and availability	✗ Lack of pure commercially available alkanes > 400 g mol ⁻¹	✗ Expensive Oligomers	✓ Cheap range of available oligomers	✓ Cheap range of available oligomers

One of the more commonly used solutes and methods for MWCO determination of OSN membranes is through the use of oligomers of polystyrene.[12, 14-16] Polystyrene oligomers having MWs between 200 and 1000 g mol⁻¹ allow a sufficient MW range to be covered to produce suitable MWCO curves for OSN membranes in various polar and non-polar solvents. Polystyrene oligomers have been used since they have four of the five essential properties of MWCO probe molecules (related to the important attributes of a MWCO method in Table 1):

- Availability:** polystyrenes are available in a wide range of MWs, unlike proposed alternative probe molecules such as alkanes [11] (which lack commercially available pure species of MW > 400 g mol⁻¹);
- Molecular similarity:** polystyrenes are available in a homologous series, enabling a range of similar molecules to be used for MWCO determination. Systems which use a selection of different compounds as probes which could vary in structure and functionalities (e.g. dyes[17] or alkanes[11]) could have differing and varied interactions with a membrane leading to a skewed increase in rejection with MW.[18]
- Robust analysis method for mixtures in different solvents:** The various MW polystyrenes when dissolved in the different solvents used in OSN can be separated by HPLC analysis and therefore a MWCO can be determined in a single filtration, instead of a series of filtrations, each with a single solute (which is often the case for MWCO methods that use different compounds).

- D. *Good resolution*: The MWCO curve must be obtained in a reasonable resolution – i.e. a small gap between the MW of molecules in the series to enable the MWCO to be determined with good accuracy. The polystyrene method is not ideal with a 104 g mol⁻¹ resolution, which may not as accurately discriminate the differences between some membranes which can have differences in MWCO less than this (such as for the DuraMem® series from Evonik which comes in close MWCOs of 150, 200 and 300) as methods with closer gaps in the molecular series.
- E. *Affordability/low cost*: The polystyrene method however fails in the last key requirement – low cost. Pure polystyrene oligomers of low MW and polydispersity are very expensive (Polystyrene 500 £153/g; Polystyrene 1000 £85.9/g; Sigma Aldrich 2016) which can mean that the use of the polystyrene MWCO method is prohibitively expensive if it is to be applied as a routine measurement and/or at large scale. The material costs can in part be ameliorated by synthesising the oligomers prior to testing if the test is to be applied at laboratory scale. However, the synthesis can be time-consuming (accruing potentially prohibitively expensive person-time costs) and may produce oligomers with varying quality and purity (e.g. mixtures of oligomers / oligomers with high polydispersity that may not be able to be properly resolved using the HPLC-UV method commonly applied).[12]

A more cost effective and higher resolution alternative to the polystyrene MWCO method is therefore needed.

Polyether-based molecular probes such as poly(ethylene) glycols (PEGs) have been proposed for determining the MWCO in both aqueous systems[6] and in polar solvents[13, 19, 20]. The analysis of polyethers (such as PEGs) is commonly done by means of reverse phase high-performance liquid chromatography (HPLC) with evaporative light scattering detection (ELSD) which gives suitable separation and detection of the individual polyether oligomers (such as PEGs, poly(propylene) glycols (PPGs) and poly(butylene) glycols (PBGs)).[21, 22] However, the insolubility of PEGs in some non-polar solvents as well as the wide range of conformations that PEG adopts in different organic solvents[23] can sometimes limit the reliability and cross-comparability of this method in OSN. This means PEGs can sometimes give quite different results for MWCO determination when compared to other methods [19] (also see further results and discussion demonstrating this in Supplementary Material, Section S1). If a closely related and inexpensive compound could be found and an analysis method can be developed to allow the oligomers to be resolved accurately in a range of solvents commonly used in OSN, an additional and further enabling OSN MWCO method to all those currently used could be developed that can help expand the MWCO determination potential where the current methods cannot be readily used. We hypothesize that poly(propylene) glycol (PPG; Figure 1) can be used as this MWCO molecular probe.

Figure 1. Chemical Structure of Poly(propylene) Glycol (PPG).

Herein we report a method for the single filtration determination of MWCO for OSN membranes utilising PPG with oligomer separation (Figure 1) by means of reverse phase HPLC coupled with an

ELSD. PPG comes as a homologous series and has the same polyether backbone as PEG, but the extra methyl groups improves the hydrophobicity of the polymer, which increase its solubility in non-polar organic solvents when compared to PEG. The method has a high resolution, with a size increment of 58 g mol^{-1} corresponding to the $\text{OCH}(\text{CH}_3)\text{CH}_2$ structural unit. Also, PPGs with a wide range of MWs are commercially available at a fraction of the cost of polystyrene oligomers. All five essential properties of MWCO probe molecules are therefore potentially satisfied.

MWCO curves have been constructed for a number of commercial OSN membranes in a range of organic solvents (polar aprotic, polar protic and non-polar) and the results have been compared to those of previously reported methods for determining MWCO in OSN. The membranes chosen are commonly used within the literature and industry, and have been selected due to their differing nominal MWCOs, as defined by the manufacturer, to probe the effectiveness of the designed method. This enables reliable comparison to both literature and industry data that have used other MWCO methods. The results indicate a reproducible, single filtration method using inert molecules of regularly incrementing size that is compatible in a range of organic solvents.

2. Materials and Methods

2.1 Materials

Tripropylene glycol (Alfa Aesar), PPG 400 (Alfa Aesar), PPG 725 (Sigma Aldrich), PPG 1000 (Alfa Aesar) of reagent grade were used as the PPG oligomer samples. Organic solvents (HPLC grade) methanol, acetone, acetonitrile and toluene were purchased from VWR and used as received. The membranes used in this study were purchased from Evonik (UK) (DuraMem® 150, DuraMem® 200, DuraMem® 500 and PuraMem® 280) and Membrane Extraction Technologies (StarMem™ 240). Ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$ at 25°C) and HPLC grade acetonitrile (Alfa Aesar) were used in the gradient elution of the HPLC method. Nitrogen (BOC, 99.998 %) was used as carrier gas for the ELSD.

2.2 Experimental Procedure

To determine the MWCO of the commercial OSN membranes, filtration experiments were conducted using a stainless steel dead end filtration cell (HP4750, Sterlitech Corporation USA; active membrane surface area of 14.6 cm^2) (Figure 2). Standard methodology that has been applied in numerous other studies was used.[6, 12, 24] A magnetic stirrer just above the membrane surface was used for mixing of the feed and minimizing concentration polarization. Typically, solutions of PPG were made up by dissolving 4 g of each PPG sample (tripropylene glycol, 400, 725, 1000) in 1 L of solvent. Before use, membranes were conditioned with the appropriate solvent at the desired applied pressure and temperature for around 2 hours until a consistent flux was achieved. For each experiment a fresh membrane was used to avoid any effects of cross contamination of samples. To perform the MWCO determination, 40 mL of feed was added to the cell of which half was permeated using an applied pressure of 30 bar, except for DuraMem® 500 where an applied pressure of 10 bar was used. The temperature was maintained at 30°C using a water bath.

Figure 2. Schematic of dead-end filtration set-up.

The concentration of each PPG oligomer was determined by the HPLC-ELSD outlined in Section 2.3. Rejection of each PPG oligomer could therefore be determined using equation 1:

$$R_{j,i} = \left(1 - \frac{C_{i,p}}{C_{i,f}} \right) \times 100 \% \quad (1)$$

where $C_{i,p}$ refers to the concentration of species i in permeate and $C_{i,f}$ refers to the concentration of species i in feed.

Mass balances were also calculated using equation 2:

$$\% \text{ recovered} = \left(\frac{V_p C_{i,p} + V_r C_{i,r}}{V_f C_{i,f}} \right) \times 100 \% \quad (2)$$

where $C_{i,f}$ refers to the concentration of species i in feed; $C_{i,p}$ refers to the concentration of species i in the permeate; $C_{i,r}$ refers to the concentration of species i in the retentate; and V refers to the volume of the permeate, retentate and feed, respectively.

2.3 Analytical Methods

Determination of the concentration of each PPG oligomer in the feed, permeate and retentate was conducted using reverse phase high-performance liquid chromatography (HPLC) equipped with an evaporative light scattering detector (ELSD). An Agilent Technologies (1260 Infinity) HPLC system consisting of a quaternary pump (G1311B), autosampler (G1329B), column oven (G1316A) and ELSD (GB1530001) was equipped with a Poroshell 120 EC-C18 (4.6 x 50 mm 2.7 μ m) column to achieve separation. The conditions utilised an injection volume of 100 μ L, a flow rate of 1 mL min⁻¹, a column temperature of 25 °C and a gradient elution of water and acetonitrile outlined in Table 2. The ELSD detector was set to a nebulizer temperature of 25 °C, a nitrogen gas (BOC, 99.998 %) flow rate of 1.8 SLM and an evaporator temperature of 25 °C. Note that this evaporation temperature is lower than is commonly used. However, evaporation temperature of ~ 30 °C are common for the ELSD used in this work (Agilent 1260, GB1530001). 25 °C was used to obtain detection of the lower molecular weight oligomers (which were undetectable at higher ELSD evaporation temperatures). Although this is the low end of usable operation, there was no noticeable effect of noise on the ELSD signal from partial vaporization of the eluent.

Table 2. Solvent gradient used for HPLC elution.

Time (min : sec)	Concentration of Water (%)	Concentration of Acetonitrile (%)
0	95	5
2:30	80	20
42:30	0	100
47:30	0	100
50	95	5
57	95	5

Before analysis, all samples in water miscible solvents were diluted with water by 1/3 (400 μL sample and 800 μL water) to give an improved chromatogram as this reduces fronting of the peaks and gives an improved baseline (see Section 3.1 for further discussion of this). Non-polar solvents were evaporated *in vacuo* and replaced with an equal amount of methanol. This mixture was then diluted with water as above before HPLC analysis.

Each PPG oligomer exhibited an exponential relationship between peak area and oligomer concentration characteristic of ELSD[21] (Equation 3):

$$y = ax^b \quad (3)$$

where y is the peak area of the response, a and b are coefficients that are dependent upon the separation and experimental conditions and x is the mass of the analyte. Calibration curves (see Supplementary Material S3.1 and S3.2) were constructed by diluting a stock solution of a mixture of PPG oligomers at a higher concentration than used ($200\% = 8\text{ gL}^{-1}$ of each sample). This gives a relative concentration which can be used for calculation of the rejection and mass balances of each PPG oligomer.

3. Results and Discussion

3.1 Development of the analytical method

Previous studies have investigated the influence of the mobile and stationary phases on the separation of PPGs using reverse phase HPLC and ELSD.[22] These methods achieved good separation of the oligomers at relatively high concentrations of PPG in methanol and therefore only required small injection volumes (10 μ L). For MWCO determination, the concentration of PPGs is required to be much lower such as to minimise the effects of concentration polarisation and fouling. To allow for this, a higher injection volume was used in the HPLC method (100 μ L); however, this led to a much larger amount of organic solvent being introduced to the column at an early stage of the separation, altering the concentration gradient. In these chromatograms peak fronting and poor baseline resolution was observed. It was found that diluting the samples with water (when water miscible solvents were used) greatly improved the separation and resolution of PPG, as this reduced the ratio of organic solvent to PPG being injected (Figure 3). Looking at the different amounts of water added (as per Figure 3) it was determined that dilution with water by 1/3 (400 μ L sample and 800 μ L water) gave an improved chromatogram with reduced peak fronting and a flat baseline, both facilitating repeatable measurements and accurate and repeatable integration of all peaks.

For determination of oligomer concentrations in non-polar and water immiscible solvents, these were solvent exchanged by removing the original solvent *in vacuo* and replacing with an equal volume of methanol. This sample was then diluted with water achieving a suitable chromatogram for MWCO determination. Mass balances showed that there was no significant loss of PPG in the solvent exchange process (< 10 %).

Figure 3. Effect of dilution of samples with water on the HPLC chromatogram of PPG dissolved in different solvents (a) methanol, (b) dimethylformamide, (c) acetonitrile, and (d) acetone. In each, percentage (%) refers to the vol% of original sample.

Each PPG oligomer can be easily identified in the chromatogram due to the regularity of elution as shown in Figure 4.a. The peak corresponding to tripropylene glycol ($\text{MW} = 192.1 \text{ g mol}^{-1}$) is first to elute and can be easily identified as it possesses shoulders due to the presence of its isomers in the purchased samples. These isomers were not able to be separated within the chromatographic method and were therefore treated as one MW due to their limited difference in sterics. The next PPG to elute is that with a MW of 250.3 g mol^{-1} ; however this oligomer was present at very low concentrations within the PPG 400 sample used and so was not used in this investigation. Each oligomer can then be identified up to PPG with a MW of $>1179.9 \text{ g mol}^{-1}$. The identification of each PPG oligomer also correlated well with the manufacturer's defined average MW distribution of each sample (Figure 4.b).

Table S2 (Supplementary Material) outlines which PPG oligomers were present within each purchased sample and typical elution times of each oligomer with the applied method.

Figure 4. Separation of PPG oligomers in methanol by the described HPLC method. (a) analysis of feed (b) analysis of individual commercial samples.

As outlined in Section 1, an essential feature of a successful MWCO determination method is the ability for the analysis to work with the MWCO probe molecules used in a number of different solvents. The PPGs were found to be soluble in all solvents investigated in this study at the intended concentration. Therefore, a study of the effect of different organic solvents on the chromatographic separation was undertaken. As can be seen from Figure 5, the method can be applied across different organic solvents which are miscible with water. Each solvent exhibits the typical separation of PPG oligomers as presented for methanol. However due to the disruption of the gradient of the mobile phase in the separation, some of the resolution of the lower MW oligomers is lost in certain solvents. For non-polar solvents (which elute in the middle of the chromatogram) and solvents that did not have

high enough resolution for the membrane to be tested, a solvent exchange can be performed where the solvent is removed *in vacuo* and replaced with the same volume of methanol before dilution with water for HPLC analysis, as outlined in Section 2.3. This allows for determination of oligomers down to a MW of 192 g mol⁻¹ if required.

Figure 5. HPLC chromatograms of PPGs in different solvents diluted with water.

3.2 Determination of MWCO in commercial OSN membranes

The MWCO of a number of commercially available OSN membranes was therefore investigated using the developed method (Figure 6). MWCO's were determined in methanol, acetone and toluene as examples of polar, polar aprotic and non-polar solvents, respectively. The MWCOs determined using PPG are within the range of those reported by the manufacturer (and closer than those determined by a PEG MWCO method – see Supplementary Material for further details), constructed using oligomers of polystyrene in acetone for the DuraMem® membranes and in toluene for PuraMem® 280 and StarMem™ 240. Importantly, the shapes of the MWCO curves are comparable to those obtained by other methods in the literature also (e.g. for StarMem™ 240 in [12]), which is essential for understanding how sharp a separation a membrane can give.[1] This is not the case for other methods, such as those using PEG (see Supplementary Material for comparison).

Figure 6. MWCO curves of (a) DuraMem® 150; (b) DuraMem® 200; (c) DuraMem® 500; (d) PuraMem® 280; and (e) StarMem™ 240 using PPGs.

Table 3. Comparison of the MWCO from the manufacturer using the polystyrene method and from the PPG method in this work.

Membrane	Manufacturers Stated MWCO: (g mol ⁻¹)		PPG MWCO: (g mol ⁻¹)		
	Acetone	Toluene	Methanol	Acetone	Toluene
DuraMem® 150	150	-	308	308	-
DuraMem® 200	200	-	308	308	-
DuraMem® 500	500	-	657	657	-
PuraMem® 280	-	280	366	-	657
StarMem™ 240	-	400	657	-	715

It is also noticeable that the rejection characteristics of StarMem™ 240 and PuraMem® 280 differ considerably between methanol and toluene. This is most likely due to a combination of the different swelling of the membrane in these two solvents (as indicated also in [12]) as well as the high degree of rotational freedom around the polymer backbone for PPG. Previous work has shown that PPGs exist as a tight coil in polar / aqueous systems and open up in non-polar solvents,[25, 26] this reflects the increased rejection observed in methanol compared to toluene. It would be expected that a tightly coiled PPG would be rejected better than an uncoiled PPG chain that could rotate to a preferred orientation to permeate through the membrane.

Figure 7 compares the MWCO of the tested membranes using the PPG method with methanol as solvent. The MWCO curves of the membranes correlate well with the increasing MWCO trends as defined by the manufacturer using the polystyrene method, however MWCO for PPGs are generally slightly higher than those reported for polystyrene (Table 3). This has been attributed to the differences in steric bulk and rotational freedom around the backbone of the polymers, as well as the differences between the polystyrene and PPG molecules and their interactions with the membranes in the solvents used. Differences in MWCOs determined using different solute systems have been noted before (e.g. [12, 17]). Different molecules may also produce different MWCOs due to differing macromolecular chain deformation, shape, membrane interactions and orientations during filtration, since rejection is not based on MW, but rather a range of shape, charge, chemical interaction and molecular orientation based phenomena. PPGs will be representative of a different set of molecules as compared to the polystyrenes used by the manufacturers of these membranes and therefore the MWCOs and MWCO curves generated by the PPG method help to explain why these membranes can give rejections that are far from the MWCO that is specified when used for separations of molecules other than polystyrenes.

Consequently, since the MWCO curves provide a further way of determining the selectivity of OSN membranes for molecules that are dissimilar to the widely used polystyrenes, this new PPG method should be used to complement the PEG and polystyrene techniques where a more robust understanding of OSN performance and selectivity is required (such as for understanding the potential range of performance of a new OSN membrane or for OSN membrane manufacturers to state a more representative range of MWCO values for client potential applications). The PPG method can also be used to ascertain MWCO in circumstances where the PEG method does not yield a single numerical value, as conventionally defined, due to poor PEG rejection creating a flattened MWCO-curve (e.g. Section S1, Supplementary Material). Moreover, in cases where only a comparative assessment of

MWCO is required and so only one MWCO method need be used, the authors propose that this method be adopted as a new standard MWCO test for OSN membranes that could be used, since compared to the current standard of polystyrene, oligomers of PPG can probe a wider range of MWCO, provide higher resolution and cost considerably less.

Figure 7. Comparison of the MWCO of different OSN membranes with methanol as solvent using the PPG method.

4. Conclusions

A new, single filtration, reproducible method for determining the MWCO of OSN membranes using PPGs has been presented. The method has been used to construct MWCO curves of commercial OSN membranes within the range of 192 – 1180 g mol⁻¹ for methanol, acetone, and toluene, indicating a method that can be applied across a number of different solvents (i.e. polar, polar aprotic and non-polar). Utilising ELSD the method can be easily adopted by many researchers already studying PEGs for characterisation of aqueous NF membranes. This method provides an alternative analysis for OSN membranes and overcomes some of the limitations of the previously reported polystyrene and PEG methods, as well as providing a complementary analysis to these methods. Consequently, the authors propose that this method be adopted as a new standard MWCO test for OSN membranes since compared to the current standard of polystyrene, oligomers of PPG can probe a wider range of MWCO, provide higher resolution and cost considerably less.

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