Theoretical model of the porosity of copolymer membranes

Simcha Srebnik*

Division of Environmental Sciences, School of Applied Sciences, The Hebrew University, Jerusalem 91904, Israel

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Abstract

A theoretical model is developed to explore the porosity and chemical morphology of copolymer membranes. The size of the leaving group during polycondensation of the cross-links is found to have unexpected effects on the porosity, leading to a nonuniform pore-size distribution. The size and formation of microdomains with different chemistries and porosities can be predicted using this model. Such knowledge of a membrane’s physical and chemical morphology is useful in the development of fouling-resistant filtration membranes. Reverse osmosis and nanofiltration membranes commonly used today frequently undergo degradation due to fouling and thus experience a diminishing water flux. Additional control over the properties of the membrane can be achieved by combining two or more polymers to form a heteropolymer network. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copolymer membranes; Nanofiltration (NF); Reverse osmosis (RO)

1. Introduction

Increasing awareness of the need of clean water over the years has led to a worldwide tendency towards stricter regulations on water quality. In the US, for example, EPA regulations [1,2] are calling for more stringent regulations on the removal of colloidal particles, bioorganisms, salts, and disinfection byproducts, requiring the development of novel separation processes that can achieve a higher degree of solute rejection. In recent years, the adaptation of nanofiltration (NF) and reverse osmosis (RO) membranes has been considered as a potential method for the removal of pollutants since it can potentially achieve better removal than conventional filtration methods such as enhanced coagulation. Indeed, today membranes are being used for a variety of applications, including desalination, disinfection, removal of turbidity and organics, water softening, and to recycle water and enrich potable water. Membrane technology is particularly attractive since initial cost estimates show that smaller plants are already competitive with conventional treatments [3,4].

A key variable influencing the operating and capital cost of membranes is permeate flux. One major obstacle with NF and RO membranes today is the formation of a cake or foulant layer on the membrane’s surface which requires frequent cleaning of the membrane and/or replacement if irreversible fouling occurs, and which leads to permeate flux decline [5,6]. Modified composite membranes are increasingly being studied as more versatile possibilities [6–9]. Very recently, experiments on nanofiltration membranes whose active surface layer is composed of copolymers of water permeable hydrophilic blocks and foulant-rejecting hydrophobic blocks have been pursued as a possible solution to overcome fouling by natural organic mat-
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>(a)</td>
<td>monomer size</td>
</tr>
<tr>
<td>(f)</td>
<td>fraction of A monomers in polymer network</td>
</tr>
<tr>
<td>(L)</td>
<td>contour length of polymer</td>
</tr>
<tr>
<td>(m)</td>
<td>microphase separation order parameter</td>
</tr>
<tr>
<td>(N)</td>
<td>total number of monomers</td>
</tr>
<tr>
<td>(N_{cl})</td>
<td>number of cross-linked monomers</td>
</tr>
<tr>
<td>(P_{cl})</td>
<td>probability of forming (N_{cl}) cross-links</td>
</tr>
<tr>
<td>(r(s))</td>
<td>spatial position of (s)th monomer from a reference point</td>
</tr>
<tr>
<td>(s)</td>
<td>contour position of (s)th monomer along the polymer backbone</td>
</tr>
<tr>
<td>(V)</td>
<td>volume of polymer network</td>
</tr>
<tr>
<td>(Z)</td>
<td>partition function</td>
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Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>(\chi)</td>
<td>size of leaving group relative to the size of the monomer</td>
</tr>
<tr>
<td>(\delta_{AA})</td>
<td>Kronecker delta (both monomers that form a cross-link are of type A)</td>
</tr>
<tr>
<td>(\mu)</td>
<td>degree of cross-linked A monomers</td>
</tr>
<tr>
<td>(\theta(s))</td>
<td>type of monomer, (+/-1) for A/B monomers</td>
</tr>
<tr>
<td>(\rho)</td>
<td>density</td>
</tr>
<tr>
<td>(\rho_A)</td>
<td>partial density of A monomers</td>
</tr>
<tr>
<td>(\rho_B)</td>
<td>partial density of B monomers</td>
</tr>
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The idea derives from the hypothesis that a proper combination of hydrophilic water permeable channels and areas on the membrane surface that interact (either favorably or unfavorably) with the fouling species will allow for more fouling-resistant membranes that still have sufficient permeate flux. A schematic depiction of such a membrane is shown in Fig. 1. Following similar arguments, membranes can be tailored for the rejection of other foulants. However, a deeper understanding of separation science is still needed before such membrane technologies can be optimized. This is in part due to the fact that membrane surfaces as well as the fouling species are still poorly characterized.

So far, the vast majority of research studies of NF and RO membranes have been experimental, leaving much room for theoretical models in this field. The few theoretical and computational efforts have mainly focused on predicting flux decline [11,12] and the effects of surface roughness on fouling [13]. The relative complexity of the problem and the necessity for immediate solutions have discouraged scientists from pursuing such theoretical research. Nevertheless, a great benefit of theory is that once the basic models are obtained, predictions for different membranes, permeates, and fouling species can be obtained simply by adjusting the appropriate parameters in the model. In addition to understanding the physics and chemistry underlying the membrane’s characteristics, molecular modeling studies could rapidly and inexpensively predict the morphology of different macromolecular networks, thereby avoiding long and costly pilot testing. In this paper, we address certain issues in membrane design through theoretical research that ultimately strives to establish engineering guidelines for designing polymeric membranes for water filtration applications. The study will address problems encountered with experimental studies already being pursued [10,14]. The results from the studies also elucidate general fundamental principles pertaining to the porosity of copolymer membranes, which plays a key role in determining the permeate flux, its mechanical properties, and its separation capabilities.

We use methods in statistical physics commonly employed in polymer science [15,16], to examine the porosity of copolymer networks, with view towards developing guidelines for the choice of molecular architectures and chemical constitution of the membrane. Such methods allow for the calculation of important macroscopic properties such as the free energy of a cross-linked network, or membrane. This kind of information, in turn, serves as inputs to
phenomenological models that aim to describe properties of engineering interest, such as porosity and chemical structure. With these findings, it should be possible to identify polymers with the needed characteristics (e.g. low fouling potential and high water flux) and from these engineer relevant composite membranes.

The paper is organized as follows. In Section 2, we provide a detailed description of the problem and develop the mathematical model for microphase separation and polycondensation of cross-linked polymer networks. In Section 3, we present and discuss our results, including their application to membrane fouling. Concluding remarks are offered in Section 4.

2. Theory

2.1. The general description of the model

Our ultimate goal in designing copolymer membranes is to find the “best possible” molecular architecture that allows for sufficient water flux, maximizes solute rejection, and minimizes fouling. A practical theoretical model should be able to capture these three properties. In general, the chemical constitution of the copolymer can be expressed as being composed of A and B monomers, where, for example, the hydrophilic monomers are of type A and the foulant-rejecting monomers are of type B. Given an appropriate distribution and fraction of A monomers, such a network will have sufficiently long channels for water permeation while maintaining anti-fouling characteristics.

The properties of the membrane depend on the chemical identity of the two constituents, the fraction of segments that are of type A, and the degree of cross-linking of the network. We will show that these three variables have a significant role in determining the physical (porosity) and chemical (AB morphology) structure of the polymer network. In addition, the model accounts for polycondensation during cross-linking implicitly by assuming densification of the network around the cross-linked sites proportional to the size of the leaving group.

We choose to study random copolymers since they are relatively cheap and easy to synthesize compared with well defined copolymers such as diblock copolymers, rendering them an attractive choice for practical applications. These polymers are composed of two types of monomers randomly distributed along the polymer chain backbone. In our model, the chemical constitution of the cross-linked polymer network enters the problem via the potentials that characterize the interactions between the different types of monomers, their functionality or ability to form covalent cross-links, and their spatial location. Given the complexity of the problem, precise analytical results cannot be obtained, and hence we treat the problem in a course-grained manner, where the precise molecular properties (e.g. bond lengths and angles) are replaced in favor of larger-scale properties, such as the persistence length of the polymer. This approach still allows for the incorporation of the essential physics and chemistry of the system while enabling an analytical route to the calculations of the free energy. Therefore, this approach does not give a detailed description of a cross-linked network on the molecular level, rather, it gives general trends in the location of the different monomers relative to one another. The initial objective of the model is to calculate the free energy as a function of the chemical composition, \( f \), and the degree of cross-linking, determined by \( \mu \). The free energy is then optimized with respect to an order parameter that is a measure of the density fluctuations across the network, and depends on \( f \) and \( \mu \). The interfacial free energy is computed within the mean field approximation, which treats all the different local interactions in the system as an average potential field acting on the system. Local density fluctuations are then introduced into the polymer network due to the polycondensation of cross-links.

2.2. Model development

2.2.1. Microphase separation

The theoretical model we consider consists of a very long polymer chain made up of a total of \( N \) segments of types A and B. Only A segments are allowed to cross-links, otherwise the \( N \) segments are identical. Therefore, there is no drive for microphase separation in the absence of cross-linking. We specify a fraction, \( f \), out of all \( N \) monomers as type A, which are randomly distributed along the backbone of the initial linear polymer chain. The remaining \((1-f)N\) monomers are of type B, and cannot cross-link. The polymer chain is allowed to form on average \( \mu/2 \) cross-links among the A segments. It has been shown...
that a long cross-linked polymer chain is a good representation of a cross-linked polymer network, since for most purposes only the concentration of the polymer is important and end effects can be neglected [17,18]. The goal of the model is to obtain expressions for the density fluctuations within the network and thus have a physical measure of the porosity and chemical morphology. Therefore, in order to concentrate on the effects of cross-linking on the structure of the polymer network, we ignore all long-range interactions between the polymer segments and with the solvent. The model is general and also allows for the study of networks where both A and B segments can cross-link, and to different extents.

The free energy of the system can be calculated from the partition function, \( Z \), of a long copolymer chain subject to \( N_{cl} \) cross-link constraints, written as a Feynman path integral over all possible configurations of the system [16].

\[
Z = \int \int D(s) \exp \left( -\frac{3}{2a} \int_0^L ds \left( \frac{dr}{ds} \right)^2 \right) \\
\times \prod_{i=1}^{N_A} \int_0^L ds_i \int_0^L ds'_i \delta(r(s_i) - r(s'_i)) \delta_{AA} 
\]

where \( \int \int \) represents the normalized path integral over all possible spatial conformations of the polymer network. \( \delta_{AA} \) ensures that only segment of type A form cross-links, and equals

\[
\delta_{AA} = \left( \frac{1 + \theta(s_i)}{2} \right) \left( \frac{1 + \theta(s'_i)}{2} \right) 
\]

\( \theta(s) \) labels the type of segment encountered at contour position \( s \) of the polymer chain, of total contour length \( L \). \( \theta(s) = 1 \) for A segments and \( -1 \) for B segments. \( r(s) \) is the spatial position of the \( i \)th segment from a reference point, with unit length \( O(s) \); \( N_{cl} \) is the total number of cross-links formed. The exponential term in Eq. (1) accounts for the connectivity between polymer segments; the product accounts for the constraints of \( N_{cl} \) cross-links. A Poisson distribution of the cross-links is a reasonable assumption [19,20], and is given by

\[
P_{cl} = \frac{e^{-\mu/2}}{N_{cl}!} \left( \frac{\mu}{2} \right)^{N_{cl}} 
\]

The identity in Eq. (4) can be used to approximate the average of the partition function over the distribution of cross-links.

\[
e^x = \sum_{k=1}^{\infty} \frac{x^k}{k!} 
\]

It is then tedious but easy to derive the averaged partition function as

\[
Z = \iint D(r) \exp \left( -\frac{3}{2a} \int_0^L ds \left( \frac{dr}{ds} \right)^2 \right) \\
\times \exp \left( \frac{1}{4} \int_0^L ds \int_0^L ds' \theta(s) \theta(s') \delta(r(s) - r(s')) \right) \\
\times (1 + 2\theta(s) \delta(r(s) - r(s'))) 
\]

The partition function of a heteropolymer with short-range interactions between the monomers has a similar form to Eq. (5), and the corresponding free energy has already been calculated [21]. The first two terms of Eq. (5) are of the same form of the partition function of [21], and the additional terms do not alter the methodology of the derivations, hence the calculations are not repeated here. The mean-field analysis results in solutions of the order parameter, \( m(r) \), as a function of \( f \) and \( \mu \) [21,22]. \( m(r) \) measures the density fluctuations (in units where \( N/V = 1 \), \( N \) being the total number of monomers and \( V \) the total volume of the polymer network) of A- and B-type monomers away from their mean values, \( f \) and \( (1-f) \), respectively, at location \( r \):

\[
m(r) = (1 - f) \rho_A(r) - f \rho_B(r) 
\]

where \( \rho_A(r) \) and \( \rho_B(r) \) are the partial densities of A and B segments at location \( r \), respectively. Microphase separation of cross-linked heteropolymer networks, or the formation of regions within the network that are rich in one type of monomer as a result of cross-linking, has been studied in other contexts [23–32]. In our work, we find that microphase separation intensifies the density fluctuations due to polycondensation, as will be discussed.
2.2.2. Polycondensation

We differentiate between three different contributions to the density of the membrane: the density of cross-linked segments of type A, the density of A-type segments that are not cross-linked, and the density of B-type segments that cannot cross-link. We assume that the variation in the local density at different regions of the membrane arises only from the first contribution. In other words, since the goal is to understand the effects of the network composition and the degree of cross-linking on the pore structure, the effects of solvent evaporation and possible interparticle coagulation due to drying are neglected. The main concern of this work is with the local density fluctuations that result from polycondensation at the cross-linked sites, which in turn lead to a pore size distribution within the polymer network. Microphase separation is found to intensify the density fluctuations.

Polycondensation of the cross-links is accompanied by the release of a leaving group of relative size $\chi$ (size of leaving group/size of monomer). Scheme 1 presents an example of an aromatic polyamide membrane, the most successful and commonly used organic polymers in nanofiltration and reverse osmosis membranes [6,33,34].

Results of the model suggest that it is the leaving group that is partially responsible for the density fluctuations and non-uniform porosity of the polymer network.

2.2.3. Surface adsorption

A strong motivation for the design of heteropolymer membranes is the minimization of surface fouling, where the fouling species are often natural organic polymers and proteins. Recent theoretical studies examined the selective adsorption of heteropolymers onto heterogeneous surfaces due to pattern recognition [35–38]. In these studies, it was found that statistical random heteropolymers (heteropolymers having a random distribution of the different monomer units) preferentially adsorb onto surfaces having a statistically similar distribution of adsorbing sites. For example, a block copolymer will strongly adsorb on a surface having a sufficiently patchy distribution of sites, while at most only weakly adsorb on surfaces having a more checkered distribution of sites. Therefore, following these studies, it can be postulated that surfaces can be designed to deter the adsorption of specific macromolecules. Therefore, once the chemical nature of the fouling species...
is known, copolymer membranes can be designed according to principles found in [35–38]. The adsorption behavior of membranes is briefly discussed in the following section. A more detailed theoretical study of membrane fouling is currently being pursued.

3. Results and discussion

3.1. Porosity

The pore structure of a membrane is as important as the chemical composition in determining its properties and applications. In this paper, the effects of several variables on the pore structure of a simple model of a copolymer membrane are discussed, namely, the chemical nature of the different monomers, the chemical composition of the copolymer membrane, the degree of cross-linking, and the relative size of the leaving group as a result of polycondensation. Manipulation of these variables allows for some control over the architecture of the network, leading to relatively uniform or non-uniform porosities, as well as microphase separation of the different monomers.

In our model, the order parameter, \( m(r) \), and the density, \( \rho(r) \), together implicitly carry information about the membrane’s chemical morphology and porosity. Qualitatively, the magnitude of the order parameter gives an indication of the membrane’s microphase structure, or the separation of the different monomers into regions rich in one type of monomer. From Eq. (6) it can be deduced that positive values of \( m(r) \) correspond to areas rich in A-type monomers (ones that can cross-link), relative to the average density of each type of monomer. On the other hand, \( \rho(r) \) indicates the fluctuations of the density across the network and is related to the membrane’s porosity. Although density fluctuations are expected in homopolymeric cross-linked systems, density fluctuations of heteropolymer networks are intensified due to microphase separation that limits polycondensation to domains within the network.

In Fig. 2 we show the effects of changing \( f \) (composition) and \( \mu \) (degree of cross-linking) on the microphase order parameter at a location in the network having a high concentration of cross-linked segments. The density fluctuations tend to peak around a symmetric monomer composition as the degree of cross-linking is increased. That is, increasing the degree of cross-linking increases the microphase separation since the cross-linkers seek each other and thus create highly cross-linked microdomains. A system described by parameters having values near the peak in Fig. 2 shows large variations in the microphase order parameter, and thus is expected to have greatest variation in the total density fluctuations and pore-size distribution for values of \( \chi < 1 \) (finite size of the leaving group). In our model, microphase separation between the different monomer units occurs as a direct result of cross-linking. Condensation due to cross-linking leads to local densification of A-rich regions, and thus variation in pore sizes across the network. Furthermore, Fig. 2 indicates that the degree of microphase separation depends not only on the fraction of cross-linkers, \( f \), but also on the fraction of these monomers that actually cross-link, determined by \( \mu \). As an example, two copolymer networks are studied in Figs. 3 and 4, having 45% of the monomers cross-linked, and an equal leaving group size. However, one is characterized by \( f = 0.5 \) and \( \mu = 0.9 \), and the other is characterized by \( f = 0.9 \) and \( \mu = 0.5 \). The modulation profiles of the pore distribution (Fig. 3) and order parameter (Fig. 3, inset) of the two scenarios are very different. The former case shows great variations in the order parameter and
pore size modulation profiles. Positive values of $m(r)$ correspond to areas rich in A-type segments, which are characterized by small pores due to the polycondensation of cross-links. These highly cross-linked regions (small pores, positive $m(r)$, A-rich) are separated from regions rich in B-type segments, described by negative $m(r)$, and having larger pores. However, for the same size leaving group, the former scenario displays much less variation in the order parameter and pore size modulation profiles. In this case the network is made up of mostly A-segments, and thus cross-linking occurs relatively evenly across the network, with small islands of non-cross-linked regions populated mainly by B-type segments. The pore size distributions of the two scenarios are plotted in Fig. 4 (networks characterized by $f = 0.5$ and $\mu = 0.9$, and $f = 0.9$ and $\mu = 0.5$). The former is characterized by a multimodal distribution, with three distinguished peaks. The strongest (center) corresponds to the average pore size of non-cross-linked domains (regions where $m(r) = 0$ in Fig. 3). The cross-linked domains are characterized by small and very large pores, as a result of polycondensation. On the other hand, the latter network which is nearly a homopolymeric system, is found to have a narrow pore distribution, and thus a relatively uniform porosity, as seen in the dashed curve of Fig. 4. Table 1 serves as a rough guide for the type of pore distribution found for networks characterized by different $f$, $\mu$, and $\chi$.

Multimodal pore distributions (non-uniform porosities) arise from high degrees of microphase separation. However, when the leaving groups is relatively small, polycondensation does not result in substantial density fluctuations, and thus even networks characterized by finite values of $m(r)$ are found to have narrow pore size distributions around the average pore size (proportional to the inverse of the mean density), indicative of a uniformly distributed porosity as of homopolymers. Regression of the difference between the maximum and minimum densities of a particular network shows that the dependence on the condensation factor obeys a power law, $\rho_{\text{diff}} \propto \chi^n$, where $n$ can equal up to 4 [22]. That is, large leaving groups create pores significantly
larger than their size, leading to highly deformed networks, while relatively small leaving groups result in more uniform networks. This strong dependence on the size of the leaving group is unexpected and may be very important in the design of membranes.

3.2. Adsorption

A common and serious problem with RO and NF membranes is surface fouling. One possible way to reduce fouling is to design copolymer membranes where one type of monomer deters fouling and the other allows for permeate flux. Previous research has shown that heteropolymers will strongly adsorb onto pattern matched heterogeneous surfaces, and will not strongly adsorb on other surfaces. For instance, a surface characterized by domains that favorably interact with one type of monomer on a copolymer chain will strongly adsorb block copolymers and only weakly adsorb copolymers with a random or alternating monomer sequence. These same concepts can be used to design membrane surfaces that will not attract fouling species. Once the chemical nature of the fouling species is known, the membrane can be designed so as not to attract the fouling species. In this paper, we discussed some parameters that can be manipulated to control the architecture of a polymer network. Using these guidelines, for example, to prevent fouling by organic homopolymeric chains, the membrane should have a random pattern of the two monomer types (water permeable and anti-fouling) so that the anti-fouling blocks are dispersed. On the other hand, if the fouling species are proteins, which can be generally classified as having a random distribution of functional segments (e.g. hydrophobic/hydrophilic) [39,40], the membrane should have a more segregated morphology of the different monomers. It is clear that the different architectures can play an important role in determining the fouling characteristics of the membrane. A more detailed examination of the subject will be presented in forthcoming research.

4. Conclusions

Copolymer membranes are currently being examined as potential nanofiltration membranes. Using mean field theory, we examined possible architectures of cross-linked copolymer networks. The model allows for the characterization of the network in terms of the pore-size distribution and formation of microdomains of the different polymer segment types. We found that the architecture of the network (i.e. pore size distribution and formation of microdomains) is unexpectedly affected by polycondensation in addition to being dependent on the chemical constitution and the degree of cross-linking. Sufficiently large leaving groups lead to networks with multimodal distributions of pore sizes. These results can be important in determining the permeate flux of the network. This line of theoretical work can be used to pursue the fouling characteristics of the surface of the membrane, which is a very important factor in determining the filtration efficiency of the membrane.

In the long term, such theoretical efforts should lead to savings in the time and money that is currently spent on experimental research studies. A complete theoretical study of membranes research should also include the effects of curvature, surface tension, and deformation, which is what distinguishes membranes from solid flat surfaces. These properties can be included in statistical mechanics models, and should be studied.
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