

Chlorine tolerant, multilayer reverse-osmosis membranes with high permeate flux and high salt rejection

Howard M. Colquhoun and David Chappell*

Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK

Andrew L. Lewis, David F. Lewis, Graeme T. Finlan and Peter J. Williams

ICI plc, The Heath, Runcorn, WA7 4QE, UK

Abstract

A new class of high molecular weight polyethersulfone ionomers is described in which the ionic content can be varied, at will, over a very wide and fully-controllable range. A novel type of coating process enables these materials to be deposited from alcohol-type solvents as cohesive but very thin (50 – 250 nm) films on porous support-membranes, giving high-flux membranes ($3.3 - 5.0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) with very good, though not outstanding salt rejection (typically 92 - 96%). A secondary layer, of formaldehyde-cross-linked polyvinyl alcohol, can be deposited from aqueous solution on the surface of the ionomer membrane, and this layer increases salt rejection to greater than 99% without serious loss of water permeability. The final multi-layer membrane shows excellent chlorine tolerance in reverse-osmosis operation.

Introduction

Pressure-driven membrane filtration is capable of removing essentially all dispersed or dissolved contaminants from water and as it involves no phase-change it is in principle (and often now in practice) very much more energy-efficient than older methods of water-purification such as distillation.¹ Membrane technologies, especially reverse-osmosis and nanofiltration, have in recent years superseded other water-treatment processes for removal of dissolved salts, notably in desalination of seawater,² of brackish water,³ and of municipal waters containing unacceptably high salt levels due, for example, to intrusion of seawater into coastal aquifers.⁴

Key parameters in defining the performance of polymeric reverse-osmosis membranes are (i) permeate flux per unit membrane area, at a given driving pressure, (ii) salt-rejection (a measure of the relative salt concentrations in feed and permeate, the value of which generally increases with pressure) and (iii) mechanical resilience and chemical stability under actual

operating conditions. Permeate flux is a function not only of the intrinsic permeability of the membrane material to water, but also of membrane thickness – the thinner the membrane the higher the flux although, in practice, reduction of membrane thickness is limited by the requirement for mechanical stability.

A very thin membrane can however be practicable if it is supported on a thicker but more porous material. The earliest commercial reverse osmosis membranes (based on the work of Loeb and Sourirajan)⁵ were derived from cellulose acetate and had a dense surface-skin grading continuously into a more open substructure.⁶ However, this "asymmetric" design was rapidly overtaken by membranes in which the active separating layer and the porous support-layer were optimised separately, from different materials (the "thin-film composite design", Figure 1)⁷ and the latter approach is adopted in most modern reverse-osmosis membranes. The real breakthrough in composite-membrane design came with the discovery by Cadotte, in 1978,⁸ that very thin aromatic-polyamide membranes could be created directly on the surface of porous polysulfone supports using interfacial polycondensation (the process known to most chemists as the "nylon rope trick").⁹ The resulting membranes have very high water-permeability (owing in part to their highly convoluted surface-structure which provides a much greater surface-area than the geometric area of the membrane would suggest).¹⁰ Moreover, the salt-rejection characteristics of these membranes are excellent, even at very low driving pressures, and the mechanical strength and stability of the aromatic polyamide enable long membrane-lifetimes to be achieved in operation. As a result (and after a regrettably bitter struggle over intellectual property rights)¹¹ the interfacial polyamide membrane has come to dominate modern, commercial reverse-osmosis technology.^{1,12}

Figure 1. Schematic of a thin-film composite membrane. Approximate thicknesses of the different layers are shown, though these vary significantly between different commercial membranes.

The only significant weakness of the interfacial polyamide membrane is its chemical instability in the presence of sanitising agents, especially chlorine,¹³ which remains (despite some drawbacks) by far the most valuable agent for preventing bacteriological contamination of potable water. Chlorinated water must therefore be filtered through activated carbon, to absorb the chlorine, before it goes to a reverse-osmosis plant using interfacial polyamide membranes (and it must then be re-chlorinated before it enters the municipal water system).

Moreover, the unprotected **membrane-plant** is itself susceptible to bacterial fouling, periodically requiring it to be chemically cleaned and disinfected to restore optimal membrane performance.

Numerous attempts have been made to develop chlorine-tolerant, thin-film composite membranes, the most successful of these being based on aromatic polyethersulfones into which sulfonic acid substituents are introduced (either pre- or post-polymerisation) to provide a degree of hydrophilicity.¹⁴ The resulting ionomers are inherently resistant to chlorine-induced degradation, at least under conditions of neutral or basic pH, and their fundamental characteristics in terms of salt and water permeability suggest that they should be capable of yielding excellent reverse osmosis membranes.¹⁵ In practice however, thin-film composite membranes fabricated using sulfonated aromatic polyethersulfones as the active, separating layer have disappointingly failed, so far, to realise the flux and rejection performance implied by materials-properties of these ionomers measured on bulk or thick-film samples.^{14,15} **This may result from poor control of ionomer-layer thickness during the coating process (especially when a simple "paintbrush" technique is used), leading to a layer which is simultaneously defective (giving poor rejection) and much thicker than necessary (giving low permeate-flux).**

In the present paper, we describe chemistry leading to the development of a new family of high molecular weight polyethersulfone ionomers, in which the ionic content can be varied, at will, over a very wide and fully-controllable range. A novel type of coating process enables these materials to be deposited from alcohol-type solvents as cohesive but very thin (< 100 nm) films on porous support-membranes, giving high-flux membranes with very good, though not outstanding salt rejection (typically 92 - 96%). However, we also show that a second polymer layer can be successfully deposited from aqueous solution on the surface of the ionomer membrane, and that this layer enhances salt rejection to ca. 99% without serious loss of water permeability. The final multi-layer membrane shows excellent chlorine tolerance in reverse-osmosis operation. Preliminary results from this work have been reported in the patent literature.¹⁶

Results and Discussion

The commercial engineering thermoplastic known as "polyethersulfone" (PES) is synthesised by nucleophilic polycondensation of 4,4'-dihydroxydiphenylsulfone (**1**) with 4,4'-dichlorodiphenylsulfone (**2**) at high temperatures (ca. 300 °C) in the presence of potassium carbonate (Scheme 1a).¹⁷ The resulting homopolymer (**3**) is essentially hydrophobic, and early attempts to increase the hydrophilic character of the polymer by sulfonation showed that the electron-withdrawing character of the sulfone linkages strongly inhibits electrophilic substitution. The polymer is, for example, inert to sulfonating agents such as 98% sulfuric acid at temperatures of up to 50 °C.¹⁸ Sulfonation *can* be achieved using more vigorous sulfonating agents such as sulfur trioxide or oleum, but the process is then extremely difficult to control and can, moreover, lead to significant degradation of the polymer chain.¹⁹ The concept of incorporating *much more readily sulfonated co-monomers* was pioneered by Rose, who showed that hydroquinone residues included in the PES structure undergo rapid and selective monosulfonation on simply dissolving the copolymer in concentrated sulfuric acid at room temperature (Scheme 1b).²⁰ The only difficulty with this system is that the hydroquinone dianion is very susceptible to oxidative degradation under high-temperature polycondensation conditions, leading to problems of synthetic reproducibility.

Scheme 1. (a) Synthesis of the polyethersulfone homopolymer **3**. (b) Regiospecific sulfonation of the hydroquinone-based copolyethersulfone **4** to give ionomer **5**.

In the present work we have explored the use of a much more stable comonomer (**6**) which we find can be readily and reliably incorporated into the PES chain-structure, where it provides a specific reaction site for sulfonation (Scheme 2). Moreover, since compound **6** is an "AB-type" monomer, it can be included in the PES polycondensation *in any proportion whatever* without affecting the stoichiometry of the reacting groups. The extent of post-polymerisation sulfonation can be controlled entirely by specification of monomer stoichiometry at the polymerisation stage, since we find that sulfonation of copolymer **7** in 98% sulfuric acid at 25 °C occurs exclusively on the biphenyl unit, *ortho* to the ether linkage (Scheme 2).

Scheme 2. Synthesis and sulfonation of copolymer **7**, affording the novel ionomer **8**.

Dropwise addition of the sulfuric acid solution to deionised water affords tough, porous beads of ionomer **8** (in the H⁺ form), from which residual sulfuric acid is readily extracted by stirring in hot water. Contrary to claims in the recent literature,²¹ we find that post-polymerisation sulfonation (at least in the present case) is completely regioselective, allows any desired level of sulfonation to be achieved (since this is fully specified by the comonomer content) and leads to no detectable chain-cleavage, cross-linking, or other form of polymer degradation. The inherent viscosity of the ionomer, measured in NMP solution, is invariably higher than that of its parent polymer, owing to expansion of the solvodynamic radius induced by mutual repulsion of the anionic sulfonate groups appended to the polymer chain.²² Typical inherent viscosity values for ionomer **8** (with an ion-exchange capacity of 0.92 meq g⁻¹) and its parent copolymer **7** were 0.96 and 0.66 dL g⁻¹ respectively. The corresponding molecular weight values for the ionomer by GPC were $M_w = 53,000$ and $M_n = 29,000$.

The extent of sulfonation in this copolymer system can be determined readily by ¹H NMR spectroscopy in DMSO-*d*₆ (Figure 2), as the resonance arising from the proton *ortho* to the position of sulfonation is clearly identifiable as a sharp singlet at 8.13 ppm. Integration of this resonance relative to all other resonances in the spectrum enables the degree of sulfonation to be calculated, and this is invariably 98 – 100% of the theoretical value. No evidence is found for sulfonation at any other position than that shown in Scheme 2.

Figure 2. (a) ¹H NMR spectrum (dmsO-*d*₆) of copolymer **7** ($n = 3m$). (b) ¹H NMR spectrum (dmsO-*d*₆) of the derived ionomer **8** ($n = 3m$) highlighting (*) the resonance assigned to the proton *ortho* to sulfonic acid. Integration of this resonance against all other resonances yields a value for the degree of sulfonation at this position (and at no other position) of 98%.

Ionomers of type **8**, with ion exchange capacities in the range 0.70 – 1.25 meq g⁻¹, proved readily soluble in 2-methoxyethanol. Non-sulfonated aromatic polyethersulfones are essentially unaffected by this solvent, so enabling thin-film composite membranes of ionomer **8** to be deposited on porous polysulfone supports. A well-established support membrane of this type is accessible by gelation in water of a solution in DMF of bisphenol-A polysulfone, coated onto a non-woven polyester paper.²³ The resulting support-membrane is asymmetric, with a thin surface layer having porosity on the nanometre scale, and it can thus retain dissolved macromolecules with molecular weights greater than ca. 20,000. Ionomers with

molecular weights higher than this are unable to enter the pores of the support-membrane and so are retained on the surface, enabling formation of a coherent ionomer film on evaporation of the solvent. Indeed, the electrostatic expansion of an ionomer's solvodynamic radius noted earlier makes ionomers ideally suited to this type of coating process (Figure 3). The final membrane structure is thus dependent on size-controlled positioning of individual macromolecules on the support-membrane surface, and such a process was realised in the present work using a small-scale bead-coater and in-line drying oven (Figure 4), capable of coating 10 × 30 cm strips of polysulfone support-membrane.

Figure 3. Schematic for ionomer coating from solution onto an asymmetric support-membrane. The key parameter is the minimum solvodynamic radius of the ionomer, which must be greater than the maximum pore radius of the support to prevent the ionomer entering and blocking these pores.

The ~~reverse-osmosis~~ performance of the resulting composite membranes in reverse osmosis was found to follow a general trend in which increasing levels of sulfonation (as measured by ion-exchange capacity, IEC) led to increasing permeate-flux but decreasing levels of salt-rejection. The best compromise was achieved with ionomer **8** of IEC 0.92 meq g⁻¹, containing one sulfonated aromatic ring to every 8 unsulfonated rings. However, the composition of the coating solvent also played a role in determining membrane performance, in that flux increased significantly (without loss of salt rejection) when lower alcohols such as methanol or ethanol replaced part of the methoxyethanol used originally as solvent. This suggests a significant dependence of membrane morphology on coating solvent, although further work is needed to establish the detailed molecular mechanisms involved.

Figure 4. Bead-coating of ionomer onto an asymmetric polysulfone support-membrane. The polished, stainless-steel coating roller rotates against the direction of travel of the membrane to generate a "bead" of ionomer solution. A high degree of control over the coating thickness is achievable with this system, as thickness increases not only with the concentration of ionomer in the coating solution, but also with the counter-rotation-rate of the coating roller and the rate of travel of the membrane.

The support-membrane was impregnated with butane-1,4-diol to maintain wettability of the internal pore-structure during composite membrane fabrication, but it was also found, empirically, that inclusion of a small proportion of sulfuric acid in the coating solution helped the final membrane to retain pore-wettability at low pressures. Thus, a composite membrane

was fabricated by coating a solution containing 0.7 wt% of ionomer **8** (IEC = 0.92 meq g⁻¹) in a solvent comprising 2-methoxyethanol (57%), methanol (38%) sulfuric acid (0.25%) and water (4.75%, v/v) onto the surface of a polysulfone support-membrane impregnated with butane-1,4-diol, and drying at 80 °C. The resulting composite structure "Membrane A", when tested in cross-flow reverse osmosis with a 2000 ppm solution of sodium chloride at 40 bar pressure, typically gave a permeate flux of 3.3 L m⁻² h⁻¹ bar⁻¹ and showed salt rejection of 96%. These figures may be compared with recently-reported values of 1.3 L m⁻² h⁻¹ bar⁻¹ and 90% for chlorine-tolerant composite membranes fabricated by brush-coating from a rather different type of polysulfone ionomer, in which the sulfonic acid groups are introduced into a co-monomer prior to polycondensation.¹⁵ Even so, it is recognised that the flux and rejection characteristics of the new membrane described here still fall well short of the performance of the best commercial polyamide thin-film composite membranes,²⁴ though the latter are of course unstable in the presence of even very low levels of chlorine.²⁵

Cross-sections of the composite membranes reported here, imaged by TEM (Figure 5), show dense, uniform films of ionomer from 50 to 250 nm in thickness (depending on the coating conditions) laminated to the surface of an obviously asymmetric support. The black line in each of these images represents an evaporated gold film which enables the surface of the membrane to be more easily located during electron microscopy. The boundary between the ionomer layer and the support is extremely sharp, confirming the idea that the surface-pores of the support membrane are sufficiently small to prevent penetration of ionomer molecules, which therefore remain exclusively on the surface to form, after evaporation of the solvent, a selective, hydrophilic layer for reverse osmosis (Figure 3).

Figure 5. Cross-sections of composite ionomer membranes showing the different coating thicknesses achievable by varying the concentration of ionomer in the coating solution. Ionomer coatings are ca. 250 nm and 60 nm thick in samples (a) and (b) respectively. A thin gold film (black line) was evaporated onto the surface of the sample prior to embedding in a light-cured resin and microtoming.

Although a salt-rejection value of 96% at 40 bar operating pressure would enable useful levels of desalination to be achieved on low-salinity waters, interfacially-polymerised polyamide membranes routinely achieve >99% rejection under similar conditions.¹² We therefore next sought to enhance the rejection characteristics of our polysulfone ionomer membranes, by applying a secondary polymer layer which was intended to improve the

rejection of the primary ionomer membrane. Early work by Cadotte had shown that aqueous solutions of polyvinyl alcohol (PVA) can be cross-linked by aldehydes on the surface of polysulfone support membranes.²⁶ The resulting composite structures showed only very limited salt-rejection but high permeate flux, and we reasoned that the formation of a *secondary* membrane of cross-linked PVA, on the surface of the polysulfone ionomer membrane, might enhance salt rejection without too drastic a loss of permeability. This idea was realised in practice, by depositing a secondary layer of PVA from aqueous solution and cross-linking it with formaldehyde. This increased the salt rejection of composite membrane **A** from 96% to 99.5%, (2000 ppm NaCl feed at 40 bar pressure) and the permeate flux decreased from 3.3 to 1.2 L m⁻² h⁻¹ bar⁻¹ (still a very acceptable value for operation in reverse osmosis).¹² The very high salt rejection of this multi-layered membrane ("Membrane **B**") also means that low-pressure reverse osmosis becomes practicable, with salt rejection of 93.5% and permeate flux of 1.3 L m⁻² h⁻¹ bar⁻¹ typically being achieved on a feed of 500 ppm NaCl at 4 bar operating pressure.

From previous work,²⁷ it seemed probable that the polysulfone ionomer would show good chlorine-tolerance, but it was by no means certain that the cross-linked PVA layer be similarly resistant. However, accelerated chlorine-tolerance tests on Membrane **B**, where the membrane was operated in reverse osmosis (500 ppm NaCl at 4 bar) in the presence of 50 ppm of active chlorine (as sodium hypochlorite) at pH 7.5, showed very good chlorine-resistance. After 1 month (38,000 ppm-hours: equivalent to 4 years in operation at the more realistic chlorine level of 1 ppm), the flux had fallen from 1.3 to 1.1 L m⁻² h⁻¹ bar⁻¹ and the rejection had decreased only very slightly, from 93.5 to 92.7%. Under the same conditions, the rejection of a commercial interfacial polyamide membrane (Filmtec FT-30) fell drastically, from 94.4% to only 19.2% confirming the massive superiority of polysulfone-ionomers over aromatic polyamides in terms of their stability to aqueous chlorine.

The chlorine stability of the cross-linked PVA layer can be accounted for on the basis that the oxidatively-sensitive primary alcohol groups in PVA are acetalised by reaction with formaldehyde, leading to much more stable ether-type linkages.²⁸ Such reactions can be both intra- and inter-molecular (Scheme 3), and the high levels of formaldehyde used in the present coating process would ensure that acetalisation of the PVA is essentially quantitative.

Scheme 3. Acetalisation and cross-linking reactions of poly(vinyl alcohol) with formaldehyde.

Experimental

Starting materials: Diphenyl sulfone, 98% sulfuric acid, 4,4'-dihydroxydiphenylsulfone and 4,4'-dichlorodiphenylsulfone and were obtained from Aldrich and were used as received. Potassium carbonate (Aldrich) was dried at 110 °C under vacuum before use. Monomer **6** was synthesised according to the literature (m.p. 272 °C, 87% yield).²⁹ Bisphenol-A polysulfone ("Udel-3500") was obtained from Amoco, and "Awa-10" non-woven polyester paper from Awa Paper Ltd (Japan). Polyvinyl alcohol (99+% hydrolysed, 65K nominal MW) and aqueous formaldehyde (37%) were obtained from Aldrich.

Instrumentation and testing: Proton NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer. Resonances were recorded in δ (ppm), referenced to residual solvent resonances. Mass spectra (EI/CI) were run on a VG Autospec instrument. Inherent viscosities were determined for 0.1 wt% solutions of polymers in NMP using a semi-automatic Schott-Geräte CT-150 viscometer. Thermal characteristics of monomers (T_m) and polymers (T_g -onset) were analysed by DSC under nitrogen, using a Mettler DSC20 system at a scanning rate of 10 °C min⁻¹. Transmission electron microscopy was carried out on a Philips 120KV FEG TEM. Membrane samples were sputtered with gold on the active surface, embedded in a light-cured resin, and microtomed in cross-section with a diamond knife before TEM analysis. Reverse osmosis measurements were carried out on discs 5.6 cm in diameter, cut from the coated membrane strips and tested in duplicate using stainless-steel reverse osmosis cells with tortuous-path spacers (active membrane area 5.4 cm²). The recirculating feed was either 2000 ppm NaCl at 40 bar pressure or 500 ppm NaCl at 4 bar pressure, and the cross-flow velocity at the membrane surface was 1.0 m s⁻¹. Salt rejection values were calculated directly from the conductivities of feed and permeate after an initial 10 cm³ of permeate had been collected and discarded. Accelerated chlorine-tolerance studies were carried out using an all-polymer membrane test system (cells, pumps, tubing etc.), to avoid the possibility of membrane damage by metal-corrosion products.

Synthesis of copolymer 7 (Scheme 2; $n = 3m$): A mixture of diphenylsulfone (56 g), 4,4'-dihydroxydiphenylsulfone (4.69 g, 18.75 mmol), 4,4'-dichlorodiphenylsulfone (5.44 g, 18.96 mmol), monomer **6** (4.31 g, 12.50 mmol) and potassium carbonate (3.52 g, 25.50 mmol) was purged with a slow stream of dry nitrogen and heated slowly (over ca. 5 h) with stirring to 280 °C. After 0.5 h at this temperature the viscous, pale brown reaction mixture was cooled

to room temperature and then ground to a fine powder in a ultracentrifugal mill. This powder was extracted successively with boiling water (3 x 100 mL) and then with methanol at reflux (3 x 200 mL), and dried to afford copolymer **7** ($m = 3n$) as a cream powder with inherent viscosity (NMP) 0.66 dL g⁻¹. Thermal analysis by DSC showed the copolymer to be amorphous, with T_g (onset) at 238 °C. The ¹H NMR spectrum of this copolymer (in dms_o-d₆) is shown in Figure 2a.

Synthesis of ionomer **8 (Scheme 2; $m = 3n$):** Copolymer **7** (3.00 g) was dissolved in 98% sulfuric acid (50 mL) with stirring under dry nitrogen, and the viscous, pale yellow solution was allowed to stand at room temperature for 24 h. Dropwise addition of the solution to stirring deionised water (350 mL) gave tough white beads of ionomer which were washed acid-free by repeated extraction with deionised water and then dried under vacuum at 70 °C, affording 3.02 g of ionomer **8** ($m = 3n$) with inherent viscosity 0.96 dL g⁻¹. The ¹H NMR spectrum of this ionomer (in dms_o-d₆) is given in Figure 2b.

Membrane fabrication: The asymmetric support-membrane was cast from a 15% w/v solution of bisphenol-A polysulfone (Udel-3500) in dimethylformamide, which was coated onto Awa-10 non-woven polyester paper and gelled in water at ambient temperature.²³ The resulting asymmetric membrane was soaked in an aqueous solution of 1,4-butanediol (10% w/v) and dried at 60 °C. Strips of this support-membrane (10 × 30 cm) were coated, using the bead-coater shown in Figure 4, with 0.5% – 2.5% w/v solutions of ionomer **8** ($m = 3n$) in a solvent comprising 2-methoxyethanol (57% v/v), methanol (38% w/v), water (4.75% w/v) and sulfuric acid (0.25% w/v), and were dried in-line at 80°C. The composite membrane formed using a 0.7% ionomer solution was over-coated in a second pass through the bead coater using an aqueous solution of polyvinyl alcohol (1% w/v), formaldehyde (4% w/v) and sulfuric acid (0.5%) and the resulting secondary coating was cross-linked and dried at 50 °C.

Acknowledgements

This work was supported in part by the Royal Society (an Industry Fellowship to HMC) and by EPSRC (Grants GR/K49560/01 and EP/G026203/1).

References

- ¹ R.W. Baker, "Membrane Technology and Applications", John Wiley, Chichester, 2nd Ed. 2004.
- ² T. Matsuura, *Desalination*, 2001, **134**, 47.
- ³ A. Asam, M. Eid, P. Cote and J. Coburn, *Desalination*, 2003, **15**, 237.
- ⁴ B. Durham, D. Yoxtheimer, C. Alloway and C. Diaz, *Desalination*, 2003, **156**, 155.
- ⁵ S. Loeb and S. Sourirajan, *Adv. Chem. Series*, 1962, **38**, 117.
- ⁶ A. Kakuta, M. Kuramoto, M. Ohno, H. Kushida, A. Tanioka and K. Ishikawa, *J. Polym. Sci, Polym. Chem. Ed.*, 1980, **18**, 3229.
- ⁷ R.L. Riley, R.L. Fox, C.R. Lyons, C.E. Milstead, N.W. Seroy and M. Tagoni, *Desalination*, 1976, **19**, 113.
- ⁸ J.E. Cadotte, R.J. Petersen, R.E. Larson and E.E. Erickson, *Desalination*, 1980, **32**, 25.
- ⁹ P.W. Morgan, "Condensation Polymers by Interfacial and Solution Methods", Interscience, New York, 1965.
- ¹⁰ S.H. Kim, S-Y. Kwak and T. Suzuki, *Environ. Sci. Technol.*, 2005, **39**, 1764.
- ¹¹ <http://www.ll.georgetown.edu/federal/judicial/fed/opinions/94opinions/94-1034.html>
- ¹² R.J. Petersen, *J. Membr. Sci.*, 1993, **83**, 81.
- ¹³ G-D. Kang, C-J. Gao, W-D. Chen, X-M. Jie, Y-M. Cao and Q. Yuan, *J. Membr. Sci.*, 2007, **300**, 165.
- ¹⁴ (a) C.L. Brousse, R. Chapurlat and J.P. Quentin, *Desalination*, 1976, **18**, 137. (b) A.E. Allegrezza Jr., B.S. Parekh, P.L. Parise, E.J. Swiniarski and J.L. White, *Desalination*, 1987, **64**, 285.
- ¹⁵ H.B. Park, B.D. Freeman, Z-B. Zhang, M. Sankir and J.E. McGrath, *Angew. Chem. Int. Ed.*, 2008, **47**, 6019.
- ¹⁶ (a) H.M. Colquhoun and D.F. Lewis, *US Pat.* 5,693,740 (1997). (b) H.M. Colquhoun, P.J. Williams and A.L. Lewis, *Eur. Pat.* 0,682,560 (1998).
- ¹⁷ R.J. Cotter, "A Handbook of Polyarylethers", Gordon and Breach, Basel, 1995, pp.11-13.
- ¹⁸ B. Bickson, M.J. Coplan and G.Gotz, *US Pat.* 4,508,852 (1985).
- ¹⁹ J.B. Rose, *US Pat.* 4,273,903 (1981).
- ²⁰ A. Bunn and J.B. Rose, *Polymer*, 1993, **34**, 1114.
- ²¹ (a) J. Pang, H. Zhang, X. Li, and Z. Jiang, *Macromolecules*, 2007, **40**, 9435. (b) F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski and J. E. McGrath, *J. Membr. Sci.* 2002, **197**, 231.

- ²² R.D. Lundberg and R.R. Phillips, *J. Polym. Sci., Polym. Phys. Ed.* 1982, **20**, 1143.
- ²³ R. Rangarajan, N.V. Desai, R.C. Mody, D. Mohan and A.V. Rao, *Desalination*, 1991, **65**, 81.
- ²⁴ Current commercial polyamide-composite membranes are typified by the Dow-Filmtec XLE membrane, which shows water permeability of ca. $7.0 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and 99% salt rejection on a 500 ppm NaCl feed, at 6.9 bar pressure. See: <http://www.dow.com/liquidseps>.
- ²⁵ J. Glater, S. Hong and M. Elimelech, *Desalination*, 1994, **95**, 325.
- ²⁶ J.E. Cadotte, *US Pat.* 4,895,661 (1990).
- ²⁷ J.E. Tomaschke, A.J. Testa and J.G. Vouros, *US Pat.* 4,990,252 (1991).
- ²⁸ B. Bolto, T. Tran, M. Hoang and Z. Xie, *Progress in Polymer Science*, 2009, **34**, 969.
- ²⁹ T.E. Attwood, D.A. Barr, R.G. Feasey, V.J. Lesley, A.B. Newton and J.B. Rose, *Polymer*, 1977, **18**, 354.