Polyaniline hollow fibres for organic solvent nanofiltration

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Intrinsically-skinned asymmetric PANi hollow fibres, fabricated using a process of directly adding large organic acids to highly concentrated PANi solutions, show stability in a wide variety of organic solvents and have shown promising nanofiltration properties, giving high rejections of nanosolutes in acetone.

Polyaniline (PANi) is widely used as a material for fabricating membranes and has been well studied, especially for gas separations.[1–5] PANi is better known for its electrical conductivity, and is obtained by doping the basic emeraldine form of PANi with acids (PANi from here will refer only to the emeraldine base form of polyaniline). However, it is this reactivity with acids that has attracted much attention in research into how the doping/de-doping of PANi with acids can introduce porosity into the structure of a piece of PANi membrane for separation applications.[6] Fig. 1 shows the mechanism for the acid doping and de-doping of PANi. The presence and subsequent removal (or partial removal) of the acid counterion has been surmised to induce porosity in PANi membranes. This effect of free volume expansion has been studied using solid state NMR spectroscopy,[6] and has been shown to vary with dopant size.[1] Thus far, studies rely mainly on the doping of as-cast membrane articles with mineral acids. Studies on such porosity generation have mainly been confined to gas permeation due to the small sizes of the mineral acids used.

In this Communication, we report the successful fabrication of porous PANi hollow fibres by using larger organic acids as dopants for organic solvent nanofiltration (OSN) applications. OSN is an emerging technology and has been shown to be useful in petrochemicals,[7] biotechnology and pharmaceutical technologies.[8] OSN membranes are typically made from dense membranes in a composite form (polydimethylsiloxane on polyacrylonitrile support) or from asymmetric membranes (polyimide).[9] OSN membranes were previously found not to be fully stable in all solvents,[10,11] but recent studies have rectified these problems through the development of membrane cross-linking techniques.[12–14] To the best of our current knowledge, OSN membranes largely owe their nanofiltration properties to the inherent packing or the structure of the membrane matrix upon membrane formation.

By using a novel method of directly adding the organic acids into the PANi solution, we could ensure adequate and even doping of it before spinning. Upon removal of the organic acid from the PANi articles, nanoporosity was induced. The PANi fibres were further stabilised by thermal cross-linking,[15] which allowed them to be used for organic solvent applications. PANi hollow fibre fabrication has relied on advancements made in previous studies on PANi processing. As a material, despite possessing many favourable qualities, PANi is known to be difficult to handle, as it dissolves in only a few organic solvents and gels readily at concentrations above 5 wt%.[16] Recent studies, however, have shown that intrinsically-skinned asymmetric PANi membranes could be fabricated by adding gel inhibitors.[17,18] These gel inhibitors are secondary amines that can complex with PANi to prevent gelation from taking place. More recently, Norris and co-workers have used these gel inhibitors to spin PANi hollow fibres.[19]

To prepare the hollow fibres, 17 wt% of PANi was dissolved in a mixture of *N*-methyl-2-pyrrolidone and 4-methylpiperidine, the gel inhibitor. This solution was stirred well before maleic acid (116.1 g mol^{-1}) was added and the solution mixed further. The amount of maleic acid added was 50 wt% of the total amount of PANi. Upon addition of maleic acid, the dark blue PANi solution turned dark green, signifying that acid doping was taking place. The hollow fibres were spun using a 2 mm outer diameter (OD) spinneret into a water coagulation bath. The inner bore coagulation fluid was also water, injected at a rate of 5 ml min^{-1}. An air gap of 20 cm was adopted, and the fibres were spun at a rate of 3 m min^{-1}.

Fig. 2 shows SEM cross-section images of a PANi hollow fibre sample. These fibres possessed a typical asymmetric structure similar to articles formed from a phase inversion process. The fibres were, on average, 2.5 mm in diameter (OD) and, as a whole, had a spongy sub-structure with macropores near both the inner and outer surfaces. Although there were

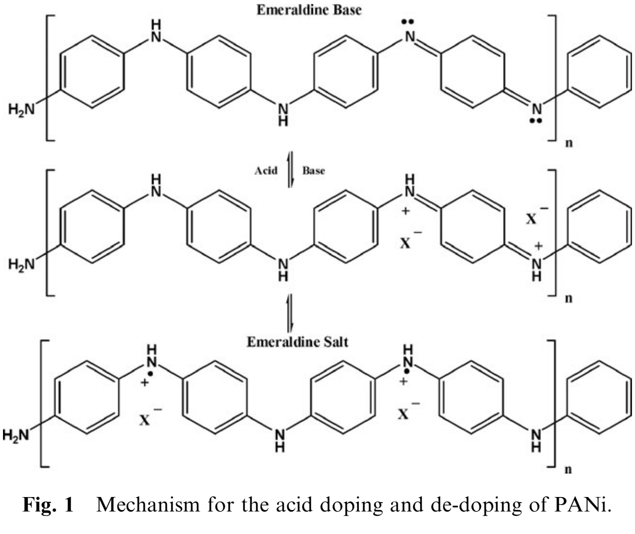

Fig. 1 Mechanism for the acid doping and de-doping of PANi.

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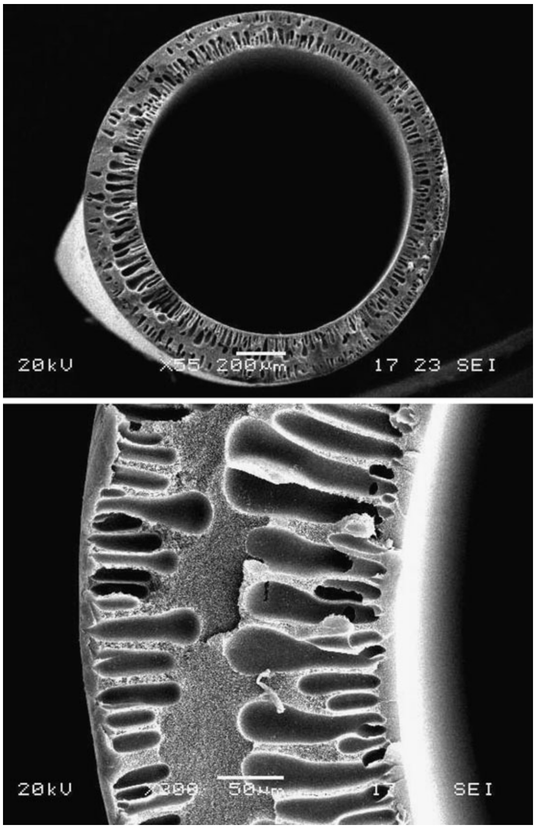

Fig. 2 SEM images of PANi hollow fibres at 55× (top) and 300× (bottom) magnification.

many macropores, a distinct top dense layer could be seen at both surfaces. Higher resolution images of the dense layer did not reveal the presence of any visible pores. These macropores could possibly be eliminated by using phosphoric acid solutions as the inner coagulant, as demonstrated by Norris and co-workers.[19]

The fibres spun from the maleic acid-doped PANi solution were dark green and possessed electrical conductivity. The acid dopant was fully removed by immersing the fibres in 1 M sodium hydroxide solutions (50 : 50 methanol/water, v/v%).[20] After acid removal, the fibres turned dark blue, which is the characteristic colour of undoped PANi. These fibres were then put into an oven at 180 °C for 1 h for thermal cross-linking. Fibres put through thermal cross-linking were stable in various organic solvents, such as acetone, methanol, tetrahydrofuran and dimethylformamide, during immersion testing. These fibres remained stable, even when re-immersed in *N*-methyl-2-pyrrolidone. The cross-linking between PANi chains occurs due to free radical generation on the imine nitrogen.[15]

Evidence for this thermal cross-linking mechanism can be indirectly seen from an FTIR-ATR (Perkin Elmer Spectrum One) spectrum of a sample of de-doped PANi membrane (Fig. 3). From the FTIR results, we saw a reduction in the intensity of the peak at 1300 cm^{-1}. This peak relates to the C–N stretch of the tertiary nitrogen present in PANi. The reduction in peak area showed a reduction in the number of imine nitrogen groups (C–N=C) present in the sample. A further indication of cross-linking could be seen from the broadening of all the peaks, especially those representing the benzoid group at 1500 cm^{-1} and the quinoid group at 1595 cm^{-1}. This had previously been attributed to an increase in the interaction of vibrational modes due to physical chain cross-linking.[21] The appearance of the peak at 1680 cm^{-1} was most striking, and is attributed to the appearance of carbonyl groups. This is possibly a side effect of thermal treatment in air, and Rannou and Nechtschein have suggested that the oxidation of PANi in air can occur either in the middle of chains or at chain ends.[22]

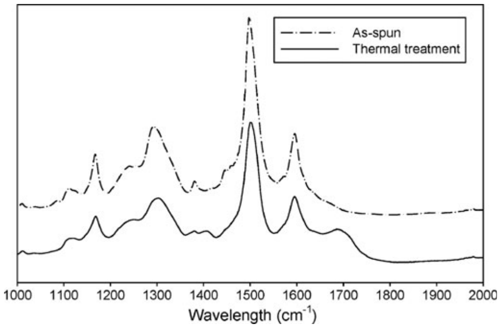

Fig. 3 Absorbance FTIR spectra of undoped PANi samples: as spun and after thermal treatment at 180 °C for 1 h.

Nanofiltration testing of these fibres was done using a series of oligostyrene test solutes in acetone.[23] A laboratory scale hollow fibre testing module was manufactured using epoxy as the sealant. Each module housed 5 × 20 cm fibres. Permeate was collected on the shell side, and the filtration was carried out at 20 °C at 6 bar pressure. Fig. 4 below shows the filtration results of two separate hollow fibre modules, and rejection, R_i, was calculated from the ratio of the test solute concentrations in the permeate and the retentate, $C_{\text{permeate},i}$ and $C_{\text{retentate},i}$, respectively (eqn 1).

$$R_i(\%) = \left(1 - \frac{C_{\text{permeate},i}}{C_{\text{retentate},i}}\right) \times 100 \qquad (1)$$

The hollow fibres gave high rejections of most species in the nanofiltration range 200–1000 g mol^{-1}, and had a molecular weight cut-off of approximately 350 g mol^{-1}. Typically, nanofiltration membranes perform at 20–30 bar pressures. At these pressures, we would expect the hollow fibres to

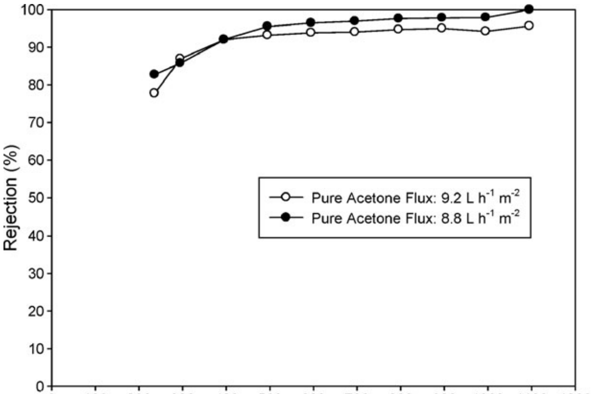

Fig. 4 Hollow fibre filtration performance in acetone at 20 °C and 6 bar pressure.

compact more, resulting in even higher rejections for these nano-sized solutes. Pure acetone fluxes through these hollow fibres were high at around 9 L h^{-1} m^{-2}. Although long-term immersion testing of the hollow fibres showed that they were stable even in harsh solvents such as dimethylformamide, only acetone was tested due to the limited stability of the epoxy sealant used. The addition and subsequent removal of maleic acid is crucial in imparting nanofiltration properties to these fibres. Fibres spun without adding maleic acid as a dopant gave little or no solvent flux. Work is in progress to identify solvent resistant sealants for the testing of these hollow fibres in various other organic solvents.

In conclusion, PANi hollow fibres have been successfully spun using a novel method of acid addition before spinning. Porosity could be induced by removing these large acids from the membrane after spinning. Preliminary immersion tests showed that these fibres were stable in many organic solvents and could be used for nanofiltration in acetone, giving a low molecular weight cut-off. Membranes in hollow fibre configurations allowed for high surface areas in small volumes, thus giving rise to the possibility of adapting these fibres for use in further industrial applications. The high rejections of these small test solutes point to the possibility of using these fibres in solvent exchange/swap processes.

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Notes and references

1 M. R. Anderson, B. R. Mattes, H. Reiss and R. B. Kaner, *Science*, 1991, **252**, 1412–1415.
2 G. Illing, K. Hellgardt, M. Schonert, R. J. Wakeman and A. Jungbauer, *J. Membr. Sci.*, 2005, **253**, 199–208.
3 L. Rebattet, M. Escoubes, M. Pinéri and E. M. Geniès, *Synth. Met.*, 1995, **71**, 2133–2137.
4 R. B. Kaner, *Synth. Met.*, 2002, **125**, 65–71.
5 S. Kuwabata and C. R. Martin, *J. Membr. Sci.*, 1994, **91**, 1–12.
6 J. Pellegrino, *Ann. N. Y. Acad. Sci.*, 2003, **984**, 289–205.
7 R. M. Gould, L. S. White and C. R. Wildemuth, *Environ. Prog.*, 2001, **20**, 12–16.
8 H. G. Hicke, I. Lehmann, G. Malsch, M. Ulbricht and M. Becker, *J. Membr. Sci.*, 2002, **198**, 187–196.
9 U. Razdan, S. V. Joshi and V. J. Shah, *Curr. Sci.*, 2003, **85**, 761–771.
10 B. Van der Bruggen, J. Geens and C. Vandecasteele, *Sep. Sci. Technol.*, 2002, **37**, 783–797.
11 J. T. Scarpello, D. Nair, L. M. F. dos Santos and A. G. Livingston, *J. Membr. Sci.*, 2002, **203**, 71–85.
12 Y. H. Seetoh, F. W. Lim and A. G. Livingston, *J. Membr. Sci.*, 2007, **301**, 3–10.
13 X. Li, P. Vandezande and I. F. J. Vankelecom, *J. Membr. Sci.*, 2008, **320**, 143–150.
14 K. Vanherck, P. Vandezande, S. O. Aldea and I. F. J. Vankelecom, *J. Membr. Sci.*, 2008, **320**, 468–476.
15 E. M. Scherr, A. G. MacDiarmid, S. K. Manohar, J. G. Masters, Y. Sun, X. Tang, M. A. Druy, P. J. Glatkowski, V. B. Cajipe, J. E. Fischer, K. R. Cromack, M. E. Jozefowicz, J. M. Ginder, R. P. Mccall and A. J. Epstein, *Synth. Met.*, 1991, **41**, 735–738.
16 K. Tzou and R. V. Gregory, *Synth. Met.*, 1993, **53**, 365–377.
17 D. Yang and B. R. Mattes, *J. Polym. Sci., Part B: Polym. Phys.*, 2002, **40**, 2702–2713.
18 P. Chapman, X. X. Loh, A. G. Livingston, K. Li and T. A. C. Oliveira, *J. Membr. Sci.*, 2008, **309**, 102–111.
19 I. D. Norris, A. G. Fadeev, J. Pellegrino and B. R. Mattes, *Synth. Met.*, 2005, **153**, 57–60.
20 A. J. Dominis, G. M. Spinks, L. A. P. Kane-Maguire and G. G. Wallace, *Synth. Met.*, 2002, **129**, 165–172.
21 A. J. Milton and A. P. Monkman, *J. Phys. D: Appl. Phys.*, 1993, **26**, 1468–1474.
22 P. Rannou and M. Nechtschein, *Synth. Met.*, 1997, **84**, 755–756.
23 Y. H. Seetoh, X. X. Loh, K. Li, A. Bismarck and A. G. Livingston, *J. Membr. Sci.*, 2007, **291**, 120–125.