

SELECTIVE MODIFICATION OF MEMBRANE PORE AND EXTERNAL SURFACES

S. Ranil Wickramasinghe, Ralph E. Martin Department of Chemical Engineering, University of Arkansas, Fayetteville, AR 72703, USA
ranil.wickramasinghe@uark.edu

Blaine M. Carter, Ralph E. Martin Department of Chemical Engineering, University of Arkansas, Fayetteville, USA

Anh Vu, Ralph E. Martin Department of Chemical Engineering, University of Arkansas, Fayetteville, USA
Xianghong Qian, Department of Biomedical Engineering, University of Arkansas, Fayetteville, USA

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Modification of membrane surfaces by grafting polymer brushes from the surface has been shown to impart unique surface properties. These polymer brushes can be used as ligands in membrane for adsorbers, they can be used to reduce membrane fouling as well as for the development of responsive membranes that can change their conformation in response to an external stimulus^{1,2}. Here we focus on magnetically responsive membranes where magnetically responsive polymer chains are grown from the membrane surface. We have developed a range of microfiltration³, ultrafiltration and nanofiltration^{4,5} membranes by grafting magnetically responsive polymer brushes from the membrane surface. Here we focus on regenerated cellulose based ultrafiltration membranes.

Atom transfer radical polymerization (ATRP) has been used to graft poly-hydroxyethyl methacrylate (polyHEMA) from the surface of the membrane. Superparamagnetic particles have been attached to the chain ends. In an oscillating magnetic field, movement of the magnetically responsive nanobrushes leads to suppression of concentration polarization resulting in higher permeate fluxes and better rejection. We have also grafted with poly(N-isopropylacrylamide) a thermo-responsive polymer that exhibits a lower critical solution temperature, using ATRP, from the surface of the membrane. By carefully choosing the frequency of the oscillating magnetic field, movement of the polymer chains can be used to induce mixing. Using much higher frequencies, around 1,000 Hz, heating will lead to collapse of poly(N-isopropylacrylamide) layer as the temperature of the grafted polymer layer increases above the lower critical solution temperature of the grafted poly(N-isopropylacrylamide).

Unlike nanofiltration and microfiltration membranes where the majority of the polymer chains are grafted from the barrier layer or the inside pore surface respectively, in the case of ultrafiltration membranes significant grafting can occur from both the barrier layer and the internal pore surface. In addition, given the smaller pore sizes compared to microfiltration membranes, pore plugging by the grafted polymer chains must be avoided. We have developed a novel technique to selectively graft from the external barrier layer or the internal membrane pore surface. We show that the magnetically responsive polymer brushes can have a significant different effect on rejection and flux of model feed streams consisting of proteins such as bovine serum albumin, depending on their location on the membrane barrier layer or in the pores. Our work highlights the importance of being able to control not only the three-dimensional structure of the grafted polymers but also their location; from the membrane barrier layer or from the inside pore surface.

References

1. D. Bhattacharyya, T. Schäfer, S. R. Wickramasinghe, S. Daunert, eds., *Responsive Membranes and Materials*, John Wiley & Sons, 2013, West Sussex, UK.
2. S. Darvishmanesh, X. Qian, Wickramasinghe, S. R. (2015), 'Responsive membranes for advanced separations', *Current Opinions in Chemical Engineering*, 8, 98-104.
3. H. H. Himstedt, Q. Yang, X. Qian, S. R. Wickramasinghe, M. Ulbricht, M., 'Toward remote-controlled valve functions via magnetically responsive capillary pore membranes', *J Membr. Sc.*, 423 (2012) 257-266.
4. Q. Yang, Q., H. H. Himstedt, M. Ulbricht, X. Qian, X., S. R. Wickramasinghe, 'Designing magnetic field responsive nanofiltration membranes', *J Membr. Sc.*, 430 (2013) 70-78.
5. X. Qian, Yang, Q., Vu, A. T., Wickramasinghe, S. R. (2016), 'Localized Heat generation from Magnetically Responsive Membranes', *Industrial & Engineering Research*, 55 (33), 9015–9027.