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Poly(ethylene oxide)-*block*-poly(methyl methacrylate) Diblock Copolymers as Functional Additive for Poly(vinylidene fluoride) Ultrafiltration Membranes with Tailored Separation Performance

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Abstract

In this work, poly(ethylene oxide)-*block*-poly(methyl methacrylate) (PEO-*b*-PMMA) diblock copolymers were established as functional additive for polyvinylidene fluoride (PVDF) ultrafiltration (UF) membranes, originally with the intention to increase their hydrophilicity and thereby decrease fouling. Additionally, however, it was found that copolymer micelles can be induced by complexing the PEO block of PEO-*b*-PMMA with specific metal salts. The formation of micelles as function of specific solution compositions was observed in dynamic light scattering and rheology experiments; the formation of PEO-metal ion complexes was shown via proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. Integration of micelle-forming compositions into typical PVDF-based casting solutions for UF membranes could lead to a higher surface porosity and a more regular barrier pore structure through microphase separation during the nonsolvent induced phase separation process used for membrane preparation. It was found that membranes containing small amounts of PEO-*b*-PMMA show a significantly higher permeance than membranes made from an otherwise equal casting solution without the copolymer, while maintaining the solute rejection properties. By using different types and amounts of metal salts to complex the PEO block it was possible to tailor the molecular weight cut-off of the membranes between 30 kDa and 110 kDa. Fouling studies in lab-scale cross-flow filtration cells showed an increased relative flux recovery compared to membranes without the functional copolymer additive. The results of this study are relevant because small fractions of a tailored diblock copolymer and metal salt as additives allow tailoring the barrier and separation properties at significantly higher overall performance within an otherwise unchanged membrane manufacturing process.