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# Fabrication and structural tailoring of reverse osmosis membranes using $\beta$ -cyclodextrin-cored star polymers

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## ABSTRACT

Here, we designed a new chemistry of fouling-resistant reverse osmosis (RO) membranes using a star polymer (CD-PAH) comprising multiple linear polymer (poly(acryloyl hydrazide), PAH) arms grafted onto a  $\beta$ -cyclodextrin ( $\beta$ -CD) core. The well-defined structure of the  $\beta$ -CD-cored star polymer enabled us to systematically synthesize CD-PAHs with different arm lengths, which were assembled into membrane selective layers via a layered interfacial polymerization technique. Increasing the PAH arm length of CD-PAH enhanced the inter-chain entanglement of PAH arms and thus the crosslinking reaction efficiency by providing a higher density of the crosslinkable amine groups of densely-packed PAH arms. Hence, longer PAH arms of CD-PAH resulted in an enhancement in NaCl rejection with a reduction in the water permeance of the CD-PAH-assembled (CD-TFC) membrane. Importantly, the CD-TFC membranes prepared using CD-PAHs with longer PAH arms exhibited RO separation performance comparable to that of a commercial RO membrane, which is not feasible by other reported branch-structured macromolecules. Furthermore, the CD-TFC membrane displayed lower organic fouling with a higher rinsing efficiency than a commercial RO membrane, because of its more negatively charged and hydrophilic surface combined with its smoother surface, overcoming a performance-fouling trade-off.

## 1. Introduction

Water treatment and desalination processes using reverse osmosis (RO) membranes are now the well-established technology for purifying water in a highly energy-efficient manner [1–3]. Conventional RO membranes adopt a thin film composite (TFC) form comprising a thin polyamide (PA) selective layer adhered to a porous support [4]. Because the selective layer primarily determines membrane performance and durability, designing an appropriate selective layer structure is critical for achieving the high separation efficiency [5].

The commercial RO selective layer is synthesized via interfacial polymerization (IP) between *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) monomers [6]. Despite its high permselectivity, the MPD/TMC-based RO membrane suffers from fouling owing to its intrinsically rough (characterized as a ridge-and-valley morphology) and insufficiently hydrophilic surface [7,8]. Extensive efforts have been dedicated to alleviating membrane fouling by tailoring the membrane surface topology or modifying the membrane chemistry through coating, grafting or incorporating antifouling materials on/into the PA selective layer [7,9–16], or employing new monomers to synthesize the selective

layer [17–19]. Although these approaches improved fouling resistance, they inevitably deteriorated separation performance, imposed by a conventional performance-fouling trade-off, which necessitating the development of a new selective layer architecture with novel materials [5,20].

Branch-structured macromolecules (BMs) with a high density of functional groups have attracted significant interest as promising building materials for the selective layer owing to their large free volume and functionality [21–23]. Although many researchers have successfully assembled BMs, including hyperbranched polymers and dendrimers, into selective layers [23–29], the separation performance of the BM-assembled TFC membranes has been limited to loose RO or nano-filtration grade because of their ineffectively crosslinked networks [25–29]. Recently, we showed that a star polymer, comprising linear polymer (poly(acryloyl hydrazide), PAH) arms on a crosslinked polymer (poly(ethylene glycol dimethacrylate), PEGDMA) core can be formed into the RO selective layer via conventional IP [30]. Compact packing of its linear PAH arms having the high-density amine groups enabled to form a tightly crosslinked network. However, our prototype PEGDMA-cored star polymer (PEGDMA-PAH) synthesized via the

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