

# Thin film composite nanofiltration membranes fabricated from quaternized poly(ether ether ketone) with crosslinkable moiety using a benign solvent



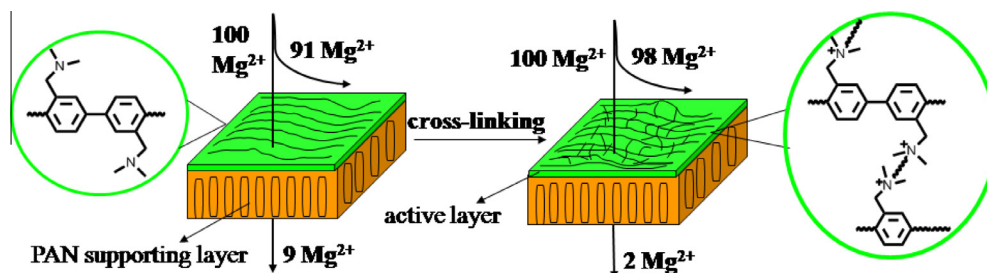
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## GRAPHICAL ABSTRACT

The cross-linked membranes showed better salt separation capability and operation stability than uncross-linked membranes.



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## ABSTRACT

Thin film composite nanofiltration membranes were fabricated through dip-coating and in situ cross-linking of quaternized poly(ether ether ketone) containing a certain amount of tertiary amine groups (QAPEEKs) on polyacrylonitrile (PAN) support. The effects of the variables in membrane formation such as the coating polymer concentration, the curing temperature, and the cross-linking agent types on resultant membrane were studied and the membrane properties such as the barrier layer chemical structure, the surface element composition and morphology were investigated. The obtained performance of uncross-linked and cross-linked QAPEEK-70 thin film composites in nanofiltration test was compared. The results indicated that the cross-linking improved the composite membranes' performance. For instance, the membrane cross-linked by bisphenol A diglycidyl ether (BPADGE) named M-C-BPADGE exhibited a  $\text{MgCl}_2$  rejection of 97.8%, a water flux of  $11.8 \text{ L m}^{-2} \text{ h}^{-1}$ , a MWCO of 800 Da and corresponding pore size of 0.69 nm, while for its uncross-linked membrane named M-U, a  $\text{MgCl}_2$  rejection of 91.2%, a water flux of  $13.5 \text{ L m}^{-2} \text{ h}^{-1}$ , a MWCO with 960 Da and a pore size of 0.77 nm were found. Furthermore, the M-C-BPADGE membrane exhibited selectivities of 16.0 for separation of mixed  $\text{Mg}^{2+}$  and  $\text{Na}^+$  cations, much larger than selectivity of 5.2 obtained for M-U, suggesting that the cross-linked membranes are promising in cation separation.

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## Nomenclature

NF	nanofiltration	QAPEEK	quaternarized poly(ether ether ketone)
TFC	thin film composite	$F$	water flux
PAN	polyacrylonitrile	$R$	rejection ratio
DABP	3,3'-dimethylaminemethylene -4,4'-biphenol	$C_p$	permeate salt concentration
BFDPA	4,4'-bisfluorodiphenylketone	$C_f$	feed salt concentration
PXDC	p-xylylene dichloride	$r_s$	Stokes radii
BPADGE	bisphenol A diglycidyl ether	MW	Molecular weight
TAPEEK	tertiary amine polyether ether ketone		

## 1. Introduction

Nanofiltration (NF) has recently gained significant attention because of advantages such as relatively low operating pressures, high fluxes and low operating and maintenance costs [1], and its typical applications including water softening, wastewater treatment, industrial separations, etc. [2,3]. Polyamide thin film composite (TFC) membranes dominate the current NF market mainly because of their combination of high water permeability and high ionic or molecular selectivity [4]. However, due to the degradation of the amide linkage, polyamide membranes suffer from poor resistance to harsh conditions found in environments with high concentration of oxidants or pH extremes [5,6]. To avoid polyamide membrane deterioration, tedious and costly steps including de-chlorination of feed water, re-chlorination of product water, and pH adjustment must be added to modern RO and NF separation processes [7,8]. Consequently, there is a strong demand for improved membranes that offer high flux and high rejection and that are also resistant to chlorine-based disinfectants, highly pH tolerant, and more resistant to fouling and are therefore more robust and durable than current materials [9].

Recently, hydrophilic modified poly(aryl ether)s, such as disulfonated poly(arylene ether sulfone) [7], sulfonated poly(ether ether ketone) [10], sulfonated polyphenylene oxide [11], have been considered as potential desalination membrane materials [9,12]. The directly copolymerized sulfonated poly(arylene ether sulfone) random copolymers (BPS-XX) based composite membranes that displayed excellent chlorine resistance over a wide range of pH values [13], have been investigated extensively by Freeman and coworkers [6]. For example, Geise et al. [12,14–17] investigated the fundamental salt and water transport properties in these copolymers membranes, and found that these followed the free volume theory. However, the practical application of these membranes has encountered several bottleneck problems. The first issue is the tradeoff between the water permeability and salt rejection which is governed by the water sorption of the polymer membranes; here, as the water uptake increases, water permeability increases and salt rejection decreases, and vice versa [6,18]. Introduction of cross-linking architectures among the polymer chains was suggested to be a useful strategy for optimization of the salt and water transport properties. Cross-linking can restrict the polymer's ability to swell, decreasing the diffusion of water and salt through the membranes; cross-linking also tends to increase membrane selectivity. Riffle et al. [19] reported that covalent cross-linking of highly sulfonated poly(arylene ether sulfone) with a multifunctional epoxy resin improved the salt rejection without significantly impairing water permeability in the RO membrane application. Kim et al. [20] also showed that thermally induced cross-linking among ethynyl end groups of sulfonated poly(arylene ether) led to remarkably improved salt rejection (up to 98.4%) compared to that of its non-crosslinked counterpart (about 90.3%) with only a small change in water permeability.

Introduction of quaternary ammonium groups is another hydrophilization strategy for poly(arylene ether)s. Compared to their sulfonated counterparts, poly(arylene ether)s that contain quaternary ammonium groups exhibit at least two advantages for membrane preparation. First, since the quaternary ammonium group is derived from the tertiary amine groups, it provides the possibility for introduction of cross-linking structure simultaneously with completion of the quaternization reaction. Second, quaternary ammonium moiety is composed of aliphatic chain segments, which is favorable for its dissolution in aliphatic solvents according to the theory of "similarity and intermiscibility". In the present study, partially quaternarized PEEKs that retain a certain amount of tertiary amine groups (QAPEEK-70) as cross-linkable moieties were synthesized and studied as candidate materials for active layer fabrication. The obtained polymer was found to be soluble in a benign ethylene glycol monomethyl ether (EGME) solvent, which has a lower boiling point (124 °C at 760 mm Hg) and lower surface tension (27.6 dyne/cm at 20 °C) than DEG, allowing the possibility of obtaining defect-free QAPEEK-70 active layer with high selectivity by use of environmentally friendly processing conditions. Two kinds of cross-linking agents, p-xylylene dichloride (PXDC) and bisphenol A diglycidyl ether (BPADGE) were used to induce cross-linking of the residual tertiary amine groups in QAPEEK-70. This study focuses on the comparison of the nanofiltration tests for uncross-linked and cross-linked QAPEEK-70 thin film composites. The effects of the major fabrication variables such as the coating polymer concentration, the curing temperature, the cross-linking agent types and concentrations on the resultant composite membrane properties are discussed in the context of their implications for the development of high performance non-polyamide based composite NF membranes.

## 2. Experimental

### 2.1. Materials and reagents

Polyacrylonitrile (PAN) ultrafiltration membranes (MWCO = 80,000 Da) were purchased from Beijing Separate Equipment Co., Ltd. PSF ultrafiltration membranes were made in our laboratory. 3,3'-Dimethylaminemethylene-4,4'-biphenol (DABP) was synthesized using the methods reported in our previous work [21]. 4,4'-Bisfluorodiphenylketone (BFDPA), Polyethylene glycol (PEG), thylene glycol monomethyl ether (EGME), dimethylacetamide (DMAC), p-xylylene dichloride (PXDC) and bisphenol A diglycidyl ether (BPADGE) were purchased from Sinopharm Group Chemical Reagent. All other reagents were obtained from commercial sources and used as received.

### 2.2. Synthesis of polymer TAPEEK and QAPEEKs

The synthesis route for the coating polymer poly(arylene ether ketone) containing pendant tertiary amine (TAPEEK) and QAPEEK-70 is shown in Scheme 1. In a typical preparation procedure for

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