
Electronic supplementary information

Benzene ring crosslinking of sulfonated polystyrene-grafted SEBS (S-SEBS-g-PSt) membrane by Friedel-Crafts reaction for superior desalination performance by pervaporation

Mengyu Yan,^a Feixiang Zeng,^b Na Li,^{*a} Wenhai Bian,^a Weiyu Shen^a and Zongli Xie^{*c}

^a School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an, 710049, China

^b Science and Technology on Reactor Fuel and Materials Laboratory, Nuclear Power Institute of China, Chengdu, 610213, China

^c CSIRO Manufacturing, Private bag 10, Clayton South, VIC 3169, Australia

Corresponding author emails: lina@mail.xjtu.edu.cn; zongli.xie@csiro.au

Experimental Section

S-SEBS-g-PSt synthesis and membrane preparation

For membrane fabrication, the as-prepared SEBS-g-PSt (S-SEBS-g-PSt) powder was dissolved in chloroform under stirring to obtain 8 wt% homogeneous dope solution. The controlled amount of dope solution was cast onto a Teflon dish and the solvent was then evaporated. The obtained membrane was sulfonated by immersing into the mixture of DCE and sulfonating reagent (acetyl sulfate) at 45 °C for 4 h, 10 h and 14 h. After being washed with deionized water till neutral pH, the S-SEBS-g-PSt membranes with SD=30%, 50% and 60% were obtained, respectively.

Membrane characterization

Table S1. Elemental analysis results of SEBS@CH₂Cl and SEBS-g-PSt

Material	C/H	Chloromethylation ratio, (%)	Grafting degree (%)
SEBS	7.1267±0.0013	—	—
SEBS@CH ₂ Cl	7.1739±0.0006	43.4	—
SEBS-g-PSt	8.0074±0.0011	43.4	272.2

Results and discussion section

Physicochemical characteristics of membrane

Mechanical and thermal stability. As shown in Table S2, in comparison with other polymeric membranes in the literature, the tensile strength and Young's modulus of the highly crosslinked membranes rank high.

Table S2. Comparison of mechanical strength of polymer-based membranes.

Membrane	Tensile strength, MPa,	Young's modulus, Mpa,	Reference
PVB/PVDF blended membrane	<10	—	[1]
SPSf/Tröger's base blend membrane	0.34±0.06	4.89±0.57	[2]
PANI/PVA membrane	33.7	—	[3]
PVB based polymer membrane	16.33	—	[4]
Phosphoric acid doped PBIANI membrane	26±3	—	[5]
PVFM/PEO blended membrane	12.81	—	[6]
PVA/PAA membrane	1.39-3.47	—	[7]
PEO membrane	37.78	310	[8]
P(AA-AMPS ₂ -crosslinked PVA/PAN nanofiber composite membrane	31.25±4.97	—	[9]
PVB-EVOH blend membrane	4-6.5	20-120	[10]
PVDF membrane	2-14	—	[11]
pDA/TpPa(W/E)-COF membrane	13.1 ± 0.2 to 17.5 ± 0.5	—	[12]
FDA crosslinked S-SEBS-g-PSt	21-32.5	194-395	This work

Pervaporation performance

Effect of operating conditions. The linear relationship between the logarithmic water permeance and the reciprocal temperature was shown in Fig.S1, by which E_p was calculated as -34.92 kJ/mol from the slope of the Arrhenius plot.

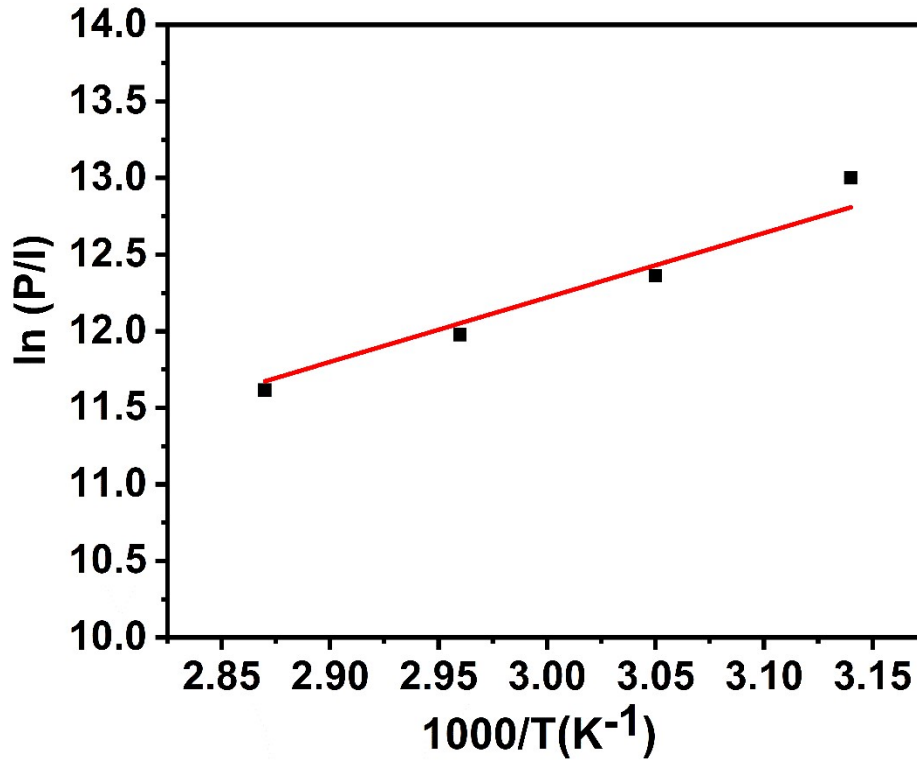


Fig.S1. The Arrhenius plot of water permeance with feed temperature in desalinating 5 wt% NaCl aqueous solution.

Comparison of membrane performance with literatures. Water permeability of the optimized membrane S1-60-2.88-80 (SD=60%) was calculated and compared to the state-of-art membranes deployed for PV desalination in the literature (as listed in Table S3). The results indicate that over a wide salt concentration range of 3.5-20 wt%, the FDA-crosslinked S-SEBS-g-PSt membrane exhibited the highest water permeability of 1,500,000–3,500,000 barrer and outperformed the other reported membranes by 1–2 orders. Our previous reported S-SEBS membrane also showed notably high water permeability (1,350,000–2,160,000 barrer). This is attributed to the advantageous features of the SAP membranes with strong hydrophilic sulfonic acid groups and inherent continuous ionic nano-channels to facilitate water diffusion. The higher water permeability of S-SEBS-g-PSt membrane than S-SEBS membrane proves the significance of polystyrene-grafting modification and FDA crosslinking.

Table S3. Comparison of pervaporative desalination performance of membranes.

Membrane	NaCl, wt%	Operating conditions	p_r (kPa)	Flux, Kg/(m ² ·h)	Water permeability, 10 ⁴ Barrer,	Salt rejection, %	Reference
ZSM-5	0.3	75 °C, vacuum	38.53	11.5	4.540	99	[13]
Silicalite-1	0.3~15	75 °C, vacuum	36.58~38.53	3~11.3	2.26~8.1	97~99	[13]
FAU zeolite membrane	3.5	50~90 °C, 10KPa	12.22~69.32	0.96~5.64	1~4.58	99.8	[14]
pure silica membrane	0.3	22 °C, vacuum	2.34	9.5	9.356	99.6	[15]
CTAB-silica membrane	4	25 °C, 0.6KPa	3.13	2.6	0.995	99.9	[16]
Ethenylene-bridged organosilica membranes	0.2~3.5	25 °C, vacuum	3.13~3.17	3.8~4.8	0.55~0.69	99.5	[17]
Inorganic membranes							
Cobalt oxide silica(CoOxSi,	1	75 °C, vacuum	38.45	1.8	0.060	99	[18]
ZIF-7	3.5	50 °C, vacuum	12.22	9.2	69.400	99.5	[19]
ZIF-8	3.5	50 °C, vacuum	12.22	8.1	61.102	99.8	[19]
Hydroxyl sodalite	3.5	30 °C, 0.3KPa	4.2	0.12	0.142	99.99	[20]
TiO ₂ /α-Al ₂ O ₃	0.3~10	75 °C, <10KPa	37.29~38.53	4~10.5	0.2~0.51	99	[21]
FAS grafted ceramic membrane	3	40 °C, 0.4KPa	7.32	5	76.596	—	[22]
maleic acid covalent-bridged MXene membrane	3.5	65 °C, 0.133KPa	24.75	79.3	0.445	99	[23]
PDA-modified GO/α-Al ₂ O ₃	3.5	90 °C, vacuum	69.32	48.4	1.287	99.7	[24]
Organic membranes							
Cellulose acetate	4~14	70 °C, vacuum	26.69~30.79	3.45~5.97	13.7~20.6	99.7	[25]
Cellulose triacetate	10	50 °C, vacuum	11.94	2.5	9.650	99	[26]
polyster	3.5	20 °C, vacuum	2.31	0.0071	10.625	99.84	[27]
polyether ester	3.2~5.2	22~28.7 °C, vacuum	2.3~4.2	0.13~0.16	28.1~41.6	—	[28]
Poly vinyl alcohol	3	70 °C, vacuum	30.89	7.4	0.110	99.9	[29]
	1	65 °C, 6KPa	24.95	22.87	216.937		[30]
S-SEBS	3	65 °C, 6KPa	24.79	20.41	195.251	99.9	[30]
	5	65 °C, 6KPa	24.63	14	135.080		[30]
PEBA	20	65 °C, 1.7KPa	23.24	0.5~1.7	9.62~14.54	99.9	[31]

	3.5	65 °C, 6KPa	24.75	69.52	341.783	99.98	This work
FDA crosslinked	5	65 °C, 6KPa	24.63	64.31	318.205	99.98	This work
S-SEBS-g-PSt	10	65 °C, 6KPa	24.2	50.6	256.284	99.991	This work
	20	65 °C, 6KPa	23.24	27.9	149.179	99.998	This work
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poly(vinyl alcohol, /polyacrylonitrile	0.5	20 °C, 0.1KPa	2.34	9.04	11.533	99.5	[32]
S-PVA/PAN	3.5	70 °C, 0.1KPa	30.84	46.3	5.554	99.5	[33]
	3.5	30 °C, 0.1KPa	4.2	14.11	12.690	99.7	[33]
poly(vinyl alcohol, /polysulfone composite	3	50~70 °C, vacuum	12.24~30.89	4.6~7.4	1.1~8.14	99.9	[29]
PVA/silica	3	60 °C, vacuum	19.75	10.4	0.558	99.9	[34]
GO/PAN	3.5	90 °C, 0.1KPa	69.32	65.1	0.433	99.8	[35]
PEI/GO LbL	20	65 °C, 1.7KPa	23.24	8.4	1.078	99.9	[36]
glutaraldehyde crosslinked GO-	5	65 °C, 6KPa	24.63	46	1.138		[37]
	10	65 °C, 6KPa	24.2	42	1.064	99.99	[37]
PVA	15	65 °C, 6KPa	23.74	34	0.883		[37]
	20	65 °C, 6KPa	23.24	27.5	0.735		[37]
glutaraldehyde crosslinked composite membranes	3.5	70 °C, 0.1KPa	30.84	69.1	1.243	99.9	[38]
S-PVA/PSF composite membrane	3.5	70 °C, 0.1KPa	30.74	60.79	10.242	99.8	[39]
GO/CS	5	81 °C, 6KPa	46.61	30	40.858	99.9	[40]
PVA/PTFE	3.5	75 °C, 0.1KPa	38.14	152.3	18.453	99.9	[41]
PVA/PVDF	10	80 °C, 5KPa	45.8	10.3	2.327	99.999	[42]
Mxene/PAN	3.5	65 °C, 0.4KPa	24.75	85.4	0.970	99.5	[43]
Sulfosuccinic acid crosslinked PVA/PAN	3.5	70 °C, 0.1KPa	30.84	27.9	20.498	99.8	[44]
P(AA-AMPS,- crosslinked	1.5	75 °C, 0.1KPa	38.38	243	21.358		
	3.5	75 °C, 0.1KPa	38.14	212	18.751		
PVA/PAN nanofiber composite membrane	10	75 °C 0.1KPa	37.29	150	13.571	99.9	[9]
	20	75 °C 0.1KPa	35.81	75	7.067		

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