Supporting Information „Highly Selective CO_2 Separation Membranes Through Tunable Poly(4-vinylphenolate)-CO_2 Interactions"

Thermogravimetric Analysis (TGA) / Differential Scanning Calorimetry(DSC)

Table 1: Glass transition temperatures (T_g) and melting points (T_m) of poly(4-vinylphenol) (**1a**), poly(2-methoxy-4-vinylphenol) (**1b**), poly(2,6-dimethoxy-4-vinylphenol) (**1c**), the respective copolymers with di(ethylene glycol methyl ether methacrylate) (**2a-2c**) and selected corresponding tetraalkylphosphonium poly(4-vinylphenolate)s (**[P_{xxxx}][1a-2c]**).

Sample	T_g[°C]	T_m [°C]
1a	169.08	-
1b	97.41	-
1c	75.40	-
2a	57.70	-
2b	44.70	-
2c	46.07	-
[P_{66614}][1a]	-64.47	31.43
[P_{44414}][1a]	-69.95	30.18
[P_{4441}][1a]	-83.35	-61.44
[P_{4444}][1a]	-75.54	104.41
[P_{66614}][1b]	-61.22	21.15
[P_{66614}][1c]	-57.88	13.04
[P_{66614}][2a]	-30.03	-
[P_{66614}][2b]	-30.08	-
[P_{66614}][2c]	-50.20	-

^1H, ^{31}P and ^{13}C-MAS NMR Spectral Data

Monomers:

4-Vinylphenol: (300 MHz, Methanol-d_4) δ (ppm) = 7.34 – 7.21 (2H, m), 6.87 – 6.72 (2H, m), 6.65 (1H, dd), 5.58 (1H, dd), 5.04 (1H, dd).

2,6-Dimethoxy-4-vinylphenol: 300 MHz, Methanol-d_4) δ (ppm) = 6.71 (2H, s), 6.62 (1H,dd), 5.61 (1H , dd), 5.07 (1H, dd), 3.84 (6H, s).

Polymers:

Poly(2-methoxy-4-vinylphenol) (1b): (250 MHz, Methanol-d_4):δ (ppm)= 6.88 – 5.80 (3H, m), 3.84 – 3.45 (3H, m), 2.40 – 0.81 (3H, m).

Poly(2,6-dimethoxy-4-vinylphenol) (1c): (300 MHz, Methanol-d_4): δ (ppm) = 5.95 (2H, m), 3.65 (6H, m), 1.68 (3H, m).

Poly(4-vinylphenol-*co*-di(ethylene glycol) methyl ether methacrylate) (2a): (250 MHz, Methanol-d_4) δ (ppm) = 7.02 – 6.38 (4H, br), 4.16 – 3.33 (11H, br), 2.75 – 1.19 (5H, br), 1.11 – 0.42 (3H, br).

Poly(2-methoxy-4-vinylphenol-*co*-di(ethylene glycol) methyl ether methacrylate) (2b): (250 MHz, Methanol-d_4) δ (ppm) = 6.93 – 5.98 (3H, br), 4.21 – 3.44 (14H, br), 2.79 – 1.21 (5H, br), 1.19 – 0.36 (3H, br).

Poly(2,6-dimethoxy-4-vinylphenol-*co*-di(ethylene glycol) methyl ether methacrylate) (2c): (1H, 300 MHz, Methanol-d_4): δ (ppm) = 1.33 (8H, br), 3.64 (17H, br), 6.24 (2H, br).

Polyelectrolytes:

Tributylmethylphosphonium Poly(4-vinylphenolate) ([P_{4441}][1a]): (31P, 360 MHz, Methanol-d_4): δ (ppm) = 33.13 (1P, s)

Tetrabutylphosphonium Poly(4-vinylphenolate) ([P_{4444}][1a]): (1H, 360 MHz, Methanol-d_4) δ (ppm) = 6.70 – 6.25 (4H, br), 2.29 – 2.15 (8H, m), 1.68 – 1.14 (19H, m), 0.96 (12H, m), (31P, 360 MHz, Methanol-d_4): δ (ppm) = 33.14 (1P, s)

Tributyltetradecylphosphonium Poly(4-vinylphenolate) ([P_{44414}][1a]): (1H, 360 MHz, Methanol-d_4) δ (ppm) = 6.70 – 6.25 (4H, br), 2.29 – 2.15 (8H, m), 1.68 – 1.14 (39H, m), 0.96 (12H, m), (31P, 360 MHz, Methanol-d_4) δ (ppm) = 33.14.

Trihexyltetradecylphosphonium Poly(4-vinylphenolate) ([P_{66614}][1a]): (1H, 360 MHz, Methanol-d_4) δ (ppm) = 6.70 – 6.25 (4H, br), 2.29 – 2.15 (8H, m), 1.68 – 1.23 (48H, m), 0.96 (12H, m), (31P, 360 MHz, Methanol-d_4) δ (ppm) = 33.13, (13C CPMAS-NMR 4mm rotor, 12 kHz, 35400 scans) δ (ppm) = 15.1, 23.8, 30.8, 33.0, 40.0, 49.7, ~119.0, ~120.0, ~132.0.

Trihexyltetradecylphosphonium Poly(4-vinylphenolate)-CO_2 ([P_{66614}][1a]-CO_2): (13C CPMAS-NMR 4mm rotor, 12 kHz, 45800 scans) δ (ppm) = 15.1, 23.8, 30.8, 33.0 40.0, ~117.0, ~127.0, ~133, 158.6, 162.2.

Trihexyltetradecylphosphonium Poly(2-methoxy-4-vinylphenolate) ([P_{66614}][1b]): (1H, 360 MHz, Methanol-d_4) δ (ppm) = 6.70 – 6.25 (3H, br), 3.81 (3H, m), 2.29 – 2.15 (8H, m), 1.68 – 1.23 (48H, m), 0.96 (12H, m), (31P, 360 MHz, Methanol-d_4) δ (ppm) = 33.15.

Trihexyltetradecylphosphonium Poly(2,6-dimethoxy-4-vinylphenolate) ([P_{66614}][1c]): (1H, 360 MHz, Methanol-d_4): δ (ppm) = 5.99 (2H, br), 3.71 (6H, m), 2.29 – 2.15 (8H, m),

1.68 – 1.23 (48H, m), 0.96 (12H, m), (31P, 360 MHz, Methanol-d_4, 300K): δ (ppm) = 56.72, 34.62.

Trihexyltetradecylphosphonium Poly(4-vinylphenolate co-di(ethylene glycol) methyl ether methacrylate) ([P_{66614}][2a]):(1H, 250 MHz, Methanol-d_4) δ (ppm) = 7.02 – 6.38 (4H, br), 4.16 – 3.33 (11H, br), 2.75 – 1.19 (5H, br), 2.29 – 2.15 (8H, m), 1.68 – 1.23 (48H, m), 1.11 – 0.42 (3H, br), 0.96 (m, 12H), (31P, 360 MHz, Methanol-d_4) δ (ppm) = 33.13.

Trihexyltetradecylphosphonium Poly(2-methoxy-4-vinylphenolate-co-di(ethylene glycol) methyl ether methacrylate) [P_{66614}][2b]:(1H, 360 MHz, Methanol-d_4): δ (ppm) = 6.70 – 6.25 (3H, br), 4.16 – 3.33 (11H, br), 3.81 (3H, m), 2.75 – 1.19 (5H, br), 2.29 – 2.15 (8H, m), 1.68 – 1.23 (48H, m), 1.11 – 0.42 (3H, br), 0.96 (m, 12H), (31P, 360 MHz, Methanol-d_4) δ (ppm) = 33.15

Trihexyltetradecylphosphonium Poly(2,6-dimethoxy-4-vinylphenolate co-di(ethylene glycol) methyl ether methacrylate) [P_{66614}][2c]: (^{1}H, 360 MHz, Methanol-d_4): δ (ppm) = 5.99 (2H, m), 3.71 (6H, m), 4.16 – 3.33 (11H, br), 2.75 – 1.19 (5H, br), 2.29 – 2.15 (8H, m), 1.68 – 1.23 (48H, m), 1.11 – 0.42 (3H, br), 0.96 (m, 12H), (^{31}P, 360 MHz, Methanol-d_4): δ (ppm) = 56.72, 34.62.

ATR FT-IR

Poly(4-vinylphenol)(1a): (ATR-IR, cm^{-1}) 3.050-3.600 broad, 3.020, 2.820,1.600, 1.510, 1.450, 1.380, 1.230, 1.170, 1.130, 1.040, 830, 720.

Trihexyltetradecylphosphonium Poly(4-vinylphenolate) ([P_{66614}][1a]): (ATR-IR, cm^{-1})1.930, 1.900, 1.840, 1.600, 1.450, 1.230, 1.170, 1040, 830, 720.

Trihexyltetradecylphosphonium Poly(4-vinylphenolate)-CO_2 ([P_{66614}][1a]-CO_2): (ATR-IR, cm^{-1})1.930, 1.900, 1.840, 1.600, 1.510, 1.450, 1.230, 1.170, 1040, 830, 720.

Density

Table 2: Density at 25 °C as determined by the solvent flotation method or a volumetric method (†)

Sample	**ρ [g / cm^3]**
[P_{44414}][1a]	0.98±0.020
[P_{4441}][1a]	0.99±0.04†
[P_{4444}][1a]	1.00±0.018
[P_{66614}][1a]	1.02±0.015
[P_{66614}][1b]	1.00±0.04†
[P_{66614}][1c]	0.98±0.05†
[P_{66614}][2a]	0.97±0.005
[P_{66614}][2b]	0.99±0.020
[P_{66614}][2c]	1.00±0.05†

Solubility and Free Fractional Volume Sheet

Substance	Count per Effective Repeating Unit								Volume Calculation										
	C [#]	H [#]	O [#]	P [#]	Nb [#]	Ra [#]	Rna [#]	∑ V_Bondi [A^3]	5.92*Nb [-]	14.7*Ra [-]	3.8*Rna [-]	V_VdW [A^3]	V_0 [A^3]	M_ru [u]	ρ [g/cm^3]	V [cm^3/g]	V [A^3/molecule]	FFV	CO2-Solubility [wt%]	CO2-Solubility [V(STP)/V]
[P4441][1a]	21	27	1	1	59	1	0	666,74	349,28	14,7	0	302,8	393,6	326,4	0,99	1,010	547,5	0,28	1,1	5,5
[P4444][1a]	24	33	1	1	66	1	0	771,91	390,72	14,7	0	366,5	476,4	368,5	0,99	1,010	618,1	0,23	0,6	3
[P44414][1a]	34	53	1	1	96	1	0	1122,47	568,32	14,7	0	539,5	701,3	508,8	0,98	1,020	862,1	0,19	2,7	13,4
[P66614][1a]	40	75	1	1	114	1	0	1405,19	674,88	14,7	0	715,6	930,3	603,0	1,02	0,980	981,7	0,05	2,3	11,8
[P66614][1b]	41	77	2	1	118	1	0	1454,96	698,56	14,7	0	741,7	964,2	633,0	1	1,000	1051,2	0,08	1,7	8,6
[P66614][1c]	42	79	3	1	122	1	0	1504,72	722,24	14,7	0	767,8	998,1	663,1	0,98	1,020	1123,5	0,11	0,7	3,5
[P66614][2a]	49	91	5	1	144	1	0	1765,06	852,48	14,7	0	897,9	1167,2	791,2	0,97	1,031	1354,5	0,14	2,6	12,7
[P66614][2b]	50	93	6	1	148	1	0	1814,83	876,16	14,7	0	924,0	1201,2	821,2	0,99	1,010	1377,5	0,13	2	10,0
[P66614][2c]	51	95	7	1	152	1	0	1864,59	899,84	14,7	0	950,1	1235,1	851,3	1	1,000	1413,6	0,13	3,4	17,2
Poly(DEGMEMA)	9	16	4	0	30	0	0	359,87	177,6	0	0	182,3	236,9	188,2	1,02	0,980	306,4	0,23	0	0,0

	C	H	O	P
Bondi radii [A] [Bondi, 1964]	1,7	1,2	1,52	1,8
VdW Volume [A^3]	20,6	7,2	14,7	24,4
Atom mass [unit]	12,01	1	16	31
V_CO2 STP [cm^3/g]	505,1			
Na	6E+23			
conversion factors				
A^3 to cm^3	1E-24			
unit to gram	2E-24			

Single Gas Transmission Rates (GTR) and Coating Thickness

Table 4: Gas transmission rates (GTR) and ideal permeability selectivities α of CO_2 and N_2 through composite membranes prepared from materials [P_{66614}][1a]-[P_{66614}][2c] at 15 °C and at 25 °C.

Polyelectrolyte	**GTR [Ld^{-1}m^{-2} bar^{-1}]**				**$\alpha_{CO2/N2}$**	
	15 °C		**25 °C**		**15 °C**	**25 °C**
	CO_2	**N_2**	**CO_2**	**N_2**		
[P_{66614}][1a]	742	35.0	770	57.0	21.20	13.51
[P_{66614}][1b]	430	28.5	463	35.0	15.09	13.23
[P_{66614}][1c]	385	17.3	487	25.7	22.23	18.95
[P_{66614}][2a]	282	6.50	303	12.2	43.38	24.85
[P_{66614}][2b]	207	4.80	160	5.34	43.13	29.96
[P_{66614}][2c]	199	2.94	347	11.3	67.69	30.71

Permeability may be substantially influenced by sorption- or pressure-induced phenomena such as plasticization and compaction. In these cases, gas permeability is no longer independent of absolute permeate- and retentate side pressure levels, which could not be varied in the permeation measurement setup. Also, potential chemical transport facilitation is sensitive to back pressure of the permeate species.

Punctual Coating Thickness Measurements according to SEM

Table 5: Coating thickness d of composite membranes prepared from materials [P_{66614}][1a]-[P_{66614}][2c] as measured punctually by scanning electron microscopy (SEM).

Polyelectrolyte	**d [µm]**
[P_{66614}][1a]	5.15
[P_{66614}][1b]	4.40
[P_{66614}][1c]	3.98
[P_{66614}][2a]	3.69
[P_{66614}][2b]	5.51
[P_{66614}][2c]	8.85

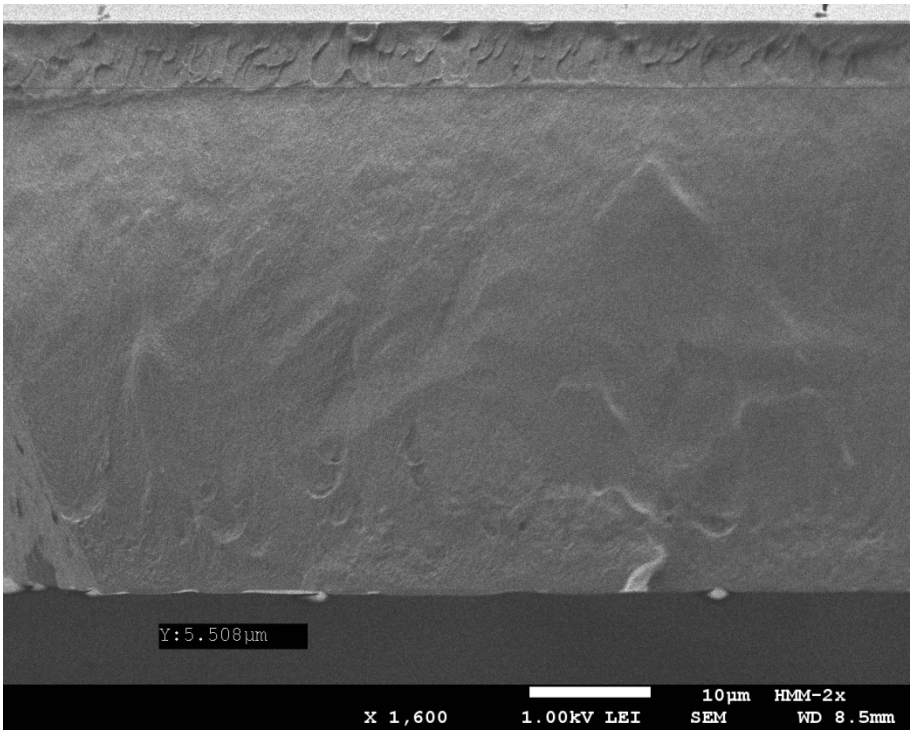

Figure 1: Exemplary cross-section SEM imageof a composite membrane composed of a polysiloxane-based flat-sheet substrate and a coating of Trihexyltetradecylphosphonium Poly(2-methoxy-4-vinylphenolate-co-di(ethylene glycol) methyl ether methacrylate) ([P_{66614}][2b])

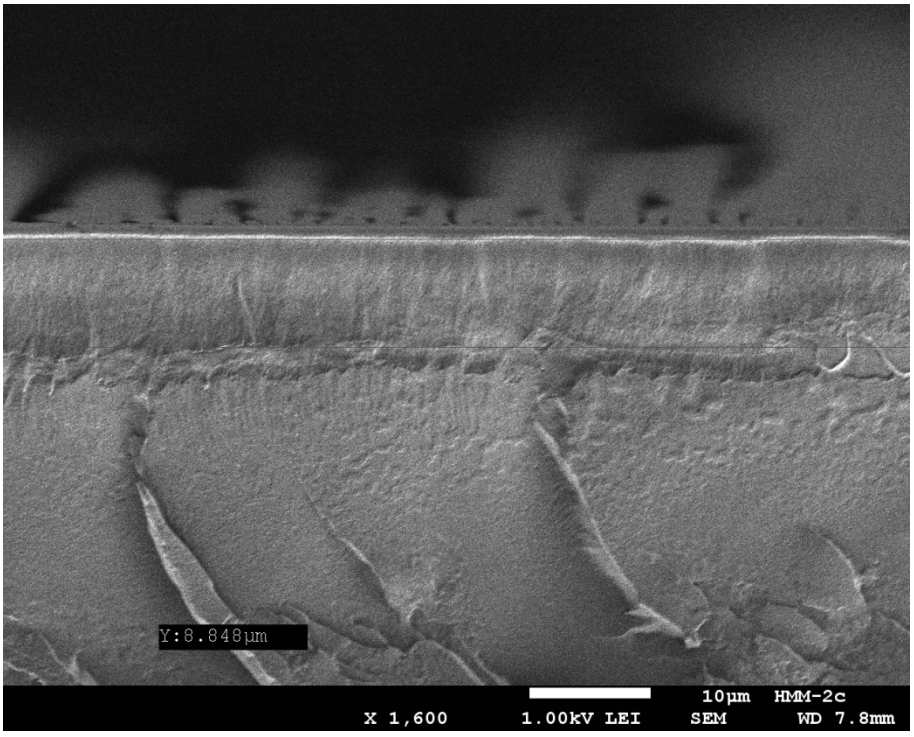

Figure 2: Exemplary cross-section SEM image of a composite membrane composed of a polysiloxane-based flat-sheet substrate and a coating of Trihexyltetradecylphosphonium Poly(2,6-dimethoxy-4-vinylphenolate-co-di(ethylene glycol) methyl ether methacrylate) ([P_{66614}][2c])

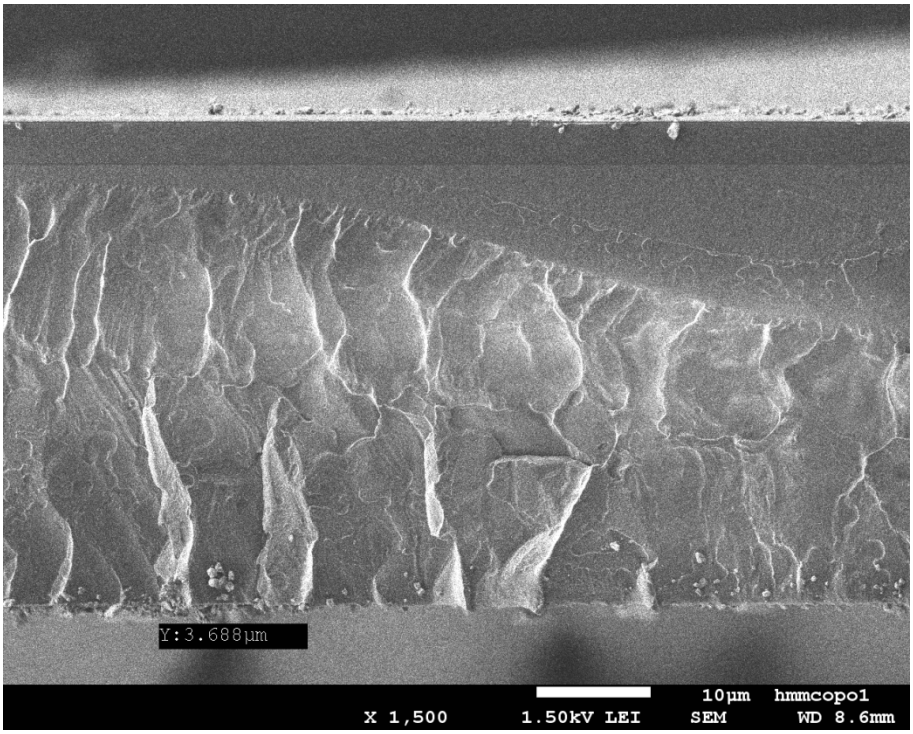

Figure 3: Exemplary cross-section SEM image of a composite membrane composed of a polysiloxane-based flat-sheet substrate and a coating of Trihexyltetradecylphosphonium Poly(4-vinylphenolate-co-di(ethylene glycol) methyl ether methacrylate) ([P_{66614}][2a])