Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Journal of
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Highly Selective CO_2 Separation Membranes Through Tunable Poly(4-vinylphenolate)-CO_2 Interactions

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A series of phenolate-containing polyelectrolytes were prepared *via* post-polymerization treatment of poly(4-vinylphenol) with tetraalkylphosphonium hydroxides (tetrabutylphosphonium hydroxide [P_{4444}][OH], tributyltetradecylphosphonium hydroxide [P_{44414}][OH] and trihexyltetradecylphosphonium hydroxide [P_{66614}][OH]) or with tributylmethylphosphonium methylcarbonate [P_{4441}][CO_3CH_3]. Also, mono- and dimethoxy-substituted vinylphenols were synthesized, polymerized and treated with [P_{66614}][OH] to 10 gain the corresponding polyelectrolytes. CO_2 absorption capacity was measured as a function of the cation species and as a function of methoxy-substituents at the phenyl ring. ATR-IR and ^{13}C MAS NMR spectroscopy confirmed chemisorption of CO_2 *via* formation of a phenol-carbonate complex at room temperature and 1 bar CO_2 partial pressure. The introduction of an oligo(ethylene glycol) methacrylate co-monomer proved to suppress the formation of crystalline domains in the resulting material, enhancing CO_2 absorption capacity and thin film stability. The polyelectrolytes reached a reversible CO_2 absorption capacity of up to 0.65 in terms of CO_2 molecule 15 per phenolate group at 35 °C and 1 bar CO_2 pressure, making them promising candidates for CO_2-selective polymeric membrane materials. Thin coatings of the polyelectrolytes atop of a polysiloxane-based membrane support exhibited excellent adhesion and homogeneity as well as a highly competitive ideal CO_2/N_2 permeability selectivity of up to 67.7 at 15 °C and 1 bar transmembrane pressure.

20 Introduction

Energy-efficient separation of CO_2 from light gases such as N_2, CH_4 and H_2, is a challenging task of great industrial as well as environmental significance. Applications include natural gas and biogas sweetening (CO_2/CH_4)[1], syngas purification (CO_2/H_2)[2] 25 and post-combustion CO_2 capture (CO_2/N_2)[3]. Conventional CO_2 separation systems are semi-continuous, adsorption-desorption setups based on aqueous alkanolamine solutions, which reversibly form carbamates with CO_2. While these systems are commercially mature and show high selectivity for CO_2, they 30 suffer from a variety of intrinsic drawbacks such as the considerable energy requirement for solvent regeneration, corrosiveness of the amine solution, and decomposition through irreversible side-reactions.[4,5] Ionic liquids (ILs) have been reported as alternative solvents for CO_2 sequestration because of 35 their remarkable and reversible solubility of CO_2, their non-volatile nature and relatively high thermal stability.[6] The high CO_2 solubility is attributed to favourable physical interactions between the ion pair of the IL and the permanent electrical quadrupole moment of CO_2, especially between the Lewis-basic 40 anion and the Lewis-acidic carbon atom of CO_2.[7-9] However, favourable physical interactions alone do not induce the desired extent of CO_2 solubility in IL at the low CO_2 partial pressures[10] that are relevant in post-combustion applications and biogas applications. In consequence, research efforts are increasingly

45 directed towards functionalized ILs with CO_2-reactive groups. Amine-functionalized ILs such as trihexyltetradecylphosphonium prolinate ([P_{66614}][Prolinate]) have been reported to absorb up to one mol of CO_2 per mol of IL at moderate CO_2 pressures.[11] More recently, Dai and co-workers reported on the controllability of 50 capacity and heat of CO_2-absorption of phenolic ILs by the presence of electron-donating or -withdrawing groups at the phenyl ring.[12]

As a promising path to a fully continuous, low-maintenance and highly modular CO_2 separation process, IL- and polyelectrolyte-55 based membranes have been the object of increasing research interest in recent years.[13-17] Since selective solubility of CO_2 is also a key material property in the membrane context, those recent advancements in CO_2 scrubbing can be transferred to membrane material development. In CO_2-separation membranes, 60 ILs are utilized as a liquid phase encapsulated in porous substrates through capillary forces, forming so-called supported ionic liquid membranes (SILMs). SILMs show high CO_2/light gas selectivities along with good CO_2 permeability.[18,19] While blowout of IL at large transmembrane pressure is a limitation of 65 some SILMs, Noble and co-workers demonstrated that membranes consisting of polyelectrolytes can be loaded with high amounts of non-polymerizable ILs, thereby greatly improving CO_2 permeability without compromising selectivity and stability at high transmembrane pressures.[20]

70 Herein, we report the preparation of poly(4-vinylphenol)-based

polyelectrolytes and their application as highly CO_2-selective separation layers in composite membranes. The polyelectrolytes are obtained *via* post-polymerization deprotonation of poly(4-vinylphenol) with quaternary phosphonium hydroxide, expanding a synthetic approach that has previously been known with regards to ILs[21] to polyelectrolytes. The synthesis provides a convenient derivation of anion-functionalized polymers from polymeric proton donors. While a variety of cation-functionalized polymers have already been implemented as CO_2 selective materials[14,22-24], to the best of our knowledge, accounts of anion-functionalized polymers as CO_2 selective membrane materials have thus far been limited to poly(styrene sulfonate). Solubility values of CO_2 at atmospheric pressure as well as permeability values of CO_2 and N_2 through composite membranes prepared from polyelectrolyte-coated composite membranes are reported. We describe the effect of tuning the phenolate-CO_2 interaction through substitution of functional groups at the phenyl ring in analogy to the monomolecular system presented by the Dai group. Furthermore, we discuss the influence of an oligo(ethylene glycol) methacrylate co-monomer on CO_2 solubility and permeability as well as on the mechanical stability of the composite membrane. We conclude that poly(4-vinylphenol)-based polyelectrolytes possess remarkable potential for CO_2-separation membrane applications.

Results and Discussion

In preliminary studies, different tetraalkylphosphonium poly(4-vinylphenolate)s, namely tributylmethylphosphonium poly(4-vinylphenolate ([P_{4441}][PVPhO]), tetrabutylphosphonium poly(4-vinylphenolate ([P_{4444}][PVPhO]), tributyltetradecylphosphonium poly(4-vinylphenolate) ([P_{44414}][PVPhO]) and trihexyltetradecylphosphonium poly(4-vinylphenolate), were prepared starting from commercially available poly(4-vinylphenol) to elucidate the influence of the cation on CO_2 absorption capacity. The results can be found in table 2. Thermal stability was found to be higher for more symmetric cations, as is shown in table 1.

Table 1: Thermal decomposition temperatures‡ of different tetraalkylphosphonium poly(4-vinylphenolate)s.

Sample	Thermal decomposition temperature [°C]	
	$T_{dec,1}$	$T_{dec,2}$
[P_{66614}][Poly(VPhO)]	179 °C	580 °C
[P_{44414}][Poly(VPhO)]	161 °C	599 °C
[P_{4441}][Poly(VPhO)]	124 °C	582 °C
[P_{4444}][Poly(VPhO)]	214 °C	583 °C

For the sake of comparability with existing literature, further investigations were limited to the use of the most common counter-cation [P_{66614}].

Synthesis

Scheme 1 shows the structures and the nomenclature of the polymers that were prepared within the scope of this work. The main parameters varied in this study were a) the degree of methoxy substitution of the phenolic monomers and b) the presence of di(ethylene glycol) methyl ether methacrylate (DEGMEMA) co-monomer.

2-Methoxy-4-vinylphenol was purchased from Sigma Aldrich. 4-Vinylphenol and 2,6-dimethoxy-4-vinylphenol were obtained in a one-step Knoevenagel-type reaction starting from the corresponding benzaldehydes, according to a literature procedure.[25] Free-radical homo- and copolymerizations with
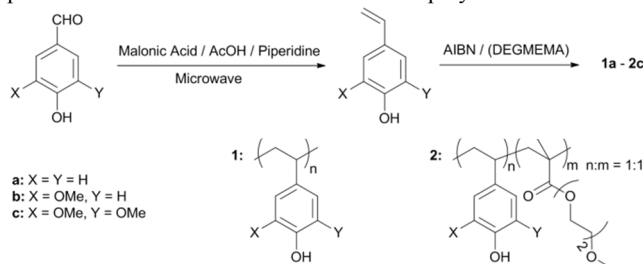
Scheme1: Preparation of poly(4-vinylphenol) (1a), poly(4-vinylphenolate-co-di(ethylene glycol) methyl ether methacrylate) (DEGMEMA) (2a) and mono- and dimethoxy substituted derivatives thereof (b and c, respectively)
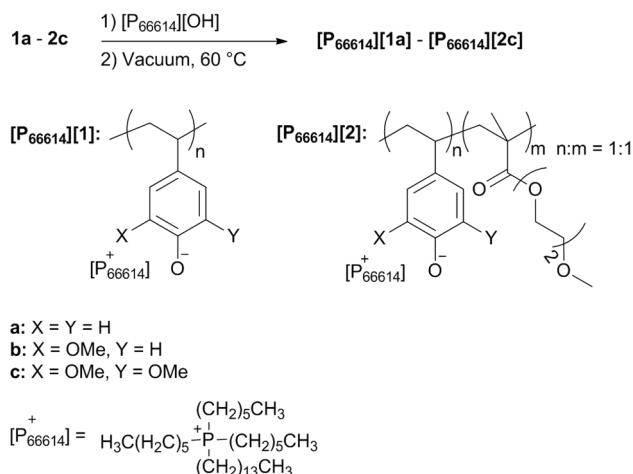
Scheme 2: Preparation of trihexyltetradecylphosphonium poly(4-vinylphenolate) ([P_{66614}][1a]), trihexyltetradecylphosphonium poly(4-vinylphenolate-co-die(ethylene glycol) methyl ether methacrylate) ([P_{66614}][2a]) and mono- and dimethoxy substituted derivatives thereof (b and c, respectively)

di(ethylene glycol) methyl ether methacrylate (DEGMEMA) were conducted using azobisisobutyronitrile (AIBN) as initiator in degassed isopropanol or benzene. The obtained polymers were treated with equimolar amounts (in terms of phenol groups) of [P_{66614}][OH] and dried for at least 24 h at 60 °C under high vacuum to yield substances [P_{66614}][1a] − [P_{66614}][2c], as is represented in scheme 2. Substances [P_{66614}][1a] and [P_{66614}][2a] are off-white in colour, substances [P_{66614}][1b] and [P_{66614}][2b] are brownish and substances [P_{66614}][1c] and [P_{66614}][2c]are of dark brown colour (please refer to supporting information for NMR and DSC results).

CO_2 absorption

The significance of CO_2 solubility in the membrane material is

highlighted by the Solution-Diffusion model, which is a simplified, yet widely accepted means to rationalize gas permeation through non-porous membranes.[26] It is built on the assumption of Fickian diffusion in the bulk and Henry-type sorption at the membrane-gas interface.

$$P_i = D_i S_i$$

$$\alpha_{i/j} = \frac{P_i}{P_j}$$

The permeability P, defined as the product of the diffusion coefficient D and the solubility coefficient S, is specific to each membrane material-gas species pair and therefore commonly used for comparison of membrane performance. It can be seen from the above equations that selective permeability can in principle be achieved by tuning both D and S to favour the permeation of one gas species over another. Since D is dominated by the kinetic diameter of the permeate gas, it is of limited use for CO_2 separation (kinetic diameter of CO_2: 3.30Å vs. 3.64 Å for N_2 and 3.80 Å for CH_4).[4,27] Therefore, the key to selective CO_2 permeability through a dense polyelectrolyte membrane is the selective and reversible dissolution of CO_2 in the membrane material. A limitation to the SD-model is that it does not account for Langmuir-type void absorption phenomena, which are known to occur in glassy polymer membranes. Here, the dual-mode sorption model provides a more detailed approach.[23,28,29]

A commercial gravimetric sorption balance was employed to measure the CO_2 absorption capacity of the polyelectrolytes. The influence of the cation on CO_2 solubility was found to be in agreement with literature results.[30] There is an increase of molar CO_2 absorption capacity with longer substituted alkyl chains and a decrease with higher cation symmetry, the latter having a slightly stronger effect. Presumably, both trends are due to their effect on steric frustration of the phosphonium/phenolate ion pair, either inhibiting or facilitating access of CO_2 molecules to CO_2-reactive phenolate moieties. Table 2 shows the equilibrium CO_2 solubility in terms of weight percent and in terms of CO_2 molecules per repeating unit of polyelectrolyte at 35 °C, respectively.

Table 2: CO_2 absorption capacity at 35 °C and 1 bar CO_2 pressure, density (ρ) and free fractional volume (FFV) at room temperature of different tetraalkylphosphonium poly(4-vinylphenolates).

Sample	ρ [g / cm³]	FFV	CO_2 absorption [wt%]	[mol%]	[V(STP)/V]
$[P_{66614}][Poly(VPhO)]$	1.02±0.02	0.052	2.3	31.9	11.8
$[P_{44414}][Poly(VPhO)]$	0.98±0.02	0.186	2.7	32.1	13.4
$[P_{4441}][Poly(VPhO)]$	0.99±0.04	0.274	1.1	8.3	5.6
$[P_{4444}][Poly(VPhO)]$	0.99±0.02	0.229	0.6	4.9	3.0

The equilibrium CO_2 solubility of 0.32 CO_2 molecules per repeating unit of polyelectrolyte $[P_{66614}][1a]$ is in the same order of magnitude as the corresponding monomolecular $[P_{66614}][Phenolate]$ system under equivalent conditions.[12] This indicates that CO_2 solubility is only slightly diminished by the attachment of the phenolate moiety to a polymer backbone.

Substances $[P_{66614}][2a]$, $[P_{66614}][2b]$ and $[P_{66614}][2c]$ showed a rather fast weight increase during the first minutes of exposure to CO_2, followed by a transition to slow weight increase, which does not reach full equilibrium during the 12 hour absorption measurement. Presumably, this behaviour corresponds to a Henry-type sorption at the polyelectrolyte-CO_2 interface accompanied by subsequent plasticization and a Langmuir-type void-filling sorption in the polyelectrolyte bulk.[31] The dual-mode sorption behaviour and long timescale of absorption are characteristic of a glassy, non-porous polymer, indicating a considerably less viscous character of the copolymers $[P_{66614}][2a]$, $[P_{66614}][2b]$ and $[P_{66614}][2c]$ in comparison to substances $[P_{66614}][1a]$, $[P_{66614}][1b]$ and $[P_{66614}][1c]$. This corresponds to the significantly lower relative volume fraction of $[P_{66614}]$ in these polyelectrolytes, which acts as a strong plasticizing agent (see table 4). The initial absorption rate as well as the rate of absorption in the second mode is also a function of
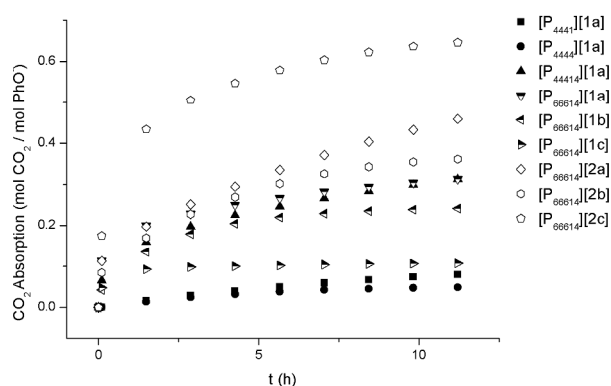

Figure 1: CO_2 absorption in terms of CO_2 molecules per phenolate group as a function of time.

the specific surface area of the samples, which was not a controlled quantity in this study.

The observed mass increase was in all cases quantitatively reversible at 60 °C under vacuum. This property can be advantageous in the use of such polyelectrolytes as CO_2 selective membrane materials, as CO_2 can be fully released under permeate side conditions, allowing for a large spatial CO_2 concentration gradient driving the CO_2 transport across the membrane. In order to elucidate the adsorption mechanism on the molecular level, gravimetric measurements were followed up by ^{13}C magic angle spinning nuclear magnetic resonance spectroscopy (^{13}C MASNMR) as well as by attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR).

^{13}C MAS NMR spectroscopy reveals the formation of a phenol-carbonate complex (δ = 162.00 ppm) upon exposure to CO_2, which is in accordance with literature results for the monomolecular system.[12] The obtained spectrum also indicates that gaseous or physically coordinated CO_2, which has a chemical shift at δ = 124.88 ppm[32], is practically absent from the polyelectrolyte sample. An additional shift at δ = 158.28 ppm is ascribed to tetraalkylphosphonium bicarbonate formation in the presence of residual moisture.[33]

The ATR-FTIR spectrum of [P$_{66614}$][1a] after exposure to CO_2 showed a pronounced COO-symmetric stretch at 1.360 cm^{-1} as well as a COO-asymmetric stretch at 1.620 cm^{-1} that can also be assigned to carbonate formation.
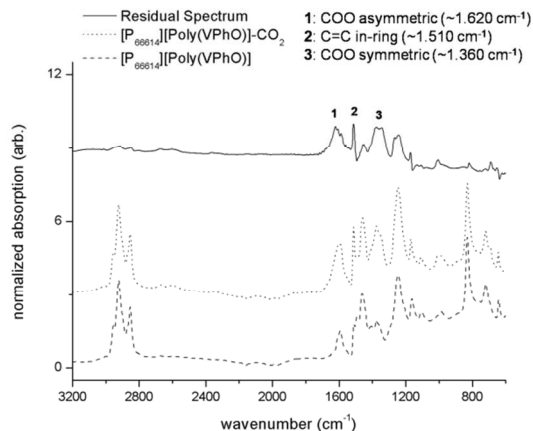

Figure 3: Change in the ATR-FTIR spectrum of [P$_{66614}$][Poly(4-vinylphenolate)] ([P$_{66614}$][1a]) upon exposure to CO_2. Observed stretch vibrations at 1.360 cm^{-1} (symmetric) and 1.620 cm^{-1} (asymmetric) are characteristic of a carbonate group.

The absence of gaseous or physically coordinated CO_2, which would exhibit a clear asymmetric stretch vibration in the spectral region between 2.400 and 2.200 cm^{-1}, affirms that a contribution of physisorption in the polymer matrix to the observed sample weight increase under CO_2 atmosphere is negligible. The formation of mobile bicarbonate anions may play a major effect on CO_2 permeability of polyelectrolyte thin films, as they could act as a mobile CO_2 carrier agent in a facilitated transport scheme.[34] A systematic study of this effect is subject to ongoing work.

Phenol Modification

The Dai group recently reported that CO_2 capacity of phenolic ILs can be tuned by substitution of electron-donating or -withdrawing groups at the phenyl ring, thereby controlling the Lewis-acidity of the phenolate moiety.[12] In an effort to further enhance CO_2 solubility, the concept was applied to the polymeric system. Surprisingly, the presence of electron-donating methoxy groups at the phenyl ring had an adverse effect on CO_2 uptake in the homopolymer (see table 2). This might be attributed to morphological changes of the polymer at room temperature that are caused by the modification. Differential scanning calorimetry (DSC) measurements show a pronounced crystalline phase transition upon heating of both [P$_{66614}$][1b] and [P$_{66614}$][1c] in comparison to [P$_{66614}$][1a], which is in support of this hypothesis, since crystalline domains are expected be less accessible to penetrant CO_2 molecules.
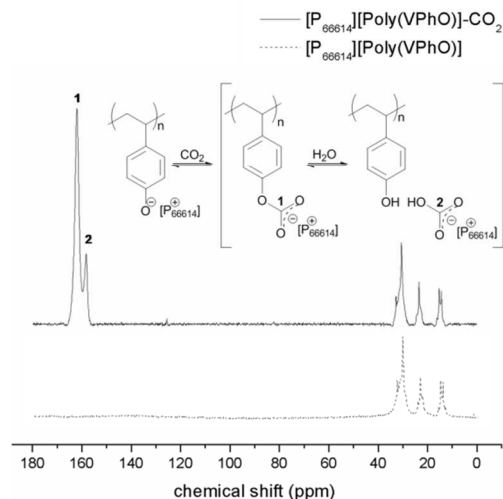

Figure 2: ^{13}C MAS NMR spectra of [P$_{66614}$][Poly(4-vinylphenolate)] ([P$_{66614}$][1a]) before (bottom) and after (top) exposure to ^{13}C-labelled CO_2. The chemical shift at δ = 162.00 ppm is ascribed to a phenol-carbonate complex. The chemical shift at δ = 158.28 ppm is ascribed to trihexyltetradecylphosphonium bicarbonate [P$_{66614}$][HCO$_3$].

Table 3: Density (ρ), free fractional volume (FFV) and CO_2 absorption capacity in unsubstituted (1a), methoxy-substituted (1b) and dimethoxy-substituted (1c) poly(4-vinylphenolate) at 25 °C and 1 bar CO_2 pressure

Sample	ρ	FFV	CO_2 absorption		
	[g / cm^3]		[wt %]	[mol %]	[V(STP)/V]
[P$_{66614}$][1a]	1.02±0.02	0.052	2.3	31.9	11.8
[P$_{66614}$][1b]	1.00±0.40	0.083	1.7	24.4	8.6
[P$_{66614}$][1c]	0.98±0.05	0.112	0.7	10.8	3.5

Morphology

Gas diffusivity in polymers is mainly a function of FFV, so a disruption of polymer chain packing can strongly enhance gas permeance, which is often desirable for membrane materials.[35,36] As a styrene derivative, poly(4-vinylphenol) can undergo π-π-stacking, and can also form intermolecular hydrogen bonds, thus minimizing FFV. Guided by these considerations, 4-vinylphenolic monomers were copolymerized with a bulky co-monomer, di(ethylene glycol) methyl ether methacrylate (DEGMEMA), in a molar ratio of 1:1 prior to treatment with [P$_{66614}$][OH]. This co-monomer was also chosen because ethylene glycols are known to interact favourably with CO_2 thanks to their polarity.[37] DSC results show the plasticizing effect of DEGMEMA on the resulting copolymers, as is reflected in lowered T$_g$ values. More importantly, DSCs demonstrate that the formation of a crystalline state of the resulting polyelectrolytes is suppressed by the introduction of DEGMEMA, since the melting transition observed in substances [P$_{66614}$][1a]-[P$_{66614}$][1c], is not observable in the copolymer-derived substances [P$_{66614}$][2a]-[P$_{66614}$][2c].

Table 4: Melting points (T_m) and glass transition temperatures (T_g) of substances $[P_{66614}][1a]$-$[P_{66614}][2c]$ and T_g of their corresponding source-polymers **1a-2c**.

Polyelectrolyte	T_m observable	T_g of corresponding Polymer [°C]	T_g[°C]
$[P_{66614}][1a]$	Yes	169.08	-21.03
$[P_{66614}][1b]$	Yes	97.41	-28.75
$[P_{66614}][1c]$	Yes	75.40	-57.88
$[P_{66614}][2a]$	No	57.7	-30.3
$[P_{66614}][2b]$	No	44.7	-30.8
$[P_{66614}][2c]$	No	46.07	-50.2

The mechanical stability of the resulting polyelectrolyte coatings has also enhanced through the copolymerization. Macroscopic cracks, which had occasionally been caused by non-uniform deformation of two composite membrane layers while handling, were no longer observed.

Table 5: Density (ρ), free fractional volume (FFV) and CO_2 absorption after 12 h in DEGMEMA-containing polyelectrolytes $[P_{66614}][2a]$, $[P_{66614}][2b]$ and $[P_{66614}][2c]$ and DEGMEMA homopolymer at 35 °C and 1 bar CO_2 pressure.

Sample	P [g / cm³]	FFV	CO_2 absorption [wt %]	[mol %]	[V(STP)/V]
$[P_{66614}][2a]$	0.97±0.01	0.138	2.6	47.5	12.7
$[P_{66614}][2b]$	0.99±0.02	0.128	2.0	36.5	10.0
$[P_{66614}][2c]$	1.00±0.05	0.126	3.4	65.2	17.2
Poly(DEGMEMA)	n.A.	n.A.	-	-	-

The DEGMEMA-containing polyelectrolytes $[P_{66614}][2a]$-$[P_{66614}][2c]$ exhibited comparable CO_2 solubility in terms of weight % as the non DEGMEMA containing species $[P_{66614}][1a]$-$[P_{66614}][1c]$. As the homopolymer poly(DEGMEMA) by itself showed no measurable CO_2 weight increase under equivalent CO_2 absorption conditions, absorption can still be exclusively attributed to the 4-vinylphenolate fraction of the copolymers. This implies that DEGMEMA aids CO_2 solubility solely through the afore-mentioned morphological effect.

Gas separation

Substances $[P_{66614}][1a]$-$[P_{66614}][2c]$ were processed into coatings of thicknesses between 4 µm and 9 µm atop of cross-linked polysiloxane supports *via* the solvent casting
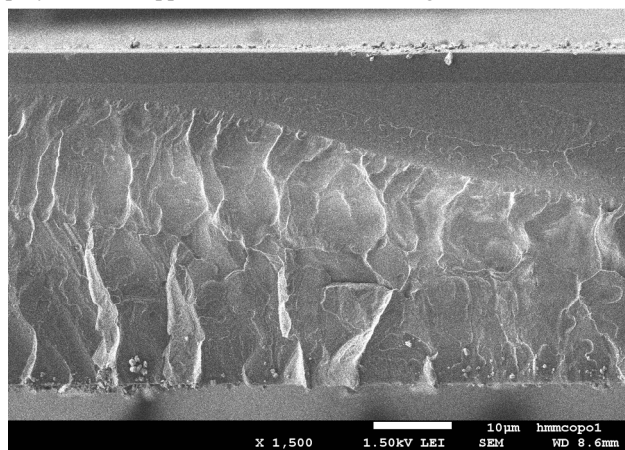

Figure 4: Exemplary SEM picture of the cross-section of a composite membrane of $[P_{66614}][2a]$ on a cross-linked polysiloxane-based membrane substrate as used for permeability measurements.

method. Polyphenols as well as poly(vinylphenols) and derivatives thereof are known to readily depose as coatings on a wide range of materials[38], which is reflected in their use as adhesives[39] and coating agents.[40,41] Consistently, the coatings of substances $[P_{66614}][1a]$-$[P_{66614}][2c]$ showed excellent adhesion to the substrate surface. The resulting composite membranes were tested for CO_2, CH_4 and N_2 gas transmission rates (GTR) in a commercial constant volume, variable pressure apparatus. The measured samples showed no decline of gas selectivity over multiple measurement runs and no hysteresis with regard to the previous measurement conditions. However, a potential increase in gas permeability and loss of permeability selectivity due to CO_2-induced plasticization, as has been reported for other polyelectrolyte-based membranes[51-53], still remains to be investigated under mixed-gas conditions.

Table 6: 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 and at 25 °C.

Polyelectrolyte	GTR [Ld⁻¹ m² 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

The GTR values of the membranes that were prepared from DEGMEMA-containing $[P_{66614}][2a]$, $[P_{66614}][2b]$ and $[P_{66614}][2c]$ substances are lower than the GTR values of the DEGMEMA-free membranes. Presumably, this corresponds to the less viscous character of these substances, owing to a lower relative volume-fraction of $[P_{66614}]$. Large discrepancies in GTR are caused in part by the varying thickness of the polyelectrolyte coating layer. Ideal permeability selectivity values are less affected by varying coating layer thickness and are therefore better suited for comparison of membrane performance. Figure 5 shows CO_2 permeability values as well as selectivities measured at 15 °C in
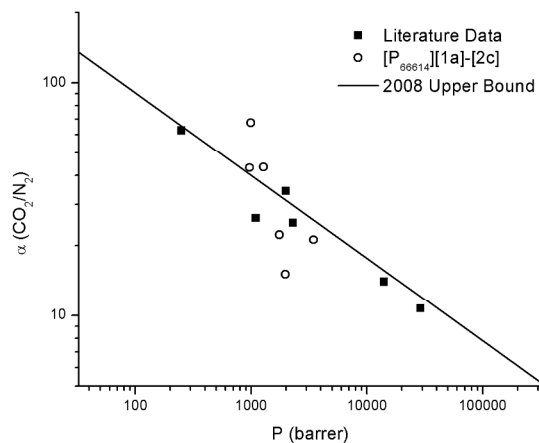

Figure 5: Empirical „Robeson upper bound"[42] with data points from literature[43-46] and from this study. Selective layer material in this order from left to right: $[P_{66614}][2c]$, $[P_{66614}][2b]$, $[P_{66614}][2a]$, $[P_{66614}][1c]$, $[P_{66614}][1b]$, $[P_{66614}][1a]$.

comparison to the 2008 Robeson upper bound[42] for the CO_2/N_2 gas pair.

DEGMEMA-containing membranes prepared from $[P_{66614}][2a]$-$[P_{66614}][2c]$ showed higher permeability selectivity values for CO_2 than membranes prepared from substances $[P_{66614}][1a]$-$[P_{66614}][1c]$. This is in agreement with their enhanced CO_2 loading capacity as observed in gravimetric measurements.

The increase of permeability selectivity, especially in the DEGMEMA-containing membranes, upon reduction of the operating temperature from 25 °C to 15 °C suggests a regime change for gas transport in this temperature range. In part, this can be ascribed to the fact that both diffusivity and solubility of the two gas species depend on temperature to a differing extent, favouring CO_2 transport over N_2 transport at lower temperatures.[47] This effect has already been exploited for polyimide-based membranes operating at low temperatures.[48] As an exotropic and exothermic process, the formation of the phenol-carbonate complex in the membrane samples is favoured at lower temperatures, allowing for a much greater relative CO_2/N_2-loading of the membrane. However, the magnitude of the temperature effect for the reported system was unexpected.

Experimental

Materials and Methods

Unless otherwise stated, chemicals were purchased in the highest available purity grade from Sigma-Aldrich and used as received. Tributyltetradecylphosphonium chloride ($[P_{44414}][Cl]$) was donated by Cytec and used as received. Anion-exchange resin Amberlyst® A26 (OH) was purchased from Sigma-Aldrich. Cross-linked polysiloxane-based membrane supports (thickness of 50 ± 5 μm) were donated by Wacker Chemie AG, Munich. Methanol was technical grade and rota-distilled prior to use. Isopropanol and benzene were degassed prior to use. All polyelectrolytes were dried under high vacuum at 60 °C for a minimum of 24 h after synthesis to remove any volatiles.

^1H and ^{31}P NMR spectra were recorded on a Bruker ARX-500 or a Bruker AVIII-300 spectrometer in methanol-d4 using tetramethylsilane and 85 wt% phosphoric acid as standard, respectively. ^{13}C MAS NMR spectra were recorded on a Bruker ARX-125 spectrometer with a scan number of at least 20.000. Decomposition temperatures were measured on a TA-Instruments TGA-Q5000 apparatus under nitrogen atmosphere. Glass transition temperatures and crystalline phase transitions were measured on a TA-Instruments DSC Q2000 using a heating rate of 10 K/min in a temperature range from at most -150 to at least 150 °C.

Density was estimated using a solvent flotation method. Dense pellets from 100 mg of sample substance were prepared in an ATR-IR press and immersed in a DMSO bath. After the pellet emerged and floated atop of the bath, toluene was gradually added and the mixture was carefully stirred. When the pellet immersed again and remained suspended in the solvent mixture, the density was estimated as the equivalent of the density of the solvent mixture. FFV was calculated according to a literature procedure.[49,50]

Gravimetric CO_2 sorption measurements were performed on a Setaram® Labsys evo TG/DSC-apparatus in flow mode. In a general gravimetric CO_2 sorption experiment, a known amount of sample was filled into an aluminium crucible and placed into the apparatus. The apparatus was then kept under high vacuum for 2 h at 120 °C for evacuation of the sample. Towards the end of the evacuation phase, the sample was allowed to cool off to 35 °C again. To start the adsorption phase, the apparatus was purged for five minutes under CO_2 flow of 200 ml/min and afterwards kept under a steady CO_2 flow of 16 ml/min for 12 h at 35 °C at atmospheric pressure. The sample weight was recorded once per second over the course of the entire experiment. Buoyancy effects on the weight signal were corrected for *via* subtraction of a blank measurement signal.

Composite membranes were prepared by casting a degassed 10 wt % solution of polymer in methanol on top of a cross-linked polysiloxane-based substrate with a 25 μm coating knife. The solvent was allowed to evaporate in a fume hood at room temperature for 24 h. Composite membrane samples were sandwiched between two glue-coated aluminium foils with a circular notch of an area of 0.785 cm^2. CO_2 and N_2 gas transmission rates of the samples were measured on a Brugger GDP-C in constant volume, variable pressure mode at Wacker AG, Munich, Germany. Measurements were repeated at least once for each sample. The coating layer thickness was determined with a Mitutoyo MDC-25 PJ micrometer. Homogeneity and intactness of the coatings was spot-checked on a JEOL-JSM 7500F scanning electron microscope.

^{13}C MAS NMR spectra were recorded before and after overnight exposure of $[P_{66614}][1a]$ to ^{13}C-labeled CO_2 at 1 bar and room temperature.

FTIR-vibration spectroscopic CO_2 sorption measurements were performed on a Bruker Vertex 70 equipped with a Platinum ATR stage. About 50 mg of polyelectrolyte was placed in a Harrick Praying Mantis DRIFT-cell and evacuated for 2 h at 120 °C under high vacuum. Afterwards the sample was allowed to cool back down to 35 °C. A sample was taken out and instantly placed on the ATR stage for recording of a spectrum. For the post-CO_2 adsorption spectrum, the DRIFT-cell was kept under 1 bar CO_2 pressure overnight. Again, a sample was taken out and immediately placed on the ATR stage for recording of a spectrum. ATR-IR Spectra were treated by blank signal subtraction and standard normal variate transformation for comparability.

Preparation of monomers, polymers and copolymers

4-Vinylphenol and 2,6-Dimethoxy-4-vinylphenol were prepared according to a literature procedure[25] from the corresponding benzaldehyde compounds. In a typical procedure, 5.68 g syringealdehyde (32.8 mmol), 13.66 g of malonic acid (132.1 mmol) and 11.16 g piperidine (132.1 mmol) were placed in a 100 ml round-bottom flask. The mixture was refluxed for 8 minutes under microwave radiation (200 W). After cooling down, the mixture was poured in ice water and extracted with ethyl acetate (3 x 40 ml), washed with saturated sodium chloride solution and then dried over sodium sulfate. The solvent was removed *in vacuo* and the residue was purified using a flash chromatograph (2:1 hexane to ethyl acetate), yielding 2.92 g (16.2 mmol, 49%) of a dark-red viscous oil. Homo- and copolymerization reactions

were free-radical polymerizationsin degassed isopropanol or benzene using AIBN as initiator.

Preparation of polyelectrolytes

Tetraalkylphosphonium hydroxide solutions were prepared using an OH-anion exchange resin and added to a stoichiometric amount of polymer (in terms of phenol groups contained), analogously to a literature procedure.[21] In a general procedure, a known amount of $[P_{66614}][Cl]$ was dissolved in methanol and passed through a column packed with at least three equivalents of freshly regenerated anion exchange resin, in terms of the number of OH-exchange groups. Residual halide content in phosphonium hydroxide solutions was excluded *via* a qualitative silver nitrate test prior to use. In the case of $[P_{4441}][CO_3CH_3]$, this OH-exchange step was omitted. 1 equivalent of poly(4-vinylphenol), in terms of the number of phenol groups, was added. Solution was stirred for 24 h at room temperature. Solvent and volatiles were removed *in vacuo* and the product was dried for at least 24 hours under high vacuum at 60 °C, yielding an off-white to brownish solid. Complete deprotonation of phenol groups upon treatment with tetraalkylphosphonium hydroxide solution was confirmed with ATR-IR spectroscopy through the absence of O-H stretch vibrations.

Conclusions

New polyelectrolyte materials containing poly(4-vinylphenolate) were synthesized using a straightforward and quantitative anion exchange method. The obtained polymeric materials show remarkable and reversible CO_2 solubility and can be processed into defect-free and stable supported thin films, which is advantageous for application as CO_2-selective composite membrane materials. ATR-IR and ^{13}C MAS NMR spectroscopy show that the phenolate groups react reversibly with CO_2 to form a phenol-carbonate complex. The extent of the complexation reaction with CO_2 is further increased through the substitution of electron-donating methoxy-groups at the phenol ring. Copolymerization with DEGMEMA is effective in stabilizing the amorphous state of the resulting polyelectrolyte and in improving thin film formation properties. Polysiloxane-based flat sheet membrane substrates coated with thin films of the poly(4-vinylphenolate)-based materials exhibit competitive CO_2 gas transmission rates and permeability selectivity over N_2. In combination, both the effects of copolymerization and of structural modification on gas permeability suggest that membrane materials based on poly(4-vinylphenolate) can be tailored to different sets of operating conditions and application requirements. The effects of bicarbonate formation in the presence of moisture and CO_2-induced plasticization on the performance of the membrane as well as on its long-term stability are subject to ongoing work.

Notes and references

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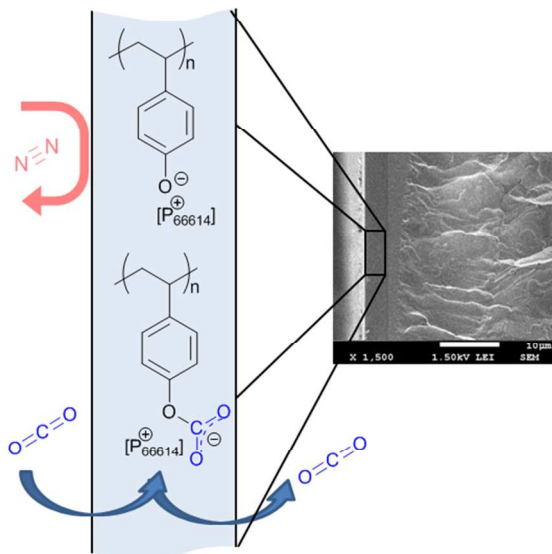
Reactive Transport Enhancement of CO2 in Poly(4-vinylphenolate)s