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Polymeric membranes composed of polystyrenes tethering amino acids for preferential CO_2 separation over H_2

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Abstract Various *N-tert*-butoxycarbonyl (*N*-Boc) amino acids, such as glycine, valine, and serine, were combined to 4-chloromethylstyrene. The resulted monomers were readily polymerized to give polystyrenes tethering an amino acid by a conventional free radical polymerization technique. After deprotection of the *N*-Boc group with trifluoroacetic acid, the obtained polystyrene derivatives were soluble in ethanol and spin-coated on a commercial poly(ether sulfone) porous membrane to fabricate a composite membrane for CO_2 separation over H_2. The CO_2 selective layer of synthesized PSt was ca. 200 nm thick, and the composite membranes showed preferential CO_2 separation over H_2, while parent polystyrene passed through H_2 rather than CO_2. Especially, the separation factor α_{CO_2/H_2} was raised after alkaline treatment to form free primary amine on the terminus of graft chain. Serine tethered polystyrene showed the highest α_{CO_2/H_2} (16) among them, which suggested the hydroxyl group would enhance the CO_2 affinity of primary amine.

Keywords Polymeric membrane · CO_2 · Gas separation · Amino acid · Polystyrene

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Introduction

With the increasing awareness of greenhouse gas effect upon global warming, urgent actions have been required to prevent the climate system from potential damage, and various approaches have been taken toward mitigation of greenhouse gas emissions, particularly CO_2 [1, 2]. CO_2 capture and storage (CCS) is thus of great importance to mitigate CO_2 emissions [3]. Since, CO_2 capturing or separation has dominated the major part of the cost [4], development of an effective CO_2 separation is of now a key in the CCS. Among various separation techniques, membrane separation with polymeric materials would be one of the promising approaches in terms of less energy consumption, technological and economic perspectives [5]. A number of investigations have been studied to separate CO_2 from other organic and inorganic gases, which were mostly larger than CO_2 [6–8]. For instance, the kinetic or sieving diameter of CO_2 was 3.3 Å, while those of N_2, O_2, or CH_4 were 3.6, 3.5, or 3.8 Å, respectively. The CO_2 separations were usually proceeded by a molecular sieving mechanism. However, CO_2 separation over a light gas, in this instance H_2, has been dedicated in this research group [9]. In a coal-fired plant, H_2 was evolved with CO_2 (ca. 40%) after the water–gas shift reaction and introduced to a steam turbine to generate electricity. Most of polymeric membrane allowed H_2 to permeate across the membrane readily rather than CO_2 [6–8]. A chemical manipulation was thus required for the preferential CO_2 separation over H_2 without reduction of H_2 partial pressure.

In this article, various amino acids were tethered to polystyrene to present primary amine, a CO_2-specific functional group, on the graft chain end. The CO_2 separation properties of the resulting polymers were investigated.

Experimental

Materials

N-Boc amino acids, *N*-*tert*-butoxycarbonyl glycine (*N*-Boc-Gly), *N*-*tert*-butoxycarbonyl-L-valine (*N*-Boc-Val), and *N*-*tert*-butoxycarbonyl-*O*-*tert*-butyl-L-serine (*N*-Boc-Ser) were purchased from Watanabe Chemical Industries (Hiroshima, Japan). 4-Chloromethylstyrene was from Tokyo Chemical Industries (Tokyo, Japan). 2,2′-Azobisisobutyronitrile (AIBN) from Wako (Tokyo, Japan) was purified by recrystallization from methanol prior to use. Trifluoroacetic acid (TFA), triisopropylsilane (TIPS), and triethylamine (TEA) were obtained from Sigama-Aldrich (MO, USA). Poly(ether sulfone) (PES) porous membrane with 5,000 in molecular weight cut-off was obtained from Millipore (MA, USA). A basic alumina was purchased from MP Biomedicals (Eschwege, Germany). Other organic and inorganic chemicals were regent grade and used without further purification. Cross-linked polydimethylsiloxane (PDMS) substrate membrane was prepared by a Sylgard 184 kit (Dow Corning Silicones, MI, USA).

Synthesis of *N*-Boc-amino acid grafted styrene

As a typical example of amino acid bearing polystyrene (PSt), synthesis of glycine grafted PSt (Gly-PSt) was described. A 57.0 mmol of *N*-Boc-Gly was dissolved in

20 mL of dimethylformamide. The solution was cooled on a crushed ice bath, and 51.8 mmol of 4-chloromethyl styrene, and 57.0 mmol of TEA were added. The reaction was kept under stirring for 3 days at ambient temperature. The reaction mixture was then diluted with ethyl acetate and rinsed with saturated $NaHCO_3$ aq. thrice, saturated NaCl aq. twice, and distilled water twice, sequentially. The organic phase containing *N*-Boc-Gly grafted styrene was collected and dried over $MgSO_4$. The product was obtained after evaporation of the solvent with 99% in yield. *N*-Boc-Val and *N*-Boc-Ser grafted styrenes were prepared by the same method with the same stoichiometry as described above. The yields of *N*-Boc-Val and *N*-Boc-Ser styrene were 99 and 76%, respectively.

N-Boc-Gly grafted styrene; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.38 (d, 2H, Ar), 7.30 (d, 2H, Ar), 6.71 (q, H, C*H*=), 5.76 (d, H, CH_2=), 5.27 (d, H, CH_2=), 5.16 (s, 2H, CH_2O), 3.95 (s, 2H, CH_2N), 1.45 (s, 9H, CH_3).

N-Boc-Val grafted styrene; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.39 (d, 2H, Ar), 7.30 (d, 2H, Ar), 6.71 (q, H, C*H*=), 5.75 (d, H, CH_2=), 5.26 (d, H, CH_2=), 5.11 (s, 2H, CH_2O), 4.27 (m, H, C*H*N), 2.14 (m, H, CH_3CH), 1.44 (s, 9H, CH_3), 0.93-0.84 (2d, 6H, CH_3).

N-Boc-Ser grafted styrene; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.38 (d, 2H, Ar), 7.30 (d, 2H, Ar), 6.71 (q, H, C*H*=), 5.75 (d, H, CH_2=), 5.25 (d, H, CH_2=), 5.12 (s, 2H, CH_2OCO), 4.43 (m, H, C*H*N), 3.56, 3.81 (d, 2H, CH_2OCCH_3), 1.44 (s, 9H, $COOC(CH_3)_3$), 1.09 (s, 9H, $CH_2OC(CH_3)_3$).

Polymerization of *N*-Boc-amino acid grafted PSt

N-Boc-amino acid grafted styrene was polymerized by free radical polymerization with AIBN. The styrene derivatives synthesized containing a radical inhibitor, hydroquinone monomethyl ether, was dissolved in toluene by 1 g/mL. The resulting solution was passed through a basic alumina column to get rid of the inhibitor right before the polymerization. To the resulting solution was added AIBN with 100/1 in monomer to initiator ratio, and the reaction mixture was subjected to Ar bubbling to remove molecular oxygen in the reaction mixture. The polymerization was carried out at 75 °C under stirring for 16 h. The polymer was collected by reprecipitation in hexane. The molecular weight was determined by gel permeation chromatography. The results as well as the yield of the PSt derivatives were summarized in Table 1. As a control experiment, 4-chloromethyl styrene was polymerized and purified by the same procedures.

N-Boc-Gly grafted PSt; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.2–6.8 (2H, Ar), 6.8–6.3 (2H, Ar), 5.3–5.0 (2H, CH_2O), 4.1–3.8 (2H, CH_2N), 1.4 (9H, CH_3), 1.5–1.1 (3H, CH_2CH).

N-Boc-Val grafted PSt; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.2–6.7 (2H, Ar), 6.6–6.1 (2H, Ar), 5.4–5.1 (2H, CH_2O), 4.4–4.2 (H, CHN), 2.2–2.0 (H, CH_3CH), 1.4 (9H, $C(CH_3)_3$), 1.5–1.1 (3H, CH_2CH), 0.9–0.8 (6H, $C(CH_3)_2$).

N-Boc-Ser grafted PSt; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.3–6.8 (2H, Ar), 6.8–6.2 (2H, Ar), 5.4–5.1 (2H, CH_2O), 4.5–4.4 (H, CHN), 3.9–3.7, 3.6–3.5 (2H, $CH_2OC(CH_3)$), 1.4 (9H, $COOC(CH_3)_3$), 1.1 (9H, $CH_2OC(CH_3)_3$).

Poly(4-chloromethyl styrene); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.2–6.9 (2H, Ar), 6.6–6.2 (2H, Ar), 4.6–4.4 (2H, CH_2O), 2.2–1.2 (3H, CH_2CH).

Table 1 Molecular weights and yields of various PSt derivatives obtained by free radical polymerization

PSt	M_w (kDa)[a]	M_w/M_n^a	Yield (%)
N-Boc-Gly PSt	98.8	1.5	79
N-Boc-Val PSt	17.1	1.4	75
N-Boc-Ser PSt	111	2.3	53
Parent PSt	24.2	2.0	82

[a] Determined by GPC

Deprotection of *N*-Boc group

The *N*-Boc protecting group was removed with TFA. For instance, *N*-Boc-Gly PSt was dissolved in TFA/TIPS/H_2O mixture (95/2.5/2.5 by vol) by 1 g/mL on a crushed ice bath to allow evolution of CO_2. After stirring for an hour, the reaction mixture was poured into diethylehter to precipitate the deprotected PSt derivatives. The deprotection reaction was confirmed by ^1H NMR. The signal of methyl proton of *tert*-butyl group disappeared after TFA treatment, which indicated the progress of deprotection. The yield was quantitative in every case.

Gly grafted PSt; ^1H NMR (600 MHz, methanol-*d4*) δ (ppm): 7.2–6.8 (2H, Ar), 6.8–6.3 (2H, Ar), 5.3–5.1 (2H, CH_2O), 4.1–3.8 (2H, CH_2N), 1.5–1.1 (3H, CH_2CH).

Val grafted PSt; ^1H NMR (600 MHz, methanol-*d4*) δ (ppm): 7.2–6.7 (2H, Ar), 6.6–6.1 (2H, Ar), 5.3–5.0 (2H, CH_2O), 4.2 (H, CHN), 2.3–2.2 (H, CH_3CH), 1.5–1.1 (3H, CH_2CH), 0.9–0.8 (6H, $C(CH_3)_2$).

Ser grafted PSt; ^1H NMR (600 MHz, dimethylsulfoxide-*d6*) δ (ppm): 7.3–6.8 (2H, Ar), 6.8–6.2 (2H, Ar), 5.3–5.0 (2H, CH_2O), 4.4–4.3 (H, CHN), 3.8–3.4 (2H, CH_2OH), 2.0–1.4 (3H, CH_2CH).

Preparation of composite membranes

The PSt derivative was first dissolved in ethanol (50 mg/mL), and the solution was filtered with a membrane filter (nominal pore size: 0.45 μm) to remove dust particles. A CO_2 selective layer of the amino acid-tethered polymers was prepared on a commercial PES porous membrane by spin-coating (1,000 rpm for 1 min, twice) of the resulting solution on an Aiden SC8000 spin-coater (Hyogo, Japan). The composite membrane obtained was dried in a vacuum oven at least 16 h. Desalination of TFA salt was carried out to immerse the composite membranes in aqueous NaOH (pH 12) for 2 h. After soaking in water for 3 h, the membranes were dried. The parent PSt, poly(4-chloromethylstyrene) (PClmSt) was not soluble in ethanol, and a control composite membrane was not available by the same method. PClmSt was thus dissolved in chloroform and placed on a PDMS substrate membrane by the spin-coating as described above.

General procedure

Chemical structures of synthesized compounds were determined by 600 MHz ^1H NMR on a JEOL JNM-ECP-600 spectrometer. The samples were dissolved in an appropriate deuterated solvent with 10 mg/mL. To determine the molecular weight of PSt derivatives, size exclusion chromatography was performed on a Shodex GPC

System 21 (Shodex, Tokyo, Japan) equipped with a Shodex RI-71S refractive index detector. KF-800RL and -804L columns (Shodex) were used in series with THF as an eluent at a flow rate of 1.0 mL/min and a temperature of 40 °C. The molecular weight was calibrated to polystyrene standards (SM-105, Shodex). X-ray photoelectron spectroscopy (Kratos 3200 electron spectrometer, Shimadzu, Kyoto, Japan) was performed to measure surface atomic composition. XPS is configured with a MgKα (1253.5 eV) 240 W X-ray source with an ultrahigh vacuum ($<10^{-6}$ Torr). The take-off angle was fixed at 45°, and all spectra were calibrated using the hydrocarbon C_{1s} peak at 284.5 eV. Scanning electron microscopic (SEM) images of the membrane were taken on a Hitachi S-4800 scanning electron microscope (Hitachi, Tokyo, Japan). The SEM samples were freeze-fractured in liquid nitrogen and coated with Pt–Pd.

Gas separation properties

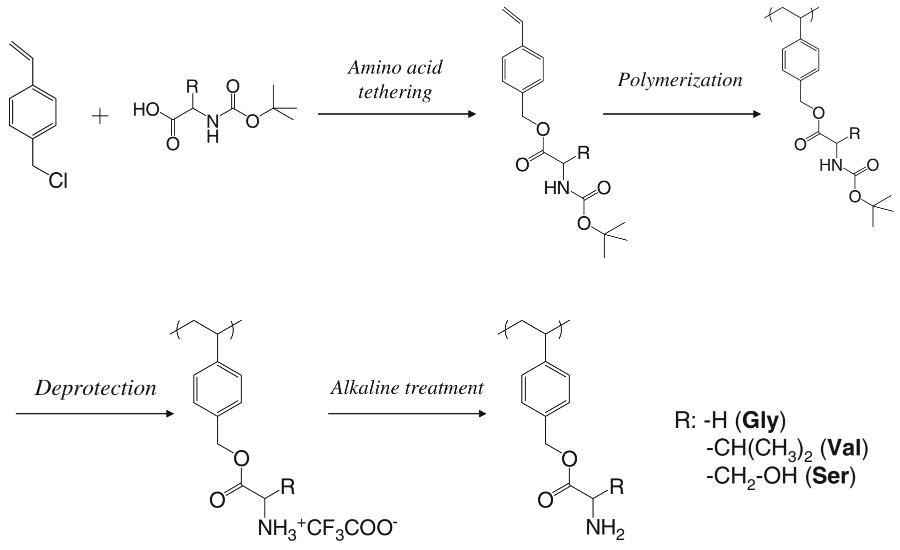
Permeation properties of the composite membranes were measured with a flat-type permeation cell at 25 °C under atmospheric pressure. The surface area of the membrane was 0.865 cm^2. A CO_2/H_2 gas mixture (CO_2 5%) was humidified (80 % relative humidity) at 25 °C prior to introducing the membrane and fed at a flow rate of 100 mL/min. Helium was supplied to the permeate side of the cell as a sweep gas at a flow rate of 10 mL/min. The gas composition of permeate and non-permeate was analyzed on a GC323 gas chromatograph with a pulsed discharge detector and a thermal conductivity detector, respectively (GL Science, Tokyo, Japan). Each measurement was conducted after at least 6 h of equilibration. Permeance Q and separation factor α_{CO_2/H_2} were determined by the following equations with Q_i permeance of i, N_i feed gas volume of i, A membrane area, Δp pressure difference of feed and permeate gas, t transmission time, x_i and y_i density of i in feed and penetrate gas.

$$Q_i = \frac{N_i}{A \cdot \Delta p \cdot t} \tag{1}$$

$$\alpha_{CO_2/H_2} = \frac{y_{CO_2}/y_{H_2}}{x_{CO_2}/x_{H_2}}. \tag{2}$$

Results and discussion

Various *N*-Boc protected amino acids were grafted to styrene to immobilize a CO_2 specific functional group, primary amine, on a polymer backbone with high density. PSt would be suitable in this study for the following reasons. Styrene derivatives were readily polymerized to give high molecular weight polymers by conventional free radical polymerization with AIBN as shown in Scheme 1. Each reaction was followed by ^{1}H NMR as represented in Fig. 1. The PSts obtained had an atactic configuration, and the resulting amorphous nature based on the configuration would provide higher free volume, where gas molecules permeated, in comparison to



Scheme 1 Synthetic route of amino acid grafted PSt

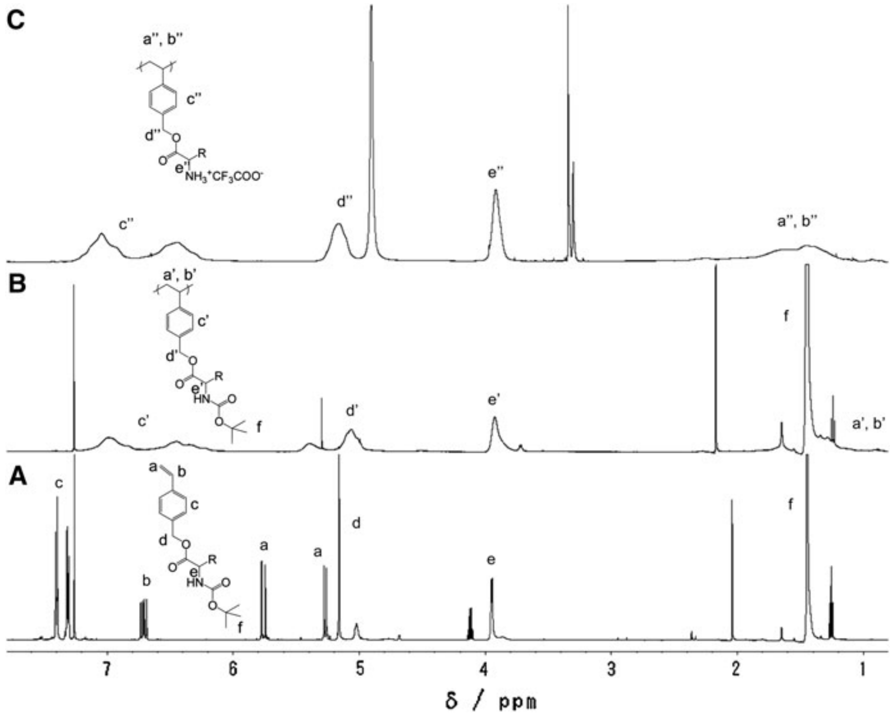


Fig. 1 ^{1}H NMR spectra of (*A*) *N*-Boc-Gly St in $CDCl_3$, (*B*) *N*-Boc-Gly PSt in $CDCl_3$, and (*C*) Gly-PSt with TFA salt in methanol-*d4*

crystalline isotactic or syndiotactic PSts. In addition, PSt exhibited excellent physicochemical and thermo resistant properties.

Various polymeric membranes for preferential CO_2 separation have been studied and developed in this research group [9–13]. It has been revealed that the chemical structure nearby amino group, as well as the amine density, showed strong relation to the CO_2 separation properties [14]. Various amino acids were commercially available and thus chosen to be tethered so as to tune the chemical environment in the vicinity of primary amine. Valine had a bulky isopropyl group on the chiral carbon, and the steric effect would be examined in comparison to glycine, while serine did another functional group, a hydroxyl group, in the β-position of amine.

The Merrifield peptide synthetic method has been well known and spread to extend amino acid sequence on a cross-linked PCmSt resin [15], and the first step reaction was to immobilize an *N*-Boc amino acid to the Merrifield resin upon ester formation between carboxylic group and chloromethyl group with elimination of hydrochloride. In this article, the procedure was traced to tether amino acids to 4-chloromethylstyrene. The yield was high and almost quantitative in the case of *N*-Boc-Gly and *N*-Boc-Val St while that of *N*-Boc-Ser St was 76 %. The obtained monomer was then polymerized with AIBN by free radical polymerization. The molecular weight and yield of the resulting PSt derivatives were summarized in Table 1. Those values were different and not consistent in the PSt derivatives, but high molecular weight polymers, enough to form a self-standing membrane, were obtained. The *N*-Boc group was then removed by TFA treatment, and the deprotection took place quantitatively. The amino group on the graft chain terminus after the deprotection formed quaternary salt with TFA, which resulted in reducing the affinity to CO_2. However, once the proton on the primary amine was taken away, the PSt derivatives became hydrophobic and insoluble in common organic or inorganic solvents. The amphiphilic nature prevented the PSt derivatives from purification by the commonly used techniques. For example, when *N*-Boc amino acid-PSt in ethanol/water was applied onto a QAE Sephadex A-25 anion exchange column (GE Healthcare, Uppsala, Sweden), the polymers could not be eluted out due to adsorption onto the resin. Deprotection was thus conducted after fabricating a composite membrane because of the insolubility of desalted polymers.

One of the major drawbacks of dense polymeric membranes was low gas permeability. With a facilitated transportation membrane, the gas selectivity and permeability showed a trade-off relation, and thus high-density inoculation of primary amine onto a polymer backbone was required to prepare a thinner polymeric membrane expressing high gas selectivity. In this research, a composite membrane was first prepared by spin-coating of the polymer solution onto a PES porous membrane. The composite membrane was then subjected to alkaline treatment to remove TFA. Due to the difficulty to determine the desalination, XPS was conducted to study the atomic composition at membrane surface before and after the alkaline treatment. A survey scan (Fig. 2) clearly demonstrated the absence of F_{1s} peak at 690 eV after the alkaline treatment whereas the other peaks remained. The atomic compositions were obtained by high resolution scan (Table 2). The weight fraction of fluorine became close to 0 after the alkaline treatment, which suggested desalination of TFA salt at the surface of composite membrane. On the

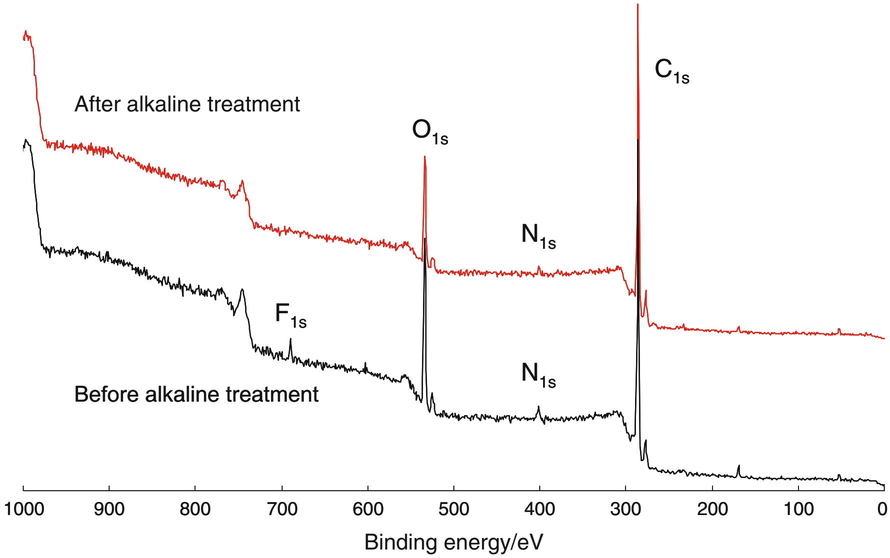


Fig. 2 XPS spectra of Gly-PSt composite membrane before (*bottom*) and after (*top*) alkaline treatment

Table 2 Surface atomic compositions of PSt derivative composite membranes before and after alkaline treatment determined by XPS

PSt	Alkaline treat.	C (wt%)	O (wt%)	N (wt%)	F (wt%)
Gly-PSt	Before	78.1 (69.2)	18.8 (15.4)	1.8 (3.8)	1.3 (11.5)
	After	77.8 (84.2)	20.0 (10.5)	1.9 (5.3)	0.0 (0.0)
Val-PSt	Before	76.1 (65.2)	20.2 (17.4)	1.9 (4.3)	1.8 (13.0)
	After	75.4 (81.3)	22.4 (12.5)	1.8 (6.3)	0.3 (0.0)
Ser-PSt	Before	77.3 (64.0)	20.8 (20.0)	1.8 (4.0)	0.1 (12.0)
	After	79.4 (77.8)	17.3 (16.7)	3.3 (5.6)	0.0 (0.0)

Theoretical values were in the parenthesis

other hand, with nitrogen, the observed weight fractions were smaller than the theoretical ones. The amino acid moieties covalently attached via ester linkage might be cleaved to some extent during deprotection in TFA. Or, under ultrahigh vacuum condition, the hydrophilic functional groups might rearrange themselves toward bulk and repel the hydrophobic polymer backbone to the surface upon surface segregation.

The carbon dioxide selective layer formed was observed by SEM (Fig. 3), and the thickness was ca. 200 nm in every case. The cross-section image indicated the PSt derivative was coated uniformly and homogeneously on a PES substrate and the absence of cracks or pinholes in the selective layer. The substantial degradation of the PSt layer was not found after the alkaline treatment. Immersion of the PSt derivatives was found in the very surface of porous substrate membrane.

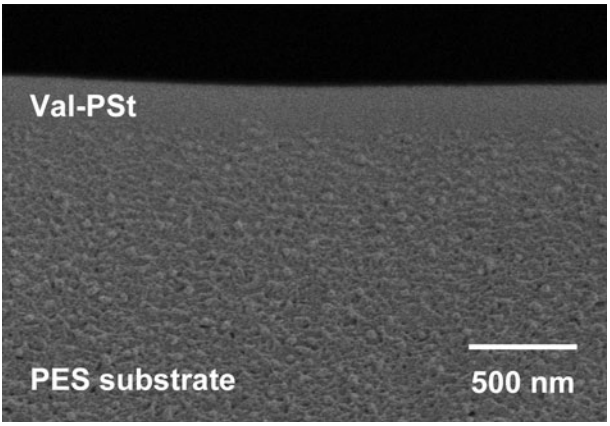


Fig. 3 SEM image of a cross-section of Val-PSt composite membrane after alkaline treatment

Table 3 CO_2 separation properties of PSt derivative composite membranes before and after alkaline treatment

PSt	10^{10} Q_{CO_2} ($m^3/(m^2$ s Pa))	10^{11} Q_{H_2} ($m^3/(m^2$ s Pa))	α_{CO_2/H_2}
Gly-PSt	4.7 (1.8)	3.7 (4.3)	11.5 (4.2)
Val-PSt	5.7 (1.8)	3.4 (4.2)	15.1 (4.2)
Ser-PSt	6.2 (4.1)	3.4 (3.8)	16.2 (10.2)
Parent PSt	– (1.1)	– (24)	– (0.5)

Values before alkaline treatment were in the parenthesis

The composite membranes were placed into a gas separation cell, and CO_2 separation properties over H_2 were investigated before and after desalination. The results were summarized in Table 3.

The permeance of CO_2 of amino acid graft PSt before alkaline treatment was larger than that of H_2, resulting in high α_{CO_2/H_2} value greater than 1. In contrast, PClmSt composite membrane showed lower separation factor (α_{CO_2/H_2} 0.5). The PDMS substrate itself showed 4 in α_{CO_2/H_2}, while PES less than 1. The preferential CO_2 permeation suggested even quaternary amine of amino acid on the graft chain showed specific affinity to CO_2. The separation factor further increased after alkaline treatment due to the increment in Q_{CO_2} whereas Q_{H_2} did not change much as shown in Table 3. Among three amino acid grafted PSts, both Val- and Ser-PSt gave a higher separation factor than Gly-PSt. Valine moiety has an isopropyl group on chiral carbon, and the steric hindrance was first assumed to reduce the affinity of amino group toward CO_2. However, the bulky side chain would rather contribute to give rise to the electron density of primary amine as an electron donating group, and the amine would present higher affinity to CO_2. The bulky isopropyl group would also contribute the higher CO_2 permeability. On the other hand, serine moiety had a hydroxyl group in the β-position of primary amine. The gas separation was conducted in humidified condition, and the amphiphilic PSt absorbed water, where CO_2 would become carbamate ion upon dissolution in the membrane. When the carbon of the resulting carbamate ion interacted with the nitrogen of primary amine,

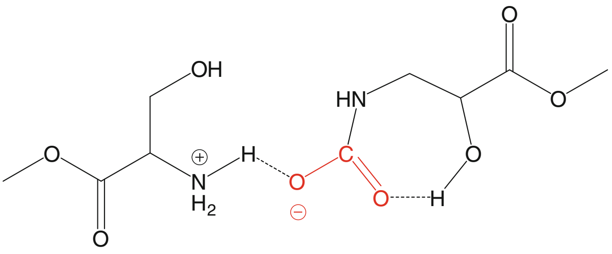


Fig. 4 Formation of a 7-membered ring on the interaction between carbamate and 2 serine moieties

the hydrogen of hydroxyl group would also interact to the oxygen of carbamate ion with the formation of a 7-membered ring (Fig. 4). In the previous research, the similar result was found with a hydroxyl substituted poly(amidoamine) dendrimer. When the hydroxyl group was attached in the β-position of primary amine, the modified dendrimer presented higher α_{CO_2/H_2} than the parent compound [14].

This ring formation could stabilize the intermediate, and as a result, serine moiety was supposed to exhibit higher separation factor in comparison to glycine.

Conclusions

Amino acid bearing PSts were successfully synthesized. A composite membrane was fabricated for CO_2 separation over H_2 by spin-coating of the PSt derivatives as a CO_2 selective layer onto a porous PES substrate. Preferential CO_2 separation properties of the resulting composite membrane were found due to the specific interaction between CO_2 and amino group of amino acid side chain. The affinity was strongly influenced not only by amino group but also by other functional groups in the vicinity. Further improvement of the separation factor and permeability of CO_2 has been required for the actual use, however, amino acid bearing PSt would be one of the promising templates in molecular design for novel CO_2 separation materials.

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