Synthesis of soluble oligosiloxane-end-capped hyperbranched polyazomethine and their application to CO\(_2\)/N\(_2\) separation membranes

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ABSTRACT

Three soluble hyperbranched polyazomethines containing oligosiloxane end group HBP-PAZ-SiO\(_n\) were successfully synthesized. HBP-PAZ-SiO\(_n\)s were used as modifiers of ethyl cellulose (EC) and polysulfone (PS) membranes. Blend membranes, HBP-PAZ-SiO\(_n\)/EC and HBP-PAZ-SiO\(_n\)/PS were prepared by blending the THF solution of HBP-PAZ-SiO\(_n\) with ethanol solution of EC and dichloromethane solution of PS, respectively. Surprisingly, the permeabilities for CO\(_2\) of the blend membranes were more than 15–16 times higher than those of pure EC and PS membranes without any drop of permselectivity to N\(_2\). This unusual improvement has been achieved by both enhancement of diffusivity for carbon dioxide and nitrogen by the oligosiloxane groups and enhancement of affinity of the amino groups with carbon dioxide at the end groups of HBP-PAZ-SiO\(_n\).

1. Introduction

Many gas permselective membranes have been reported in the past three decades as energy saving separation process because they can solve recent environmental problems [1–12]. Among them, membranes permeating carbon dioxide selectively are very important in view of solving the global warming problem. For example, they can eventually remove CO\(_2\) from flue gas [3,13–17].

In general, requirements for polymer materials as a practical gas permselective membrane are the following three: 1) a high gas permeability coefficient for a Gas A (\(P_\text{A}\), such as \(P_{\text{CO}_2}\)), 2) a high gas permselectivity of Gas A to Gas B (\(P_\text{A}/P_\text{B}\), such as \(P_{\text{CO}_2}/P_{\text{N}_2}\)), and 3) good membrane-forming ability giving an ability to yield a thin membrane. However, trade-off relationships between the permeability and permselectivity have been often observed [18]. In addition, polymers which may have high permeability and permselectivity tend to have low membrane forming ability. To overcome these problems, more precise design of chemical structures of polymers used for permselective membranes is needed. Polyazomethines (PAZ) are known for their excellent thermal stability, good mechanical strength, environmental resistance, and optoelectronic property [19–23]. PAZs are usually synthesized from diamine and dialdehyde and therefore they have amine end groups. Since amine groups have strong interaction with CO\(_2\), they are useful for CO\(_2\) separation [16]. However, due to the aromatic conjugated structures, the solubility of aromatic PAZ is very low. Hyperbranched polymers (HBP) have been reported, and they have high solubility compared with the corresponding linear ones [24–34]. Since insoluble polymers are not suitable for permselective membranes materials, we selected HBP of PAZ (= HBP-PAZ).

In this paper, in order to enhance solubility of HBP-PAZ, we introduced oligosiloxane chains with a different length by reaction with an oligosiloxane end capping reagent to the end of HBP-PAZ to give HBP-PAZ-SiO\(_n\). Their performances as CO\(_2\) permeation membrane materials were estimated by using blend membranes of HBP-PAZ-SiO\(_n\) with substrate polymers, ethyl cellulose (EC) and polysulfone (PS).

2. Experimental

2.1. Materials

All the solvents used for monomer synthesis and polymerization were distilled as usual. Melamine and isophthalaldehyde were purchased from Aladdin Industrial
Corporation. The silicon containing reagents purchased from TCI chemical Co., Inc., were used as received.

2.2. Measurements

2.2.1. Measurements of carbon dioxide and nitrogen permeability

Carbon dioxide and nitrogen permeability coefficients ($P_{CO_2}$ and $P_{N_2}$: cm$^3$(STP)·cm$^2$·s$^{-1}$·cmHg$^{-1}$) and the carbon dioxide separation factor ($P_{CO_2}/P_{N_2}$) were measured by a gas chromatographic method by using YANACO GTR-11 MH according to our previous report.[30,32,35,36]

The mixture of carbon dioxide and nitrogen (50/50 (v/v)) was used for the feed gas. The $P_{CO_2}$ and $P_{N_2}$ were calculated by the following equation:

$$P = \frac{Q \times l}{A \times \Delta p \times t}$$

where $Q$, $l$, $A$, $\Delta p$, and $t$ are the amount of the permeated gas, the thickness of the membrane, the permeation area of the membrane, the pressure difference across the membrane and the permeation time, respectively. Disc-type membranes were used. The $A$ and $l$ of the membranes were 1.77 cm$^2$ and around 120–310 $\mu$m, respectively. The $\Delta p$ was 1 atm and the measurement temperature was 25°C.

The schematic view of the experimental setup is shown in Figure S1. A polymer film was placed in the membrane cell and exposed to vacuum to remove the gases from the polymer and membrane cell for 10 min by pull ‘VAC’, and then, the mixed CO$_2$/N$_2$ test gas was feed to membrane cell through ‘In’. After the retention time and wait for steady state, the permeate gas in the ‘permeate storage tube’ was measured by gas chromatography through the time lag. The residue gas in ‘Membrane cell’ was released through ‘Retentate’. The amount of the permeated gas ($Q$) was calculated from the peaks of gas chromatogram.

2.2.2. Other measurements

$^1$H NMR (600MHz) spectra were recorded on an AVANCE III spectrometer. The average molecular weights ($M_n$ and $M_w$) were evaluated by gel permeation chromatography (GPC) by using Polymer Laboratories (Varoam) liquid chromatography instruments (with MIXED-E, MIXED-B, MIXED-A, MZ-Gel SDplus columns, THF eluent, polystyrene calibration). The infrared spectra were recorded on Spotlight 400.

2.3. Synthesis of soluble oligosiloxane-end-capped hyperbranched polyazomethines HBP-PAZ-SiOn

Soluble oligosiloxane-end-capped polyazomethines HBP-PAZ-SiOn were synthesized according to Scheme 1. All the following reaction procedures were conducted under dry nitrogen.

2.3.1. Synthesis of oligosiloxane end capping reagent precursor 2

n-Butyllithium (35.3 mL, 70.6 mmol, 2.0 N in hexane) was added dropwise to the tetrahydrofuran (THF) (50.0mL) solution of hexamethyldisiloxane (11.5mL, 70.6mmol) at 0°C. After refluxing for 24h, THF was removed by evaporation and the crude product 1 was purified by vacuum drying.

The mixture of hexamethylcyclotrisiloxane (D3) (n = 9: 7.25g, 37.5mmol; n = 18: 14.5g, 65.0mmol; n = 39: 28.9g, 130mmol) and cyclohexane (50.0mL) was stirred for 30min at room temperature. Then, compound 1 (1.20g, 10.0mL) was add to the mixture, and after 1h stirring at room temperature, THF(25.0mL) was add to the mixture followed by stirring at room

![Scheme 1. Synthesis of soluble oligosiloxane end capped hyperbranched polyazomethine HBP-PAZ-SiOn (n = 9,18 and 39).](image-url)
temperature for 24 h. Finally, the dimethylchlorosilane (5.01 mL, 5.00 mmol) was injected into the mixture and stirred for another 3 h at room temperature. The mixture was filtered, THF was removed by evaporation. The crude product was purified by vacuum drying to give 2 as a yellowish transparent liquid.

\[ n = 9: \text{Yield: } 65.3\% \text{ (5.52 g). } \]
\[ \begin{align*} \text{H NMR (CDCl}_3, \text{ ppm): } & \delta = 4.70 \text{ (m, 1H, (CH}_3)_2\text{SiH), 0.05–0.09 (br, 69H, (CH}_3)_2\text{SiO).} \\
\text{H NMR (CDCl}_3, \text{ ppm): } & \delta = 4.70 \text{ (m, 1H, (CH}_3)_2\text{SiH), 0.05–0.09 (br, 136H, (CH}_3)_2\text{SiO).} \\
\text{H NMR (CDCl}_3, \text{ ppm): } & \delta = 4.70 \text{ (m, 1H, (CH}_3)_2\text{SiH), 0.05–0.09 (br, 273H, (CH}_3)_2\text{SiO).} \\
\end{align*} \]

2.3.2. Synthesis of oligosiloxane end capping reagent(SIO\(_n\))

The resulting compound 2 (1.71 mmol) was added to the toluene (8.10 mL) solution of allylamine (759 μL, 10.1 mmol) and 3-divinyl-1,1,3,3,3,3-tetramethyldisiloxane platinum (0) complexes (453 μL, 1.01 mmol). The mixture was stirred at 45°C for 24 h, and then, the mixture was filtered, solvent was removed by evaporation. The crude product was purified by vacuum drying to give 3 as a brown transparent liquid.

\[ n = 9: \text{Yield: } 70.7\% \text{ (11.1 g). } \]
\[ \begin{align*} \text{H NMR (CDCl}_3, \text{ ppm): } & \delta = 2.66 \text{ (t, 2H, CH}_2\text{NH}_2), 1.45 \text{ (m, 2H, CH}_2\text{CH}_2\text{NH}_2), 0.53 \text{ (m, 2H, SiCH}_2\text{CH}_2\text{NH}_2), 0.05–0.09 \text{ (br, 75H, (CH}_3)_2\text{SiO).} \\
\text{H NMR (CDCl}_3, \text{ ppm): } & \delta = 2.66 \text{ (t, 2H, CH}_2\text{NH}_2), 1.45 \text{ (m, 2H, CH}_2\text{CH}_2\text{NH}_2), 0.53 \text{ (m, 2H, SiCH}_2\text{CH}_2\text{NH}_2), 0.05–0.09 \text{ (br, 136H, (CH}_3)_2\text{SiO).} \\
\text{H NMR (CDCl}_3, \text{ ppm): } & \delta = 2.66 \text{ (t, 2H, CH}_2\text{NH}_2), 1.45 \text{ (m, 2H, CH}_2\text{CH}_2\text{NH}_2), 0.53 \text{ (m, 2H, SiCH}_2\text{CH}_2\text{NH}_2), 0.05–0.09 \text{ (br, 273H, (CH}_3)_2\text{SiO).} \\
\end{align*} \]

2.3.3. Synthesis of HBP-PAZ

A typical procedure for synthesis of HBP-PAZ was as follows: A solution of melamine (A\(_3\)) (305 mg, 2.43 mmol) and isophthalaldehyde (B\(_2\)) (500 mg, 3.73 mmol) (A\(_3\)/B\(_2\) = 0.65) in 1,3-dimethyl-2-imidazolidinone was stirred for 2 h at 65°C. Then, the mixture was poured into a 100 mL beaker containing 50.0 mL ethyl acetate. After precipitation, the liquid was filtered. The crude solid product was purified by vacuum drying to give a white solid.

Other polymerizations of melamine and isophthalaldehyde were carried out similarly. The results are shown in Table 1.

| No. | /[B\(_3\)] | Yield (%) | THF | DMF | DMSO |
|-----|------------|-----------|-----|-----|-----|
| 1   | 0.65       | 58.1      | 19.5| 18.6| 20.9|
| 2   | 0.60       | 63.3      | 18.9| 17.6| 18.4|
| 3   | 0.55       | 68.4      | 13.8| 11.8| 20.5|
| 4   | 0.50       | 56.6      | 13.4| 7.80| 13.2|

\( ^a \text{The feed ratio of melamine (A}\(_3\) \text{) with isophthalaldehyde (B}\(_2\) \text{).} \)
\( ^b \text{Soluble part in THF, by GPC correlating polystyrene standard (eluent: THF).} \)

2.3.4. Synthesis of HBP-PAZ-SiO\(_n\)

A typical procedure for synthesis of HBP-PAZ-SiO\(_n\) was as follows: To a mixture of HBP-PAZ (5.0 mmol) and THF (1.20 mL), oligosiloxane end capping reagent 3 (n = 9) (175 mg, 0.200 mmol) was added and refluxed for 48 h. The mixture was filtered, solvent was removed by evaporation. The crude product was purified by vacuum drying to give HBP-PAZ-SiO\(_n\) as a brown viscous liquid.

Other end capping reactions of HBP-PAZ with 3 were carried out similarly. The yields of HBP-PAZ-SiO\(_n\) (n = 9, 18 and 39) were 94.5%, 94.2% and 93%, respectively.

HBP-PAZ-SiO\(_n\): IR(KBr): 3469 & 3133 cm\(^{-1}\) (NH\(_2\)), 1671 cm\(^{-1}\) (C = O), 1543 cm\(^{-1}\) (C = N), 1438 cm\(^{-1}\) (C-N), 1263 cm\(^{-1}\) (Si-C), 1091 cm\(^{-1}\) (Si-O), 788 cm\(^{-1}\) (Si-C).

2.4. Preparation of HBP-PAZ-SiO\(_n\)/EC and HBP-PAZ-SiO\(_n\)/PS blend membranes

HBP-PAZ-SiO\(_n\)/EC and HBP-PAZ-SiO\(_n\)/PS blend membranes, were fabricated as follows: a solution of HBP-PAZ-SiO\(_n\) in THF (1.5 mg/mL) and a solution of the substrate EC in ethanol (30 mg/mL) (for PS, in CH\(_3\)Cl\(_2\)) were blended together, and then the resulting blend solution was cast on a Teflon sheet. After evaporating the solvent for 24 h at room temperature, the membrane was detached from the sheet and dried in vacuo for 24 h. And then the carbon dioxide and nitrogen permeability were measured by a gas chromatographic method by using YANACO GTR-11 MH [35,36]. The active permeation area was 1.77 cm\(^2\) and the thickness of the membranes were 120-310 μm.

3. Results and discussion

3.1. Synthesis of oligosiloxane end-capping reagents

Three kinds of oligosiloxane end-capping reagents SiO\(_n\) (n = 9, 18 and 39) were synthesized by living polymerization in the different feed ratio of hexamethylcyclotrisiloxane/lithium trimethylsilanolate with
yield of 52.1, 34.7 and 34.4%, respectively. The n of SiO\textsubscript{n} were 9, 18 and 39 which were confirmed by the integral ratio of OSi((CH\textsubscript{3})\textsubscript{2}) to the terminal SiH in the \textsuperscript{1}H NMR spectra of 2. The observed values were consistent with the theoretical calculation values.

3.2. **Synthesis of hyperbranched polyazomethine**

Hyperbranched polyazomethines (HPB-PAZ) were successfully synthesized by condensation polymerization of melamine (A\textsubscript{3}) and isophthalaldehyde (B\textsubscript{2}) with yields higher than 56.6%. The chemical structures were confirmed by FT-IR spectra (Figure 1) because they had insoluble part. The =C = N- stretching vibration band around 1543cm\textsuperscript{-1}, the NH\textsubscript{2} and =HC = O stretching vibration band of end groups around 3469-3133cm\textsuperscript{-1} and 1671cm\textsuperscript{-1} were observed. It indicates the condensation polymerization between amine and aldehyde was achieved to form HPB-PAZ. Many amine and aldehyde end groups remain in HPB-PAZ.

By changing the A\textsubscript{3}/B\textsubscript{2} feed ratio from 0.50 to 0.65, the solubility and molecular weight (THF soluble part) were changed, the results are shown in Table 1. When the A\textsubscript{3}/B\textsubscript{2} feed ratio reaches to 0.65, the HPB-PAZ shows the highest solubility of 19.5% in THF and 20.9% in DMSO. The \(M_n\) and \(M_w\) values of the soluble part were also the highest among the four HPB-PAZ: \(M_n = 3,500, M_w = 3,600, \text{DP} = 15\).

3.3. **Synthesis of soluble oligosiloxane-end-capped hyperbranched polyazomethine HBP-PAZ-SiO\textsubscript{n}**

Soluble oligosiloxane-end-capped hyperbranched polyazomethines (HBP-PAZ-SiO\textsubscript{n}) were synthesized by reaction of the aldehyde end groups of HBP-PAZ with the amine group of the oligosiloxane end capping reagent SiO\textsubscript{n} \((n = 9, 18, 39)\). The yields of the resulting HBP-PAZ-SiO\textsubscript{n} were higher than 94%. From the FT-IR spectra of HBP-PAZ-SiO\textsubscript{39} (Figure 1), the new Si-C and Si-O stretching vibration bands around 1263 and 1091cm\textsuperscript{-1} are found and the =C = O stretching vibration band of the aldehyde end group of HBP-PAZ decreased. It indicates that the end capping reaction has been achieved. Judging from these data, an example of chemical structure is shown in Figure 2.

3.4. **The CO\textsubscript{2}/N\textsubscript{2} separation of HBP-PAZ-SiO\textsubscript{n}/EC and HBP-PAZ-SIO\textsubscript{n}/PS blend membranes**

A 5wt% of soluble oligosiloxane-end-capped hyperbranched polyazomethine (HBP-PAZ-SiO\textsubscript{n}) was blended with EC and PS to give a self-standing membrane. The CO\textsubscript{2}/N\textsubscript{2} permeation experiments were carried out and the results are shown in Table 2. By adding HBP-PAZ-SiO\textsubscript{9}, the permeability \(P_{CO2}\) of EC and PS were enhanced and reached more than 9 times higher values without any drops of the permeability \(P_{CO2}/P_{N2}\) (Table 2, Nos. 2 and 6). In addition, with increasing the length of oligosiloxane...
of HBP-PAZ-SiO
 from 9 to 39, the $P_{\text{CO}_2}$ increased and reached values about 15–16 times higher than those for EC and PS substrates (Table 2, Nos. 4 and 8).

The extremely high enhancements of $P_{\text{CO}_2}$ were caused by the enhancements of diffusivity by the introduction of the SiO
 chains. Although these enhancements of $P_{\text{CO}_2}$ were usually reported, simultaneous large decreases in $P_{\text{CO}_2}/P_{\text{N}_2}$ were usually observed. In this study, surprisingly no decreases were observed. This may be caused by the interaction of amino groups in HBP-PAZ-SiO
 with CO$_2$, a weak acid. The interaction avoided decreasing the selectivity.

### 4. Conclusions

Three soluble oligosiloxane-end-capped hyperbranched polyazomethines HBP-PAZ-SiO
 (n = 9, 18 and 39) were synthesized by reaction of aldehyde end group of HBP-PAZ with the amine group of oligosiloxane end capping reagent SiO
 (n = 9, 18, 39). The permeability of EC and PS substrate membranes were enhanced more than 15 times by using the HBP-PAZ-SiO
 as modifiers without any drop on permeability. In the three HBP-PAZ-SiO
, HBP-PAZ-SiO
 showed the highest performance due to the longer oligosiloxane chain end. This unusual improvement has been achieved by both enhancement of diffusivity for carbon dioxide and nitrogen by the oligosiloxane groups and enhancement of affinity of the amino groups with carbon dioxide at the end groups of HBP-PAZ-SiO
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### Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Lau C, Li P, Li F, Chung T, Paul D. Reverse-selective polymeric membranes for gas separations. Progr Polym Sci. 2013;38:740–766.

[2] Yampolskii Y. Polymeric gas separation membranes. Macromolecules. 1999;45:3298–3311.

[3] Sanders D, Smith Z, Guo R, Robeson L, McGrath J, Paul D, Freeman B. Energy-efficient polymeric gas separation membranes for a sustainable future: a review. Polymer. 2013;54:4729–4761.

[4] Ghosal K, Freeman B. Gas separation using polymer membranes: an overview. Polym Adv Technol. 1994;5:673–697.

[5] Freeman B, Pinnau I. Separation of gases using solubility-selective polymers. Trends Polym Sci. 1997;5:167–173.

[6] Liaw D, Wang K, Huang Y-C, Lee K, Lai J, Ha C. Advanced polyimide materials: syntheses, physical properties and applications. Prog Polym Sci. 2012;37:907–974.

[7] McKeown N, Budd P. Polymers of intrinsic microporosity. ISRN Mater Sci. 2012;2012:150–151.

[8] Zhang J, Kang H, Martin J, Zhang S, Thomas S, Merkel T, Aoki T, Jin J. The enhancement of chain rigidity and gas transport performance of polymers of intrinsic microporosity via intramolecular locking of the spiro-carbon. Chem Commun. 2016;52:6553–6556.

[9] Rose I, Carta M, Malpass-Evans R, Ferrari M, Bernardo P, Clarizia G, Jansen J, McKeown N. Highly permeable benzotriptycene-based polymer of intrinsic microporosity. ACS Macro Lett. 2015;4:912–915.

[10] Yampolskii Y. A current position of polyacetylenes among other highly permeable membrane materials. Polym Rev. 2017;57:200–212.

[11] Aoki T. Macromolecular design of permeselective membranes. Progr Polym Sci. 1999;24:951–993.

[12] Zang Y, Aoki T, Teraguchi M, Ferrari M, Bernardo P, Clarizia G, Jansen J, McKeown N. Synthesis and oxygen permeation of novel polymers of phenylacetylenes having two hydroxyl groups via different lengths of spacers. Polymer. 2015;56:199–206.

[13] Adewole J, Ahmad A, Ismail S, Leo C. Current challenges in membrane separation of CO2 from natural gas: A review, Int J Green Gas Con. 2013;17:46–65.

[14] Lin H, Freeman B. Materials selection guidelines for membranes that remove CO2 from gas mixtures. J Mol Struct. 2005;739:57–74.

[15] Liu J, Hou X, Park HB, Lin H. High-performance polymers for membrane CO2/N2 separation. Chem Eur J. 2016;22:15980–15990.

[16] Taniguchi I, Duan S, Kazama S, Fujioka Y. Facile fabrication of a novel high performance CO2 separation membrane: immobilization of poly(ami doacocine) dendrimers in poly(ethylene glycol) networks. J Membr Sci. 2008;322:277–280.

[17] Vinoba M, Bhagiyalakshmi M, Alqaheem Y, Alomair A, Pérez A, Rana M. Recent progress of fillers in mixed matrix membranes for CO2 separation: A review. Sep Purif Technol. 2017;188:431–450.

[18] Robeson L. The upper bound revisited. J Membr Sci. 2008;320:390–400.

[19] Iwan A. An overview of LC polyazomethines with aliphatic-aromatic moieties: thermal, optical, electrical and photovoltaic properties. Renew Sust Energ Rev. 2015;52:65–79.

[20] Iwan A, Sek D. Processible polyazomethines and polyketamils: from aerospace to light emitting diodes and other advanced applications. Prog Polym Sci. 2008;33:289–345.

[21] Iwan A, Sek D. Polymers with tripheny lamine units: photonic and electro-active materials. Prog Polym Sci. 2011;36:1277–1325.

[22] Jeevadason A, Murugavel K, Neelakantan M. Review on Schiff bases and their metal complexes as organic photovoltaic materials. Renew Sust Energ Rev. 2014;36:220–227.

[23] Hussein M, Abdel-Rahman M, Asiri AM, Asiri A, Alamry K, Aly K. Review on: liquid crystalline polyazomethines polymers. Basics, syntheses and characterization. Des Monomers Polym. 2012;15:431–463.

[24] Voit B, Lederer A. Hyperbranched and highly branched polymer architectures synthetic strategies and major characterization aspects. Chem Rev. 2009;109:5924–5973.

[25] Gao C, Yan D. Hyperbranched polymers: from synthesis to applications. Prog Polym Sci. 2004;29:183–275.

[26] Kwak G, Masuda T. Synthesis, characterization and optical properties of a novel Si-containing α-α-conjugated hyperbranched polymer. Macromol Rapid Commun. 2002;23:68–72.

[27] Gradwell S, Kepler L. Preparation of novel polyluminescent oligocarposilanes by hydroxilylation. Macromolecules. 2002;35:2871–2872.

[28] Kwak G, Masuda T. Synthesis and thermal properties of regio- and stereoregular poly(silylene-1,4-phenylenevinylene)s. Macromol Rapid Commun. 2001;22:1233–1236.

[29] Lach C, Frey H. Enhancing the degree of branching of hyperbranched polymers by postsynthetic modification. Macromolecules. 1998;31:2381–2383.

[30] Wang J, Li J, Aoki T, Kaneko T, Teraguchi M, Shi Z, Jia H. Subnanoporous highly oxygen permeable membranes from poly(conjugated hyperbranched macromonomers) synthesized by one-pot simultaneous two-mode homopolymerization of 1,3-bis(silyl)phenylacetylene using a single Rh catalytic system: control of their structures and permeabilities. Macromolecules. 2017;50:7121–7136.

[31] Li J, Wang J, Zang Y, Aoki T, Kaneko T, Teraguchi M. Enhanced gas perme selectivity of copoly(hyperbranched macromonomer) synthesized by one-pot simultaneous copolymerization of dimethylsil- containing phenylacetylene. Chem Lett. 2012;41:1462–1464.

[32] Kaneko T, Yamamoto K, Asano M, Teraguchi M, Aoki T. Synthesis of poly(phenylacetylene)-based polydendrons consisting of a phenylethynylene repeating unit, and oxygen/nitrogen permeation behavior of their membranes. J Membr Sci. 2006;278:365–372.

[33] Aoki T, Kaneko T, Teraguchi M. Synthesis of functional n-conjugated polymers from aromatic acetylenes. Polymer. 2006;47:4867–4892.

[34] Kaneko T, Asano M, Yamamoto K, Aoki T. Polymerization of phenylacetylene based monodendrons and structure of the corresponding polydendrons. Polym J. 2001;33:879–890.

[35] Kawakami Y, Aoki T, Hisada H, Yamamura Y, Yamashita Y. Poly(p-diolosaine substituted styrene)s as materials for oxygen permeable membranes. Polym Commun. 1985;26:133–136.

[36] Aoki T, Toyoshima Y, Oikawa E. Synthesis of poly(p-(1H,1H,2H,2H-perfluorooalkyloxy)alkylsiloxyl)styrene)s and oxygen perme selectivity of their membranes. Polym J. 1994;26:1142–1153.