SYNTHESIS AND OXYGEN PERMEATION OF SOPHISTICATEDLY MODIFIED POLYPHENYLACETYLENE-BASED 2D MEMBRANES

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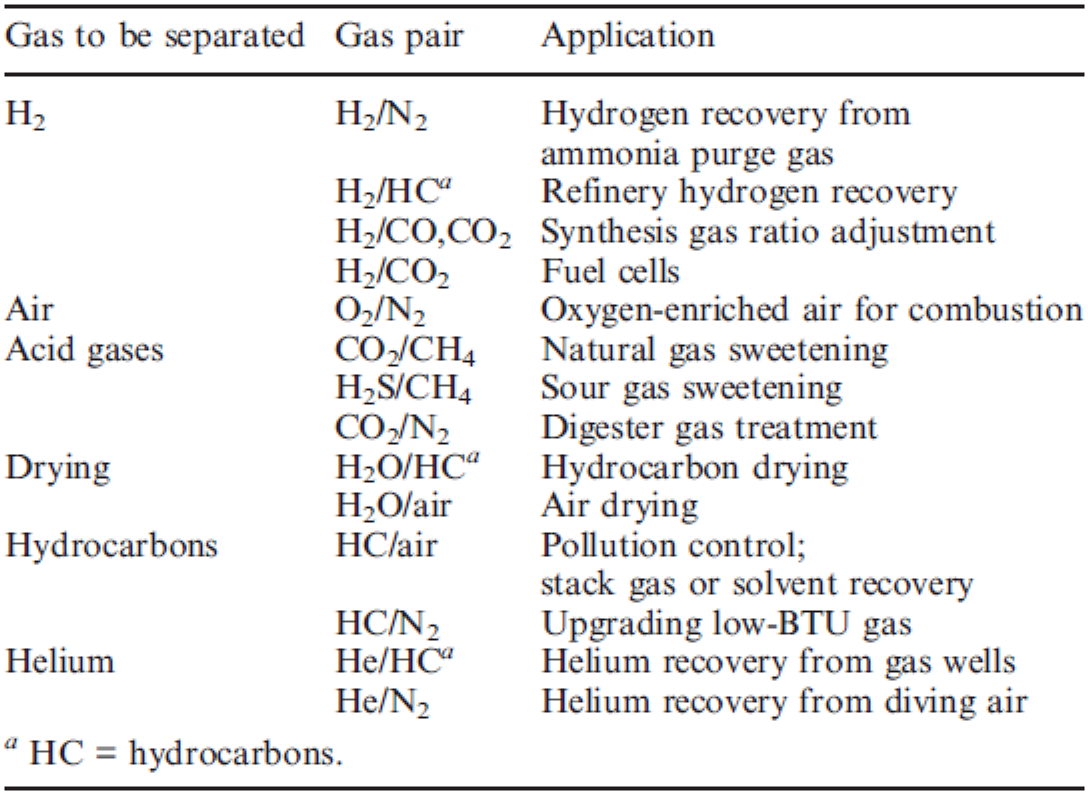
General introduction

Ⅰ. Gas separation membranes

Gas separation occupies a central position in the chemical feedstock industry: oxygen and nitrogen enrichment of air, hydrogen recovery, natural gas separation and removal of volatile compounds from effluent streams are all current applications. Gas separation by membranes has acquired great economic importance because of its energy efficiency. Some typical examples of membrane gas separations are summarized in Table 1. In particular, the non-cryogenic nitrogen production and hydrogen purification are already present at the industrial level.[1]

Table 1 Current applications of gas separation membranes



Gas to be separated	Gas pair	Application
H_2	H_2/N_2	Hydrogen recovery from ammonia purge gas
	H_2/HC^a	Refinery hydrogen recovery
	$H_2/CO,CO_2$	Synthesis gas ratio adjustment
	H_2/CO_2	Fuel cells
Air	O_2/N_2	Oxygen-enriched air for combustion
Acid gases	CO_2/CH_4	Natural gas sweetening
	H_2S/CH_4	Sour gas sweetening
	CO_2/N_2	Digester gas treatment
Drying	H_2O/HC^a	Hydrocarbon drying
	H_2O/air	Air drying
Hydrocarbons	HC/air	Pollution control; stack gas or solvent recovery
	HC/N_2	Upgrading low-BTU gas
Helium	He/HC^a	Helium recovery from gas wells
	He/N_2	Helium recovery from diving air

[a] HC = hydrocarbons.

Commercial gas separation membranes are composed of synthetic polymeric materials. Polymers provide a range of desirable properties that are important for gas separation processes including low cost, high permeability, good mechanical, stability, and easy processability.[2] Membranes of polymeric material have been recognized in a number of separation processes of gas, liquid and mixed phases.[3,4] The basic principle of gas separation by polymeric membranes is the solution diffution mechanism. In this model, the tansport of a gas mixture component through the polymer matrix occurs under a gas phase partical pressure gradient(or chemical potential gradient) of that component across the membrane. The diffution consists of three steps: (a) adsorption at the surface and dissllution into the polymer in the high pressure face of the membrane; (b) diffution across the membrane thickness to the low pressure side and (c) desorption of the gas and vaporization into the gas phase.

Phenylacetylenes with bulky spherical substituents show extremely high gas permeability. This is because the combination of their stiff main chain composed of alternating double bouds and the steric repulsion of the bulky substituents make their membranes sparse. Therefore, poly(substituted acetylene)s are promising materials for gas separation membranes. A large number of poly(substituted acetylene)s have been synthesized so far, and the gas permselectivities of their membranes has been investigated.[5-10] The incorporation of functional groups into poly(substituted acetylene)s is the great interest in the various fields due to their potentional applications as polymer light-emitting devices, sensors, enantioselective materials and separation membranes for specific gases.

Robeson’s group have punlished the newest upper bound line in 2008 for gas separation through polymeric membranes, in this doctor thesis, we summarized the the most highest plots for oxygen permeation through the polymer membranes and achieved the the new upper bound curve.(Figure 1). It contains the permeation data with a higher permeability exceed 4000 barrer that havn’t be contained in Robeson’s upper bound line, but in this area, there also have no plot with permselectivity higher than 2.0. The structure of the polymers in this upper bound curve was shown below.

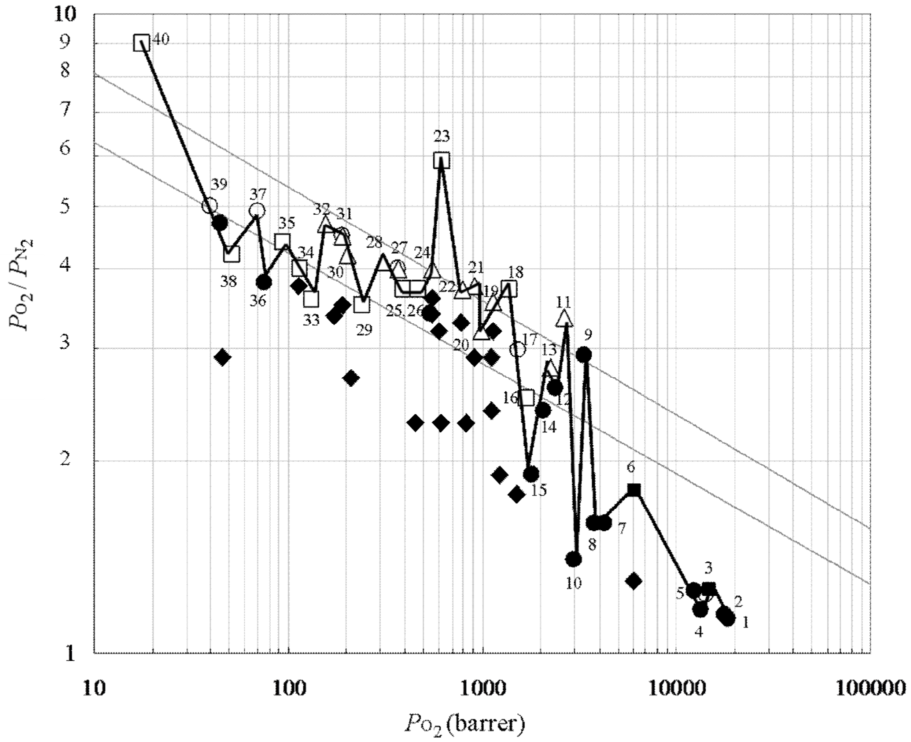
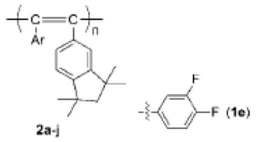
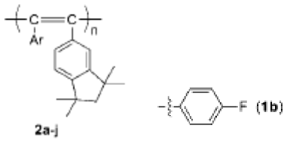


Fig.1. Upper bound curve for O_2/N_2 permeation through the **all the polymer** membranes(numbers in the figure were accordance to that in Table 1). ●： PDPA; ■:PTMSP; △ : PIMs ; □:PI(polyimides).



1



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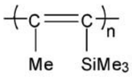

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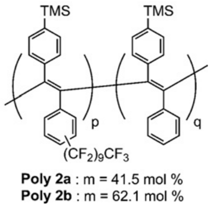
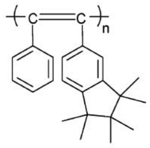


4(poly(2b))



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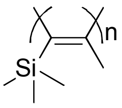

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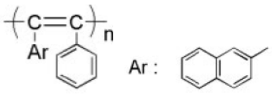

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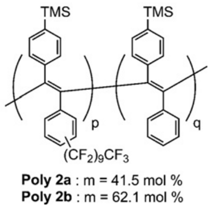
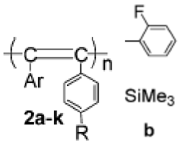
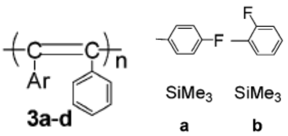


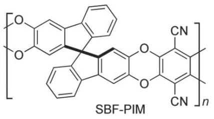
9(poly(2a))



8(2b)



10(3a)



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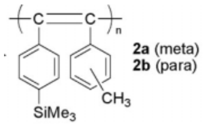

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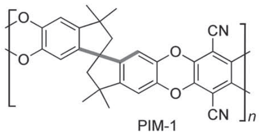

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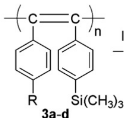
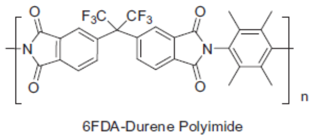
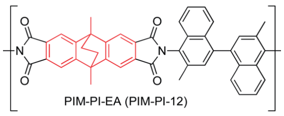


15(3a, R=H)



16 (with 30 wt% ZIF-7)



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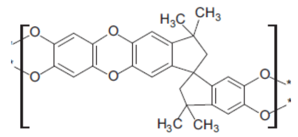
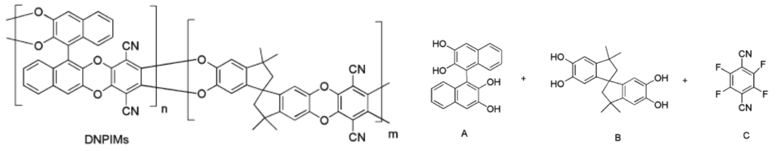
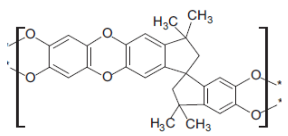


20(0.5 wt% f-MWCNT/PIM)

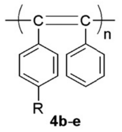


19 (copolymer, A:B:C = 1:3:4)

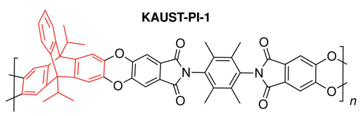
21(copolymer, A:B:C = 1:2:3)



22 (3.0 wt% f-MWCNT/PIM)



14(4e, R=t-C_4H_9)



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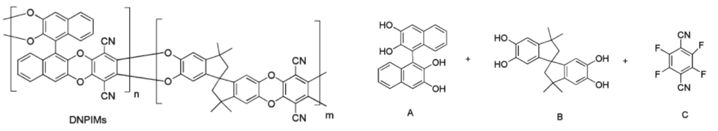
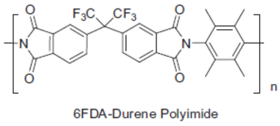
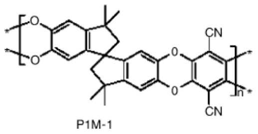


24 (copolymer, A:B:C = 1:1:2)



25 (with 30 wt% ZIF-8)
26(with 15 wt% ZIF-8)



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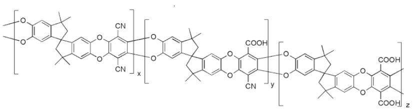
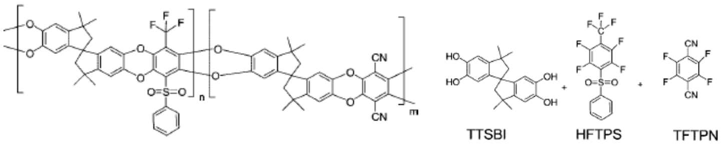
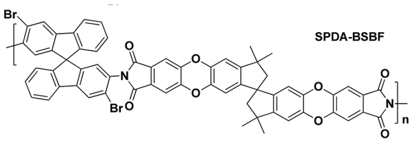


30 (PIM-1 hydrolysis at 120℃, 3h)



28 (TTSBI: HFTPS: TFTPN = 3:2:1)



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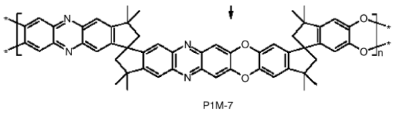

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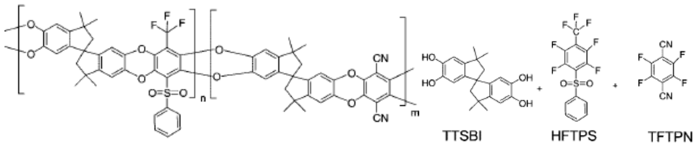
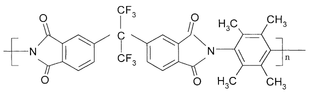


32(TTSBI: HFTPS: TFTPN = 1:1:0)



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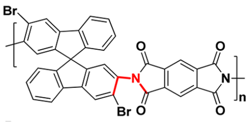

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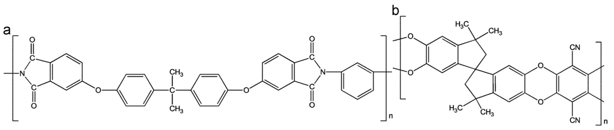
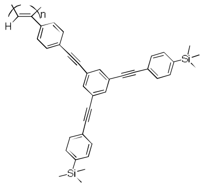


35 (a: b = 30:70)



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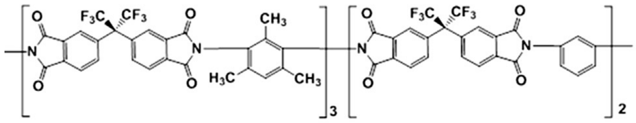

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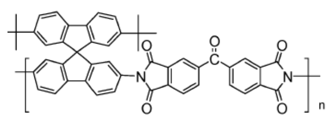


40

Gas permselective membranes are very important and valuable because the necessity to remove impurities or purify mixtures of gases whose molecular size are very similar in enhacing because solving the recent environmental problems has been focus on.In general, trade-off relationship between permeability and permselectivity is usually observed. To over come this, more control of chemical structures of the side groups in the polymer used for permselective membranes are needed.

In general, structural changes which lead to increases in polymer permeability also cause losses in permselectivity. This so-called “trade-off” relationship is well described in the literature.[9,10]

Ⅱ. Hyperbranched polymers

Hyperbranched (hb) polymers are a special type of dendritic polymers and have as a common feature a very high branching density with the potential of branching in each repeating unit. They are usually prepared in a one-pot synthesis, which limits the control on molar mass and branching accuracy and leads to “heterogeneous” products with a distribution in molar mass and branching. This distinguishes hyperbranched polymers from perfectly branched and monodisperse dendrimers.

In the last 20 years, both classes of dendritic polymers, dendrimers as well as hb polymers, have attracted major attention because of their interesting properties resulting from the branched architecture as well as the high number of functional groups.[11]

This term now not only cover the “classical” products based on Flory’s AB_x approach but is extended to variously highly branched structures including those prepared by the A_2 by monomer combination[12, 13, 14, 15] prepared by self-condensing vinyl polymerization(SCVP)[16], ring-opening multibranching polymerization(ROMBP) or self-condensing ring-opening polymerization(SCROP), or proton transfer polymerization,[17,18] and those prepared by various copolymerizations and methodology combinations including self-assembly aspects which lead to linear highly branched hybrids like dendronized polymers, dendrigrafts and hyperbranched core-branched strctures and nanocapsules.

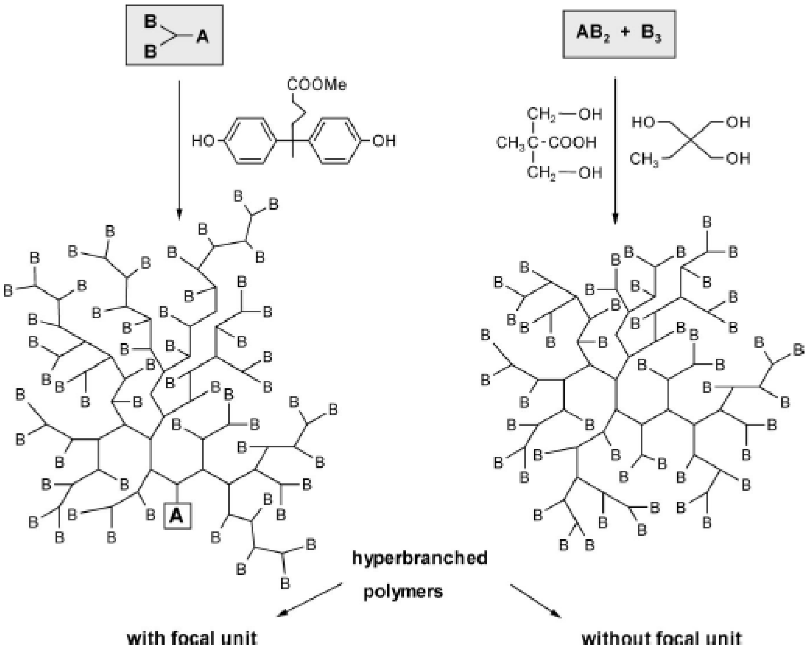


Figure 2. Schemetic representation of the synthesis of hp polymers through AB_x and $A_x + B_y$ approach(here: x=2, y=3)

Previous comprehensive reviews like that of Gao and Yan[19] provide an excellent overview of the different synthetic approaches to hb polymers. Gao and Yan pointed out that the first hyperbranched structures, based on an $A_2 + B_3$

approach, go back as early as Berzelius,[12] followed by an early paper on hb polyethers through AB_3 monomers by Hunter and Woolett.[20] Considering the A_2 + B_y, many resins actually fit the term “hyperbranched” in the form of a soluble precursor polymer ready for curing. Thus, an early example for hyperbranched structures was introduced by Korshak, who described the synthesis of branched polyphenylenes through cyclotrimerization of various diethynylbenzenes with phenylacetylenes.[21]

In the classical approach toward hyperbranched polymers, which goes back to Flory’s[22] early description as a special type of polycondensation, AB_x monomers with equal reactivity of the B functionalities are reacted (Figure 2). The reaction involves the typical features of a step-growth reaction of multifunctional monomers and the formed oligomers but without the possibility of crosslinking. Dendritic (fully reacted B functions), terminal (no reacted B function), and linear (one reacted B function) units and one focal unit (A function) should be present in the resulting, highly branched macromolecule.

Ⅲ. Highly selective photocyclic aromatization (SCAT) of cis-cisoid helical poly(phenylacetylene)s in the membrane state

A novel highly selective photocyclic aromatization (SCAT) of π-conjugated polymers from phenylacetylene having two hydroxyl groups to exclusively yield a 1,3,5-trisubstituted benzene derivative was developed by our groups and its success was confirmed by ^{1}H-NMR, GPC, and TOF-MS (Figure 3).[23] The

SCAT reaction had many unique characteristics, such as unusual selectivities, as follows. 1) It is a quantitative reaction: it gave only the corresponding cyclic trimer, *i.e.*, a 1,3,5-trisubstituted benzene derivative, quantitatively(= 100%). No by-products were produced under the best condition. 2) It is an intramolecular reaction: it occurred between adjacent three monomer units in one macromolecule. 3) It is a stereospecific and topochemical or template reaction: the reactivity strongly depended on the configuration and conformation of the starting polymer substrates. 4) It is a photoreaction: high selectivity (= 100%) was observed only by the use of visible light irradiation, not by heating. 5) It is a solid state reaction: high selectivity(=100%) was observed only in the solid state, not in solution. *In addition*, 6) the resulting cyclic trimers had the ability to form a self-supporting membrane, in spite of their low molecular weights. This new approach resulted in a new class of supramolecular polymers consisting of a 1,3,5-trisubstituted benzene derivative, numbers of which were linearly linked by hydrogen bonds and stacked benzenes. Since SCAT has such high selectivities and is useful for the preparation of a self-supporting supramolecular polymer membrane, many kinds of applications can be expected.

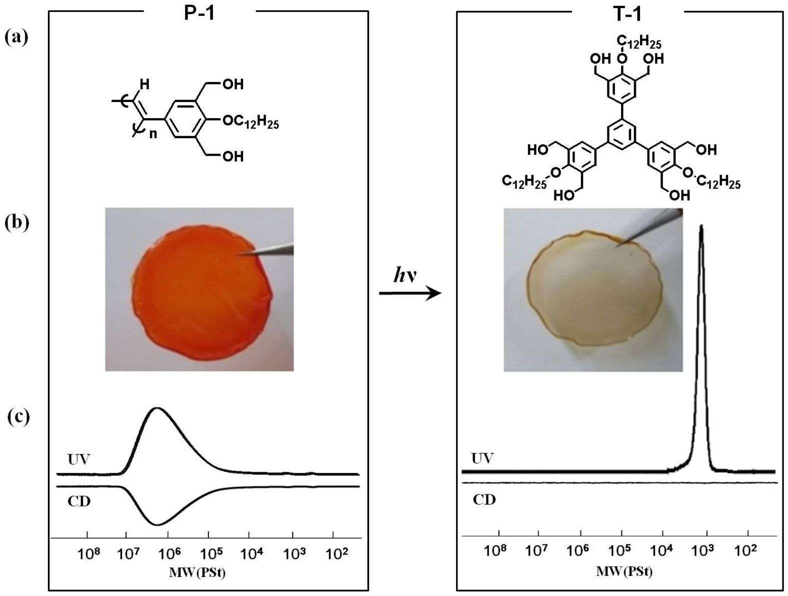
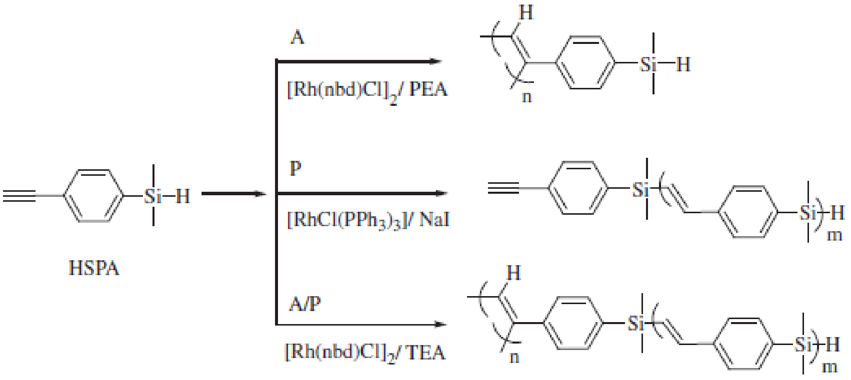


Figure 3. SCAT of **P-1** to **T-1** (a) chemical structures of the starting polymer(**P-1**) and the SCAT product(**T-1**). (b) Photographs of **P-1**(a polymer membrane) and **T-1**(a supramolecular polymer membrane), (c) GPC curves detected by UV and CD of **P-1** and **T-1**.

IV. Purpose of this thesis

In chapter 1, Three types of homopolymerizations of *p*-(dimethylsilyl)-phenylacetylene (HSPA) having a terminal triple bond and a SiH group were selectively carried out by using three kinds of polymerization catalysts(Scheme 3). Among them poly(HSPA) synthesized by addition polymerization of its triple bond using [Rh(nbd)Cl]$_2$ (nbd: norbornadiene)/phenylethylamine (PEA) showed a good membrane forming ability. The copolymerizations of HSPA with *p*-(trimethylsilyl)phenylacetylene (SPA) were carried out using [Rh(nbd)Cl]$_2$/PEA and the resulting copolymers were fabricated to self-supporting membranes. These membranes, including the homopolymer of HSPA, showed higher permselectivities for oxygen and carbon dioxide over nitrogen than those of poly(SPA). Incorporation of HSPA unit to poly(SPA) effectively enhanced its permselectivities with only small decrease in its permeability.



Scheme 2. homopolymerizations of *p*-(dimethylsilyl)- phenylacetylene (HSPA).

In chapter 2, An amphiphilic 1,3,5-trisubstituted benzene as a new 2D surface modifier (T-EO) which has six hydroxy groups and three oligoethylene groups was successfully and easily synthesized by selective photocyclic aromatization in high conversion and selectivity for the first time. We prepared four kinds of blend membranes based on PVA or poly(trimethylsilylphenylacetylene) (poly(SPA)) containing the new amphiphilic cyclic trimer (T-EO) or the corresponding polymer (P-EO) by two different methods, membranes structure and gas permselectivity through these membranes wew also been discussed in this research.

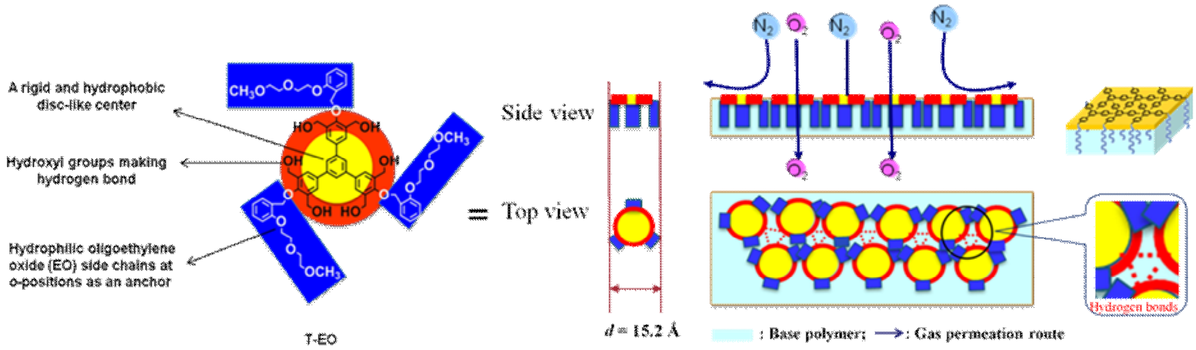


Figure 4. Structure of the 2D amphiphilic surface modifier and the surface modifer membranes

In chapter 3, A facile synthesis of novel five 2D (planar) surface modifiers having a triphenylbenzene derivatives as a 2D structure has been achieved by the highly selective photocyclic aromatization reaction. Efficient enhancement of oxygen permselectivities through the three polymer membranes has been achieved by adding a small amount (<5.0 wt%) of the 2D surface modifiers. Among the five 2D surface modifiers, a modifier compound having oligoethylene oxide groups showed the best performance for the enhancement. These improvements were thought to be caused mainly by improvement of the solution selectivity on the membrane surface where the 2D surface modifiers were accumulated.

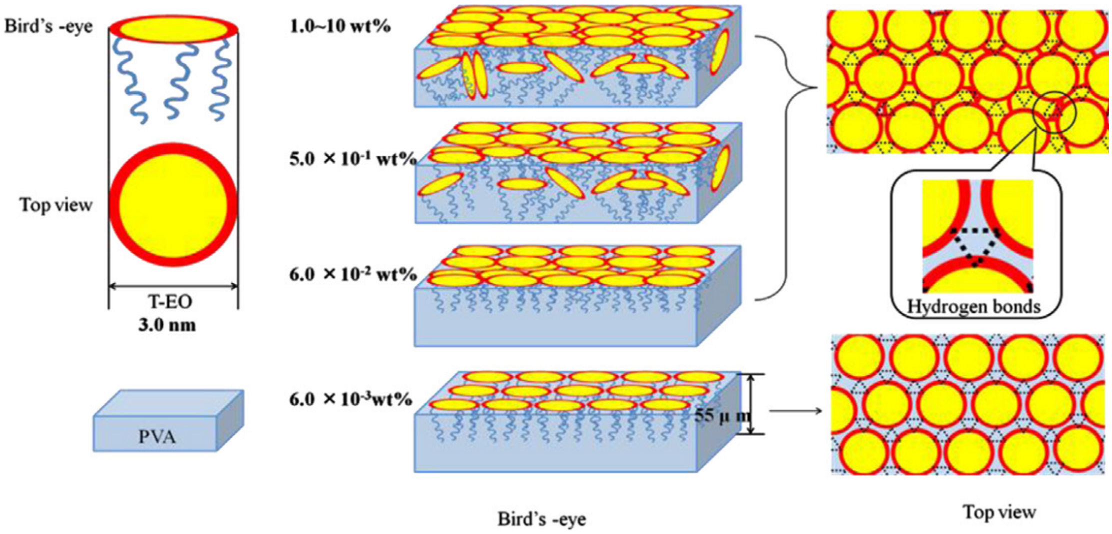


Figure 5. Possible membrane structures of T-EO/PVA membranes having different amount of T-EO.

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PART I

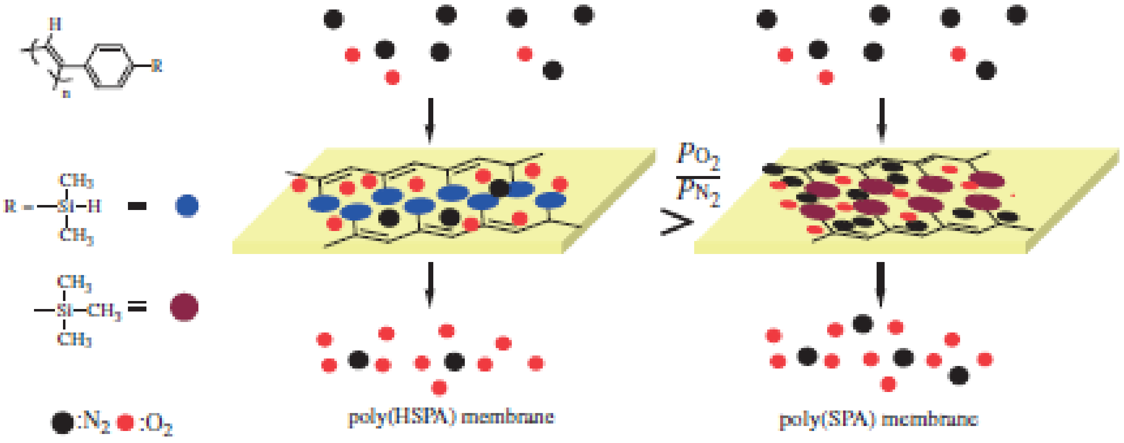
One-pot Synthesis of 2D Poly(Phenylacetylene type Macromonomer) by Simultaneous Polymerization for Gas Permselective Membranes

Chapter 1

Selective Polymerization of Dimethylsilylphenylacetylene and the Gas permselectivity of the Resulting Polymer Membranes

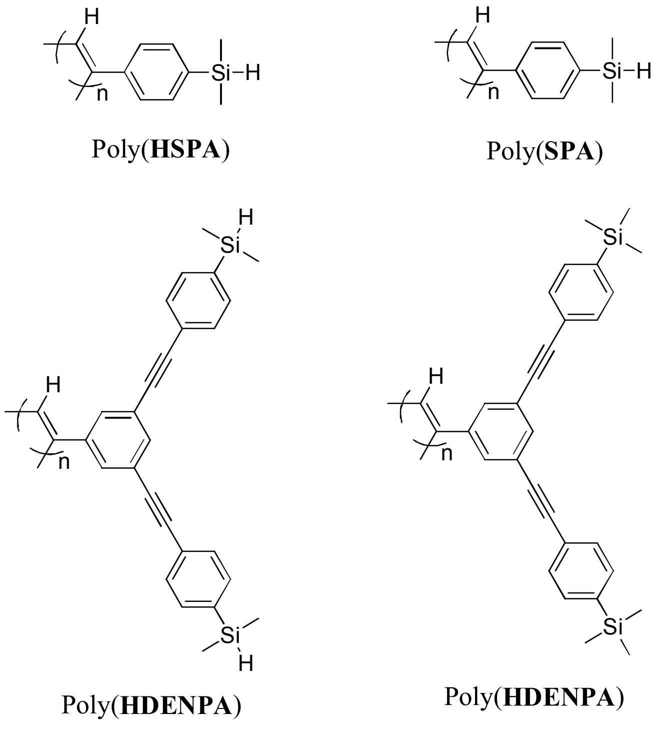
1.1 Abstract

Three types of homopolymerizations of *p*-(dimethylsilyl)-phenylacetylene (HSPA) having a terminal triple bond and a SiH group were selectively carried out by using three kinds of polymerization catalysts. Among them poly(HSPA) synthesized by addition polymerization of its triple bond using $[Rh(nbd)Cl]_2$ (nbd: norbornadiene)/phenylethylamine (PEA) showed a good membrane forming ability. The copolymerizations of HSPA with *p*-(trimethylsilyl)phenylacetylene (SPA) were carried out using $[Rh(nbd)Cl]_2$/PEA and the resulting copolymers were fabricated to self-supporting membranes. These membranes, including the homopolymer of HSPA, showed higher permselectivities for oxygen and carbon dioxide over nitrogen than those of poly(SPA). Incorporation of HSPA unit to poly(SPA) effectively enhanced its permselectivities with only small decrease in its permeability.



1.2 Introduction

We reported the synthesis and good performance as oxygen permselective membrane materials of poly[*p*-(trimethylsilyl)-phenylacetylene] (poly(**SPA**), Chart 1.1).[1-3] Poly(**SPA**) having a good self-membrane-forming ability was synthesized by the polymerization of **SPA** by using $[Rh(nbd)Cl]_2$ (nbd: norbornadiene)/triethylamine (TEA) and showed relatively high oxygen permeability (P_{O_2} =171 barrer) and permselectivity (P_{O_2}/P_{N_2} = 2.36). The good properties were thought to be caused by the rigid conjugated backbone and bulky symmetrical round-shape trimethylsilyl ($SiMe_3$) substituents. We also reported the higher P_{O_2}/P_{N_2} of polydendron (poly(**DENPA**), Chart 1.1), which has a rigid conjugated backbone and $SiMe_3$ terminal substituents via regularly branched side groups, than that of poly(SPA).[4]



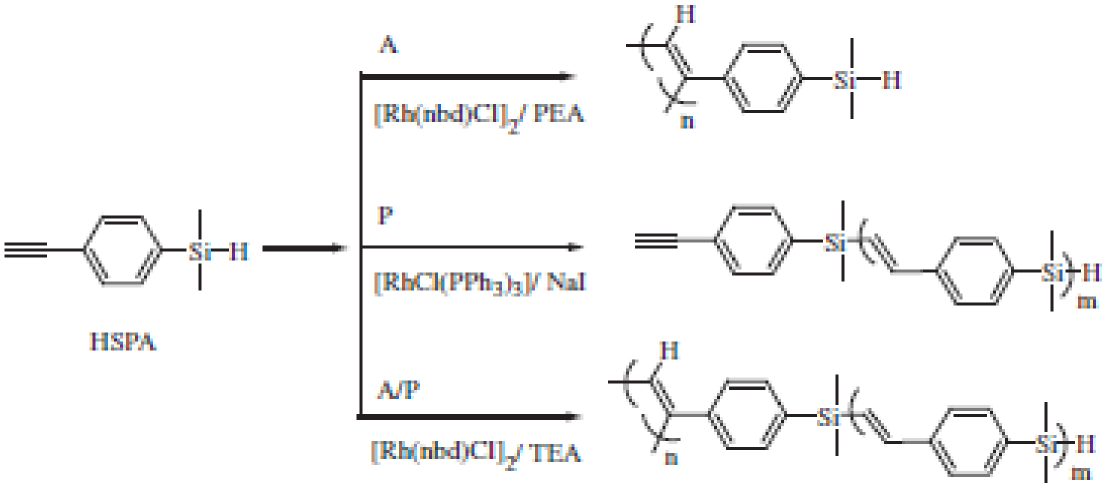
Poly(**HSPA**) Poly(**SPA**)

Poly(**HDENPA**) Poly(**HDENPA**)

Chart 1.1 Structure of the polymers in this research.

In addition, recently we reported the synthesis of copoly (hyperbranched macromonomer) (poly(**HDENPA**), Chart 1.1) by the simultaneous two-mode copolymerization of a monomer having a terminal triple bond and two SiH groups, and their good performance as gas permselective membranes.[5] However, the control of the two polymerizations, i.e., the addition polymerization of the triple bond and the polyaddition between the triple bond and SiH groups, was difficult and in particular, it was difficult to obtain homopolymers having good membrane forming ability. For example, we could not obtain (co)polymers containing HSPA units as the main component and having good membrane-forming ability.

In this study, to obtain new silicon-containing polymers having better oxygen and carbon dioxide permselectivity with maintaining high permeability ($P\mathrm{O_2} > 100$, $P\mathrm{CO_2} > 1000$) and better self-membrane-forming ability than other silicon-containing polymers having high $P\mathrm{O_2}$ such as poly(**SPA**), we designed a silicon-containing polymer (poly(**HSPA**), Chart 1.1) having smaller silicon-containing groups, i.e., dimethylsilyl ($\mathrm{SiHMe_2}$) instead of trimethylsilyl group ($\mathrm{SiMe_3}$) in poly(**SPA**). Because the increase of the part of polyaddition products decreases the membrane-forming ability, we examined the control of the two polymerizations, i.e., the addition polymerization of the triple bond and polyaddition between the triple bond and SiH groups (Scheme 1.1). In addition, the copolymerizations of **HSPA** with **SPA** were synthesized using $[\mathrm{Rh(nbd)Cl}]_2)$/PEA and the resulting copolymers were fabricated to self-supporting membranes. The permeabilities of oxygen, carbon dioxide, and nitrogen were measured through these pure polymer membranes.



Scheme 1.1 Three modes of polymerization of HSPA.

1.3 Experimental

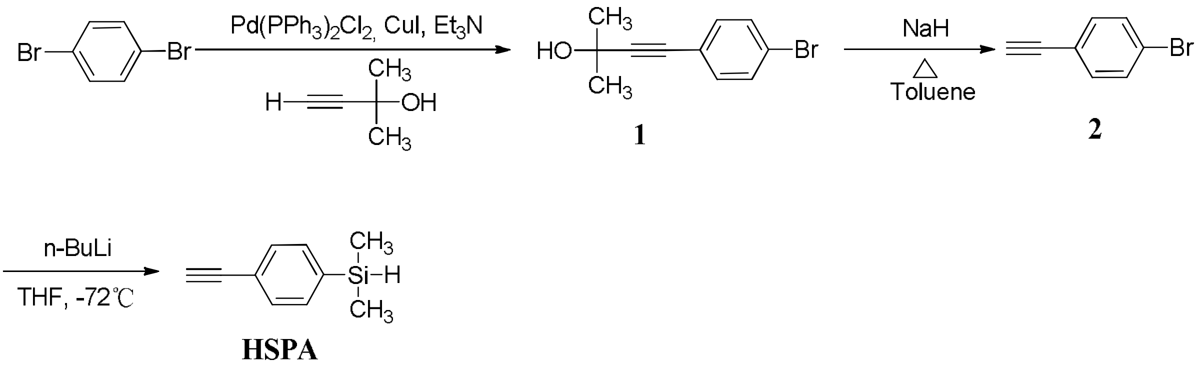
1.3.1 Materials

All the solvents used for monomer synthesis and polymerisation were distilled as usual. The polymerisation initiator, [Rh(nbd)Cl]$_2$ (nbd=2,5 norbornadiene), purchased from Aldrich Chemical Co., Inc., was used as received. The silicon-containing reagent, trimethylsilylacetylene was purchased from Shinetsu Chemical Co., Ltd., and used as received.

1.3.2 Measurements

^{1}H-NMR (400 MHz) spectra were recorded on a VARIAN-400 spectrometer. The average molecular weights (Mn and Mw) were evaluated by gel permeation chromatography (GPC) by using JASCO liquid chromatography instruments with PU-2080, DG-2080-53, CO-2060, UV-2070, CD-2095, and two polystyrene gel columns (Shodex KF-807 L, THF eluent, polystyrene calibration). The infrared spectra were recorded on FT/IR-4200 (JASCO). Oxygen and nitrogen and carbon dioxide/nitrogen permeability coefficients (P_{O_2} P_{CO_2} and P_{N_2} : cm^3(STP) cm cm^{-2} s^{-1} $cmHg^{-1}$) and the oxygen separation factor ($\alpha = P_{O_2}/P_{N_2}$, P_{CO_2}/P_{N_2}) were measured by a gas chromatographic method at 25℃ using YANACO GTR-10. The area of membrane is 1.77 cm^2, and the initial feed gas pressure 1atm.

1.3.3 Synthetic procedures of the monomers HSPA(Scheme 1.2)



Scheme 1.2 synthesis route of monomer **HSPA**.

1.3.3.1 4-(4-bromophenyl)-2-methyl- 3- butyn-2-ol(**1**)

1,4-dibromobenzene (6.8 g, 24.4 mmol), dry triethylamine (100 mL) and 2-methyl-3-butyn-2-ol (3.1 mL, 31.7 mmol) were added to a mixture of triphenylphosphine (256 mg, 0.95 mmol), cuprous iodide (279 mg, 1.45 mmol) and bis (triphenylphosphine) palladium (Ⅱ) chloride (171 mg, 0.25 mmol). Then the solution was refluxed for 15 h at 90℃ and extracted with diethyl ehter. washed with water, and dried over anhydrous sodium sulfate. Diethyl ether was evaporated, and the crude product was purified by silica gel column to give compound 1 as yellow solid. Yield: 87% (5.1 g); TLC (Hexane / AcOEt = 4 / 1, R_f = 0.6).

^{1}H-NMR (400 MH$_Z$, CDCl$_3$, ppm): δ 7.43 (d, 2H, Ar-*H*), 7.32 (d, 2H, Ar-*H*), 3.60 (s, 1H, -O*H*), 1.41 (s, 6H, -C*H*$_3$).

1.3.3.2 3,5-dibromophenylacetylene (**2**).

1 Sodium hydride (0.97 g, 22.3 mmol) was added to a toluene solution (70 mL) of compound **1** (5.1 g, 21.2 mmol). The mixture was heated to 90℃ and stirred under a nitrogen flow for 2 h. It was allowed to room temperature slowly. The reaction mixture was filtered. The solvent of the filtrate was concentrated by evaporation. The crude product was dissolved in diethyl ether, and the ether layer was washed with 10% HCl(aq) and then water, and dried over anhydrous sodium sulfate. The crude product was purified by silica-gel column chromatography with hexane as an eluent to give **2** as a white solid. Yield: 82%(3.0 g); TLC (hexane, Rf = 0.5).

^{1}H-NMR (400 MH$_Z$, CDCl$_3$, ppm): δ 7.45 (d, 2H, Ar-*H*), 7.36 (d, 2H, Ar-*H*), 3.12 (s, 1H, C≡C*H*).

1.3.3.3 Synthesis of *p*-dimethylsilylphenylacetylene (**monomer HSPA**).

p-bromophenylacetylene (4.3 g, 24.0 mmol) and dry THF (70 mL) were placed in the flask at -75 °C. At the same temperature, a hexane solution of *n*-butyllithium (35.5 mL, 57.5 mmol) was added dropwise, and the reaction mixture was stirred for 4 h at this low tempreture. A solution of dimethylchlorosilane (2.7 g, 25.2mmol) in dry THF (20 mL) was added dropwise, and it was alloweded warm to room temperature slowly and kept overnight. After excess water was added to the reaction mixture, the stirring was continued for 1 h. The mixture was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. Diethyl ether was evaporated, and the crude product was purified by silica-gel column to give monomer HSPA as colorless viscous liquid. Yield: 27% (1.1 g); TLC (hexane, R_f= 0.5).

^{1}H-NMR (400 MH_Z, $CDCl_3$, ppm): δ 7.48(q, 4H, Ar-*H*), 4.42(s, 1H, Si-*H*), 0. 34 (s, 6H, Si-CH_3).

1.3.4 Polymerization of the monomers HSPA by three different modes (Scheme 1.1)

1.3.4.1 Addition polymerization of **HSPA** using $[Rh(nbd)Cl]_2$/PEA catalytic system.

A typical polymerization procedure was as follows: To a solution of **HSPA** **(**160 mg, 1. 0 mmol) with PEA (242 mg, 2.0 mol) in dry toluene (8.0 mL) at 25 °C under nitrogen, a solution of $[RhCl(nbd)]_2$(2.3 mg, 5.0 μmol) in dry toluene (2.0 mL) was added. The mixture was kept at room tempreture for 4h. The formed polymer was purified by precipitation of the toluene solution in a large amount of methanol and dried in vacuum to give a yellow solid. Yield: 92%. Mn = 9.2×10^4 (Table 1.1, no. 1).

Copolymerization of **HSPA/SPA** follows the same procedures as above.

1.3.4.2 Polyadditon of **HSPA** using $RhCl(PPh_3)_3$/NaI catalytic system.

A typical polymerization procedure was as follows: To a solution of **HSPA** **(**160 mg, 1. 0 mmol) in dry toluene (8.0 mL) at 25 °C under nitrogen, a solution of $[RhCl(PPh_3)_3$ (2.3 mg, 5.0 μmol) and NaI in dry toluene (2.0 mL) was added. The mixture was kept at room tempreture for 12h. The formed polymer was purified by precipitation of the toluene solution in a large amount of methanol and dried in vacuum to give a yellow solid. Yield: 40%. Mn = 9.9×10^3 (Table 1.1, no. 2).

1.3.4.2 Simultaneous polymerization of **HSPA** using $[Rh(nbd)Cl]_2$/TEA catalytic system.

A typical polymerization procedure was as follows: To a solution of **HSPA**

(160 mg, 1. 0 mmol) with TEA (0.2 mL, 2.0 mmol) in dry toluene (8.0 mL) at 25 °C under nitrogen, a solution of $[RhCl(nbd)]_2$(2.3 mg, 5.0 μmol) in dry toluene (2.0 mL) was added. The mixture was kept at room tempreture for 4h. The formed polymer was purified by precipitation of the toluene solution in a large amount of methanol and dried in vacuum to give a yellow solid. Yield: 75%. Mn = 3.2×10^4 (Table 1.1, no. 3).

1.4 Results and discussions

1.4.1 Selective Polymerization of HSPA by different catalytic systems

In order to obtain polymers having a good self-supporting membrane forming ability from HSPA, which bears one terminal triple bond and one SiH group, three kinds of catalytic systems were used for its homopolymerizations (Scheme 1.1). First, when $[Rh(nbd)Cl]_2$/TEA was used as we reported previously,[3-5] both the polymerizations, i.e., the addition polymerization of the triple bond and polyaddition between the triple bond and SiH groups happened to yield a poly(macromonomer) as shown in Scheme 1.1 (A/P). The structure of the poly(macromonomer) was confirmed by NMR (Figure 1.1, A/P). Unfortunately, the resulting product had a poor self-supporting membrane-forming ability and it indicates no control of the three modes of polymerizations (Scheme 1.1).

Then when $[RhCl(PPh_3)_3]$/NaI was used,[6] only the polyaddition between the triple bond and SiH groups happened to yield a macromonomer as shown in Scheme 1.1, **P**, which was confirmed by NMR (Figure S1.1). The resulting product had a poor self-supporting membrane forming ability.

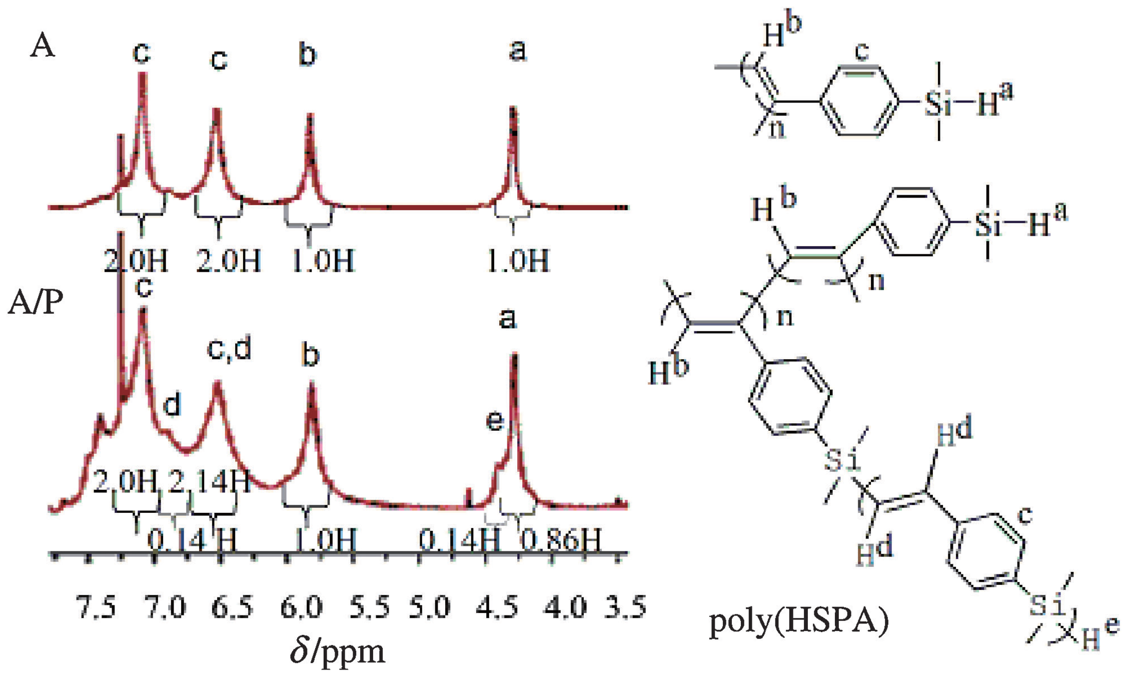


Figure 1.1 ^{1}H-NMR spectra of poly(HSPA) prepared by using two kinds of cocatalysts. **A** by [Rh(nbd)Cl]$_2$/phenylethylamine(PEA) and **A/P** by [Rh(nbd)Cl]$_2$/triethylamine (TEA).

Finally when [Rh(nbd)Cl]$_2$/PEA was used, only the addition polymerization of the triple bond happened to yield a poly(substituted acetylene) having dimethylsilyl (SiHMe$_2$) instead of trimethylsilyl group (SiMe$_3$) in poly(**SPA**) as shown in Scheme 1.1 (A). The structure was confirmed by NMR (Figure 1.1, A) and IR (Figure S1.1). The cocatalyst **PEA** was very effective in selecting the addition polymerization. The resulting polymer had a good selfsupporting membrane-forming ability. These results of the three modes of polymerizations of **HSPA** are summarized in Table 1.1. Poly**(HSPA**) prepared by using [Rh(nbd)Cl]$_2$/**PEA** showed the highest M*w* and the best membrane-forming ability. The degree of polymerization for addition polymerization (n) and polyaddition (m) were determined by GPC and NMR (Figure 1.1 and Figure S1.1).

In summary, we obtained poly(**HSPA**) having high Mw, good membrane forming ability, and well-controlled chemical structure by using $[Rh(nbd)Cl]_2$/PEA. Since the polymer has a main chain structure similar to poly(**SPA**) and smaller substituents than poly(**SPA**), good oxygen permeation behavior was expected. In fact, P_{O_2}/P_{N_2} for poly(**HSPA**) was two times higher than that for poly(**SPA**) (Table 1.2 and Figure 1.3, Nos. 1 and 6).

1.4.2 Copolymerization of HSPA with SPA by $[Rh(nbd)Cl]_2$/PEA catalytic system

To obtain a better gas permselective membrane than poly(SPA) and investigate the effect of $SiHMe_2$ on permselectivity, the copolymerizations of HSPA and SPA with different feed ratios using a $[Rh(nbd)Cl]_2$/PEA catalytic system were carried and the results are listed in Table 1.2. Copoly(HSPA/SPA) with less than 20 mol% of HSPA unit had a high Mw and good membrane forming ability similar to poly(SPA) (Nos. 4 and 5) and poly(HSPA), and copoly(HSPA/SPA) with more than 20 mol% of HSPA unit had a little a lower Mw and membrane forming ability compared with poly(SPA) (Nos. 13), but they could endure one atom pressure difference during permeation experiment.

Table 1.1 Selective polymerization of *p*-(dimethylsilyl)phenylacetylene (**HSPA**).

No.[a]	Polymerization[a] mode	Catalyst	$M_w/\times10^3$ [b]	M_w/M_n [b]	n[b]	m[c]	n/m	Membrane-forming-ability[d]
1	A	$[Rh(nbd)Cl]_2$/PEA	91.2	2.5	222	0	∞	++
2	P	$[Rh(PPh_3)_3Cl]$/NaI	9.9	4.5	1	14	0.07	−
3	A/P	$[Rh(nbd)Cl]_2$/TEA	32.2	4.8	36	6	6	+

[a]The numbers and codes correspond to those in Scheme 1 and Figure 1. [b]For *n*, see Scheme 1, determined by GPC. [c]For *m*, see Scheme 1, determined by ^{1}H NMR. [d]++: tough, +: brittle, −: poor.

Table 1.2 Oxygen and carbon dioxide permeation through copoly(**HSPA**/**SPA**) membranes prepared by using $[Rh(nbd)Cl]_2$/PEA catalytic system[a]

No.	HSPA unit in copolymer/mol %[b]	Yield[c] /%	M_w[d] /$\times10^4$	M_w/M_n[d]	P_{O_2}[e] /barrer	P_{O_2}/P_{N_2}	P_{CO_2}[e] /barrer	P_{CO_2}/P_{N_2}	Density[f] /g cm^{-3}	Membrane forming ability[g]
1	100 (= poly(HSPA))	84	8.9	2.5	76	4.17	—	—	0.886	++
2	50	82	9	2.6	98	4.03	554	16.1	0.871	++
3	24	90	16	3.0	107	3.35	—	—	0.852	++
4	19	92	16	2.8	122	3.13	1180	13.2	0.835	+++
5	10	91	29	2.7	160	3.06	1380	12.3	0.826	+++
6	0 (= poly(SPA))	94	24	2.7	171	2.36	1640	11.1	0.810	+++

[a]The polymer membranes were fabricated using solvent-casting method from $CHCl_3$ solution. [b]From ^{1}H NMR spectra. [c]Methanol-insoluble part. [d]Determined by GPC correlating polystyrene standard with THF eluent. [e]In 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} cmHg^{-1}. [f]By the floating method. [g]+++: very tough, ++: tough.

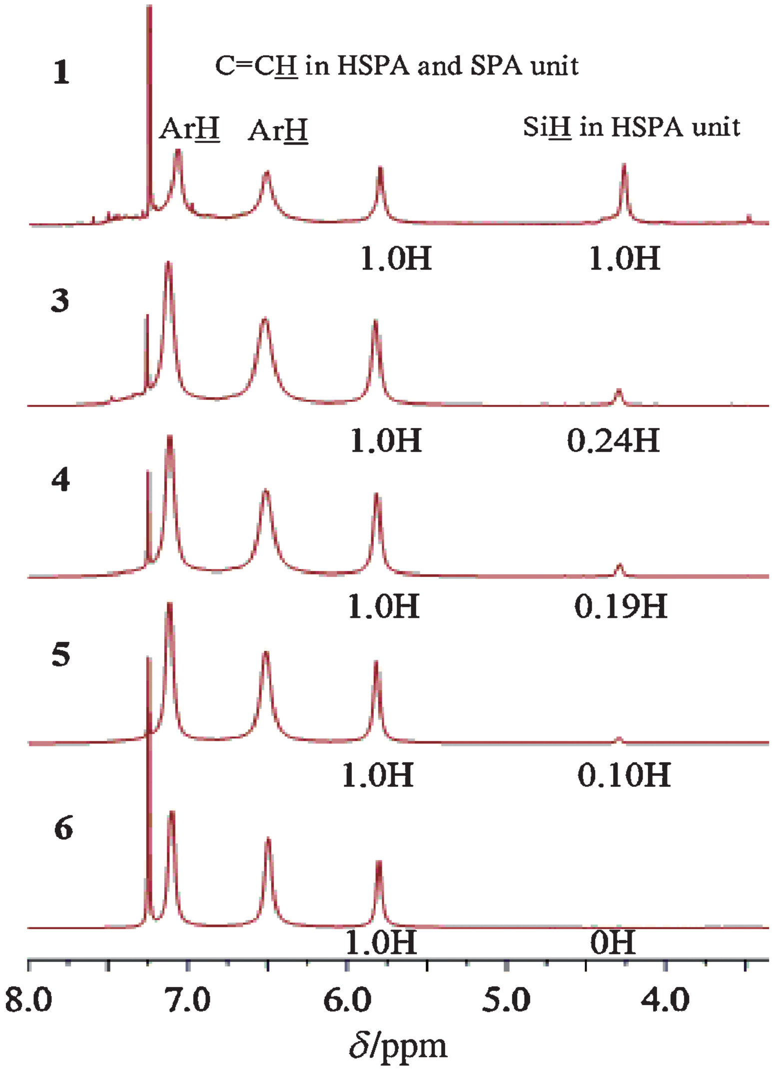


Figure 1.2. ^{1}H-NMR spectra of copoly(**HSPA/SPA**) (**3-5**) and poly(**HSPA**) (**1**) and poly(**SPA**) (**6**). The numbers (**1-6**) correspond to those in Table 1.2.

Figure 1.2 shows the ^{1}H-NMR of these copolymers with the two homopolymers. Their compositions were easily and clearly determined by HC= and SiH in the ^{1}H-NMR as shown in Figure 1.2. The ^{1}H-NMR spectra shows that no side reactions, which we described above, happened. The IR spectra (Figure S1.3) also show no side reactions. The copolymers having 10-50 mol% of **HSPA** unit were successfully synthesized because a unimodal peak was observed in the GPC (Figure S1.2). They all have a good membrane-forming ability and could be used for gas permeation measurement where a 1-atom pressure difference was applied, although they became more brittle when the HSPA unit increased.

1.4.3 Gas permselectivity through the poly(HSPA) and copoly(HSPA/SPA) self-supporting membranes

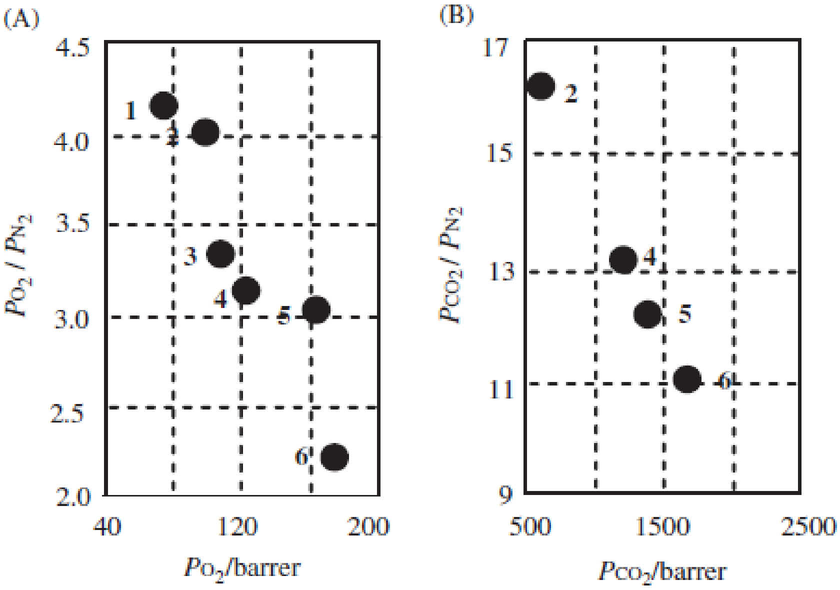


Figure 1.3 Relationship between the permeability and permselectivity of (**A**) O_2 and (**B**) CO_2 through the membranes of copoly(**HSPA/SPA**). The numbers (1-6) in the figure correspond to those in Table 1.2.

Results of the oxygen permeation through copoly(**HSPA/SPA**) membranes are shown in Table 1.2. Figure 1.3 shows the relationship between the oxygen permeability and permselectivity of the membranes. With increasing the **HSPA** unit in the copolymer, the P_{O_2}/P_{N_2} of the membranes increased while the P_{O_2} decreased. However, the degree of decrease in P_{O_2} was relatively low and smaller than that of the increase of P_{O_2}/P_{N_2}.

Especially, in the case of copoly(**HSPA**/**SPA**) (No. 5) containing 10 mol% of **HSPA** unit, the P_{O_2}/P_{N_2} was 1.5 times higher than that of poly(**SPA**) (No. 6) with almost no decrease in P_{O_2} (No. 6 to 5). Results of the CO_2 permeation through copoly(**HSPA**/**SPA**) membranes are also shown in Table 1.2. Figure 1.3 shows the relationship between the carbon dioxide permeability and permselectivity of N_2 through the membranes, similar to the oxygen permeation. With the increasing of the **HSPA** unit in the copolymer, the permselectivity of the polymeric membranes increased while the permeability decreased similar to the case of oxygen.

The density of poly(**HSPA**) was higher than that of poly(**SPA**) and when the content of **HSPA** unit in the copolymer increased, their densities (Table 1.2) increased resulting in the increase of P_{O_2}/P_{N_2} and the decrease in P_{O_2}. This may be caused by the size difference between $SiMe_3$ and $SiHMe_2$.

1.5 Conclutions

In conclusion, dimethylsilyl ($SiHMe_2$) group-containing polymers, i.e., poly(**HSPA**) and copoly(**HSPA**/**SPA**) having self-membrane forming property were synthesized by selective addition polymerization using $[Rh(nbd)Cl]_2$ (nbd: norbornadiene)/ phenylethylamine (PEA) without polyaddition for the first time.

Membranes from the copoly(**HSPA**/**SPA**)s showed higher permselectivities for oxygen and carbon dioxide over nitrogen than poly(**SPA**).

References and Notes

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Supporting Information (SI)

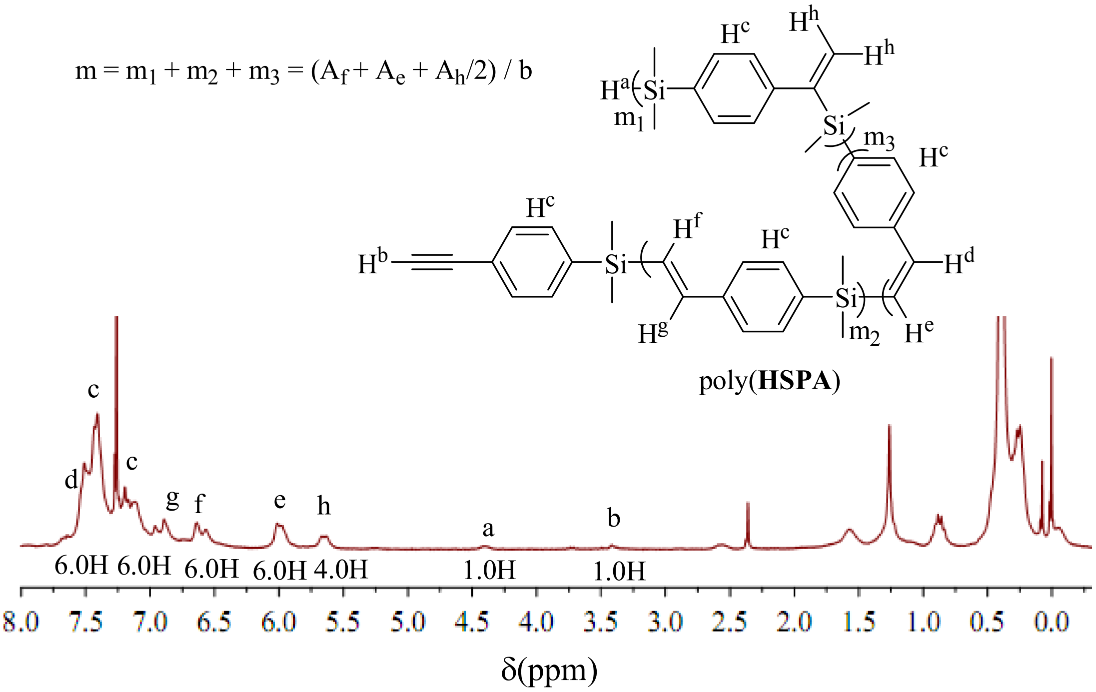


Figure S1.1 ^{1}H-NMR spectra of poly(**HSPA**) prepared by using [RhCl(PPh$_3$)$_3$] / NaI.

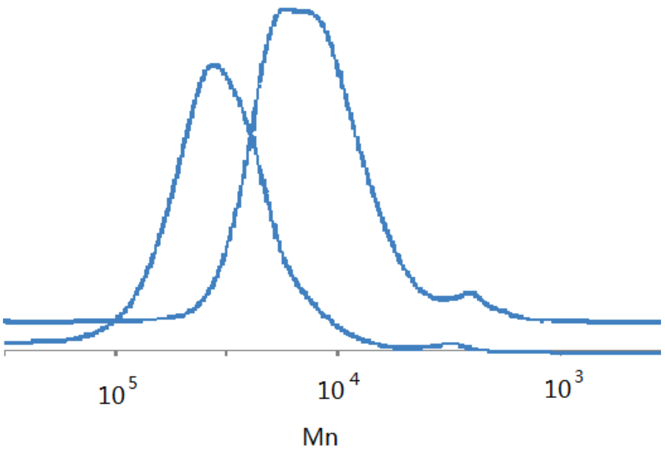


Figure S1.2 GPC trace of poly(**HSPA**) **(1)** and copoly(**HSPA**/**SPA**) **(3)** containing 24mol% **HSPA** unit.

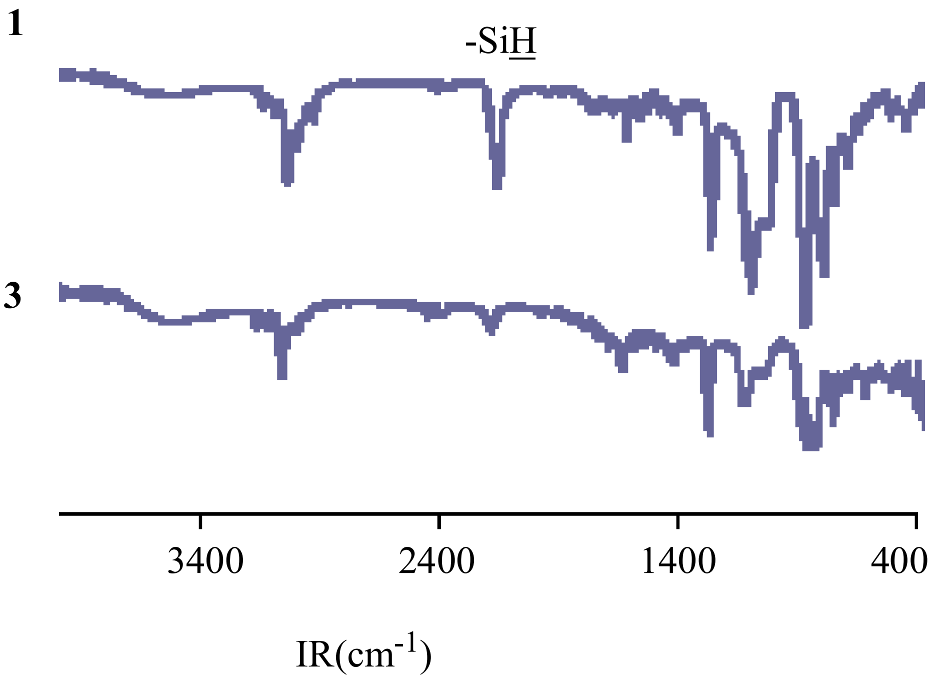


Figure S1.3 FTIR spectra of poly(**HSPA**)(**1**) and copoly(**HSPA**/**SPA**)(Table 1.2, no. **3**) containing 24mol% **HSPA** unit.

PART Ⅱ

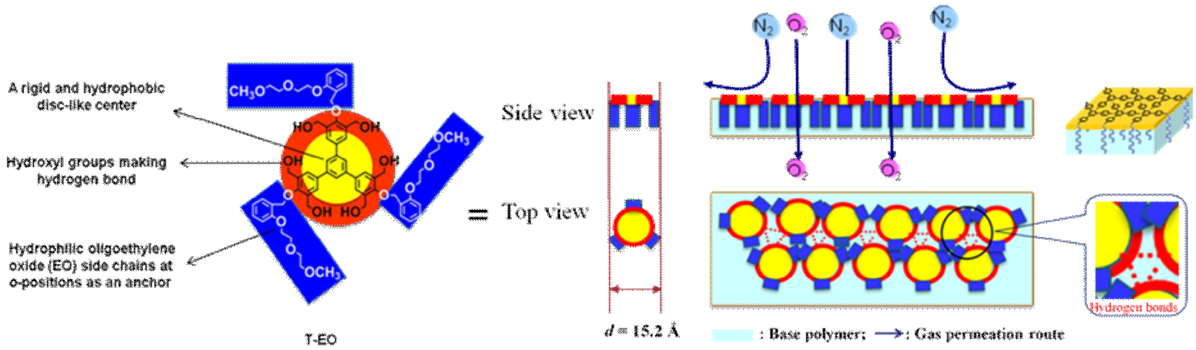
Enhancement of Oxygen Permselectivity by Surface Modification Using 2D Surface Modifer by SCAT of Poly(Substituted Phenylacetylene)s.

Chapter 2

Facile Synthesis of an Amphiphilic 1,3,5-Trisubstituted Benzene as a Novel Surface Modifier by Selective Photocyclic Aromatization and Efficient Improvement of Oxygen Permselectivity by the Addition of the Surface Modifier

2.1 Abstract

In this research, An amphiphilic 1,3,5-trisubstituted benzene as a new 2D surface modifier (**T-EO**) which has six hydroxy groups and three oligoethylene groups was successfully and easily synthesized by selective photocyclic aromatization in high conversion and selectivity for the first time. We prepared four kinds of blend membranes based on **PVA** or poly(trimethylsilylphenylacetylene) (poly(**SPA**)) containing the new amphiphilic cyclic trimer (**T-EO**) or the corresponding polymer (**P-EO**) by two different methods, membranes structure and gas permselectivity through these membranes wew also been discussed in this research.

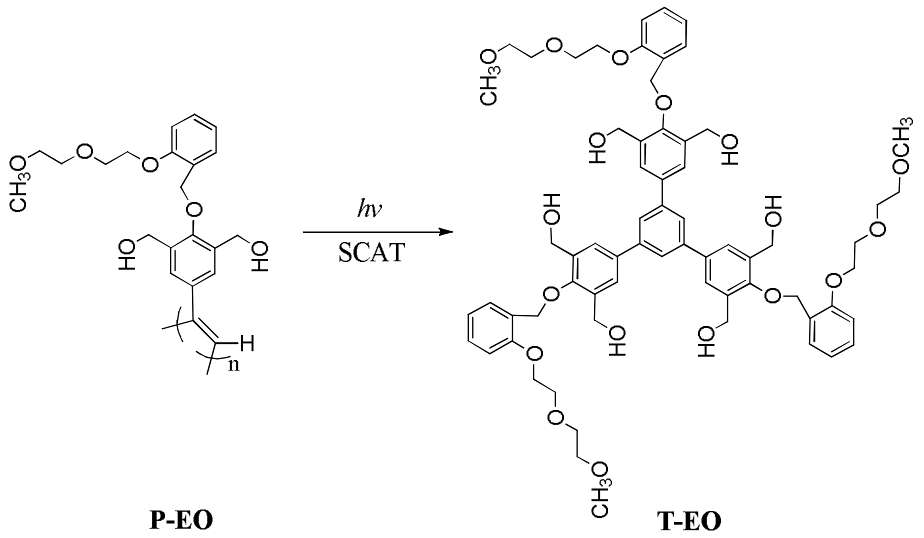


Structure of the 2D amphiphilic surface modifier and the surface modifer membranes

2.1 Introduction

Permselective membranes separating gases such as oxygen and nitrogen are very useful for many practical use to solve environmental and energy problems. So many studies have been reported on such membranes form not only organic polymers but also inorganic compounds.[1] The requirements for oxygen permselective membranes are (1) high permeability coefficient (Po_2 : cm^3(STP)·cm/cm^2·s·cmHg), (2) high separation factor ($\alpha = Po_2 / PN_2$), and (3) good membrane forming ability (high mechanical strength). However, the three requirements were not be able to be realized at the same time in almost all membrane materials reported. For example, membranes having higher Po_2 had lower α and membranes having higher α had lower Po_2, that is, Po_2 and α showed a tradeoff relationship.[1a] Also membranes having higher Po_2 tended to show too flexible and membranes having higher α tended to show too brittle.

To overcome the above problems, that is, to obtain materials satisfying the three requirements simultaneously, we reported surface modifications of conventional polymer membranes having enough mechanical strength by solvent casting of the mixture of small amounts of surface active polymers and the conventional base polymers.[2] It was an effective method to enhance α with a small decrease in Po_2 and giving no change to the good membrane forming abilities of the base polymers. However, the extent of enhancement in α was not enough.



Scheme 2.1 Selective photocyclic aromatization(SCAT) of P-EO.

In this study, to improve effectiveness of the surface modifiers, a new surface active compound, T-EO (Scheme 2.1) was designed. T-EO is a 1,3,5-trisubstituted benzene derivative which has a triphenylbenzene as a hydrophobic planer (2D) part and *ortho*-substituted three oligo(ethylene oxide) groups as hydrophilic parts and in addition it has six hydroxyl groups which can make hydrogen bonds. If T-EO was used as a surface modifier of hydrophilic polymer membranes, the hydrophilic surface exposed by hydrophobic air can be covered by the hydrophobic 2D part of T-EO, because the triphenylbenzene part tends to be accumulated on the surface and the oligo(ethylene oxide) groups can work as an anchor segment. In addition, if the six hydroxyl groups make hydrogen bonds between the molecules, a planar i.e, 2D supramolecular surface can be formed. However, since the molecular structure of T-EO is complicated and has three kinds of functional groups, it is difficult to obtain it in a high yield by a simple synthetic route. For example, the direct cyclization from EO

(Scheme S2.1) to T-EO is difficult because the catalyst using for the direct cyclyzation reaction has low tolerance to functional groups.

We found and reported recently a novel polymer reaction called SCAT (highly selective photocyclic aromatization reaction).[3] The SCAT reaction has many advantages.[3a] Among the advantages, high conversion, high selectivity, and simple procedure (only light irradiation) are very useful for synthesis of T-EO and therefore we selected SCAT as the synthetic route. In this communication, a facile synthesis of T-EO by the SCAT reaction and enhancement of α by surface modification by using T-EO are reported.

2.3 Experimental

2.3.1 Materials

All the solvents used for monomer synthesis and polymerization were distilled as usual. The polymerization initiator, $[Rh(nbd)Cl]_2$ (nbd=2,5 norbornadiene), purchased from Aldrich Chemical Co., Inc., was used as received. Poly(vinyl alcohol) (PVA) (M_w = 1500, degree of hydrolysis = 86.0~90.0 mol%) purchased from Wako Pure Chemical Industries, LTD., were used as received. Poly(1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene) (PSPA) ($M_w = 5.72\times10^6$) was synthesized according to our previous report.

2.3.2 Measurements

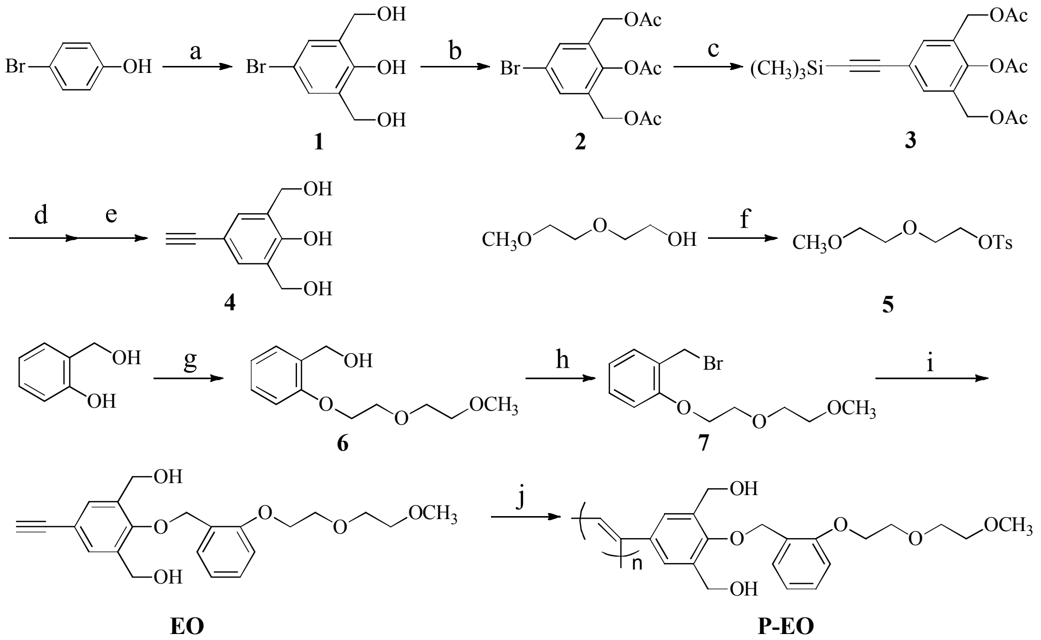
2.3.2.1 Measurement of oxygen and nitrogen permeability

Oxygen and nitrogen permeability coefficients (P_{O_2} and P_{N_2}: cm^3·(STP)·cm cm^{-2}·s^{-1}·cm·Hg^{-1}) and the oxygen separation factor ($\alpha = P_{O_2}/P_{N_2}$) were measured by a gas chromatographic method using YANACO GTR-10 according to Ref. [11]The gas permeability coefficient and can be explained on the basis of the solution-diffusion mechanism ($P = DS$), where D is the diffusion coefficient and S is the solubility coefficient. The diffusion coefficient was calculated by the time-lag method represented by $D = L^2 / 6\theta$, where L is the thickness of the membrane and θ is the time-lag.

2.3.2.2 Other measurements

^{1}H NMR (400MHz) spectra were recorded on a JEOL LEOLEX-400 spectrometer. The average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography (GPC) by using JASCO liquid chromatography instruments with PU-2080, DG-2080-53, CO-2060, UV-2070, CD-2095, and two polystyrene gel columns (Shodex KF-807 L, THF eluent, polystyrene calibration). CD spectra were recorded by using a JASCO J-720WI spectropolarimeter with a Peltier controller for temperatures at 20°C (a quartz cell of 1 mm path length; sample concentration: 0.100 to 2.00 mM based on the monomer unit). The infrared spectra were recorded on FT/IR-4200 (JASCO). MALDI-TOF-MS spectra were recorded using a Bruker Reflex II mass spectrometer (Bruker Daltonics). Contact angles of distilled water droplets on the membranes were measured with a DM-301， Kyowa Interface Science Co., LTD.

2.3.3 Synthesis of the monomer EO (Scheme 2.2)



Scheme 2.2. Synthesis and helix-sense-selective polymerization(HSSP) of EO. (a) HCHO, 2-propanol, and KOH; (b) Ac_2O and pyridine; (3) PPh_3, CuI, $PdCl_2(PPh_3)_2$, trimethylsilylacetylene, and Et_3N; (d)$LiAlH_4$, dry THF; (e) H_2O; (f) NaH, *p*-toluenesulfonyl chloride, and dry THF; (g) **5**, K_2CO_3, 18-crown-6, and acetone; (h) CBr_4, PPh_3, and CH_2Cl_2; (i) **4**, K_2CO_3, 18-crown-6, and acetone; (j) $[Rh(nbd)Cl]_2$, chiral phenylethylamine, and $CHCl_3$.

4-bromo-2,6- bis(hydroxymethyl)-1-phenol (**1**)

According to the literature procedure **1** was prepared. Yield: 56.8% (114g). ^{1}H-NMR (400MHz, DMSO-d_6): $\delta = 8.76$ (s, 1H, PhO*H*), 7.29(s, 2H, Ph*H*), 5.31(t, 2H, $J = 5$Hz, CH_2OH), 4.51(d, 4H, $J = 5$Hz, CH_2OH).

2,6-bis(acetoxymethyl)-4-bromo-1-phenyl acetate (**2**)

To a pyridine solution (50 mL) of **1** (10 g, 42.9 mmol), acedic anhydride

(30 mL, 317 mmol) was added dropwise at 0℃. The solution was stirred for 1.5h at room tempreture and then ethyl acetate (100 mL) was added to the mixture. The mixture was washed with saturated aqueous solution of $CuSO_4 \cdot 5H_2O$ to remove pyridine. The organic layer was dried over anhydrous $MgSO_4$. After concentration, the crude product was purified by silica-gel column chromatography to give **2** as a white solid. Yield: 78.4% (12.1 g). Rf = 0.3 (ethyl acetate / hexane = 1 / 2). ^{1}H-NMR (400MHz, DMSO-d_6): δ = 7.56 (s, 2H, PhH), 4.97(s, 4H, Ph(CH_2O)$_2$), 2.34(s, 3H, PhOCOCH_3), 2.09(s, 6H, Ph(CH_2OCOCH_3)$_2$).

2,6-bis(acetoxymethyl)-4-(trimethylsilylethynyl)-1-phenyl acetate (**3**)

A mixture of **2** (11.8 mg, 32.9 mmol), triphenylphosphine (610 mg, 2.33 mmol), copper (Ⅰ) iodine (752 mg, 3.95 mmol) and trimethylsilylacetylene (6.46 mL, 45.7 mmol) in triethylamine (130 mL) was refluxed for 24h. After the mixture was filtered, the solvent was removed by evaporation and the crude product was purified by silica-gel column chromatography to give **3** as a brown liquid. Yield: 95.6% (11.8 g). Rf = 0.3 (ethyl acetate / hexane = 1 / 3). ^{1}H-NMR (400MHz, $CDCl_3$, TMS): δ = 7.53 (s, 2H, PhH), 4.98(s, 4H, Ph(CH_2OAc)$_2$), 2.32(s, 3H, PhOCOCH_3), 2.06(s, 6H, Ph(CH_2OCOCH_3)$_2$), 0.22(s, 9H, Si(CH_3)$_3$).

2,6-bis(acetoxymethyl)-4-ethylphenol (**4**)

To a mixture of lithium hydride (3.0 g, 79.1 mmol) and tetrahydrofuran (120 mL), a tetrahydrofuran solution (15 mL) of **3** (14.92 g, 39.5 mmol) was added dropwise at 0℃. After the mixture was stirred for 2h at room tempreture, deionized water (140 mL) was added dropwise into the reaction mixture at 0℃. The mixture was stirred for 12h at room tempreture. The reaction mixture was treated with 2N HCl aq to precipitate aluminum salts. After the mixture was filtered, tetrahydrofuran was removed by evaporation. The product was dissolved in ethyl acetate and the solution was washed with water. The organic layer was dried over anhydrous $MgSO_4$. The crude product was purified by silica-gel column chromatography to give **4** as a white solid. Yield: 70.3% (4.9 g). Rf = 0.39 (ethyl acetate / hexane = 2 / 3). ^{1}H-NMR (400MHz, DMSO-d_6): $\delta =$ 8.98(s, 1H, PhO*H*), 7.27(s, 2H, $Ph(CH_2OH)_2$), 4.52(s, 4H, $Ph(CH_2OH)_2$), 3.91(s, 1H, *H*C≡C).

2-(2-Methoxyethoxy)ethyl-4-methylbenzenesulfonate (**5**)

To a mixture of sodium hydride (3.5 g, 87.6 mmol) and THF (50 mL), 2,6-bis(acetoxymethyl)-4-ethylphenol (7.8 mL, 65.7 mmol) was added dropwise at 0℃. Then *p*-toluenesulfonyl chloride (10.44 g, 54.75 mmol) dissolved in THF (20 mL) was added dropwise at 0℃. The solution was stirred for 9h at room tempreture and then deionized water was added to the mixture. The reaction mixture was treated with 4N HCl aq until the PH = 4 and it was extracted with CH_2Cl_2, and the organic layer was dried over anhydrous $MgSO_4$.

The crude product was purified by silica-gel column chromatography to give **5** as a colorless viscous liquid. Yield: 64.3% (9.6 g). Rf = 0.39 (ethyl acetate / hexane = 1 / 1). ^{1}H-NMR (400MHz, $CDCl_3$, TMS): δ = 7.8 (d, 2H, *J* = 8.5 Hz, Ph*H*), 7.34(d, 2H, *J* = 8.5 Hz, Ph*H*), 4.17(t, 2H, $S(=O)_2OCH_2$), 3.69(t, 2H, $S(=O)_2OCH_2CH_2O$), 3.58-3.48(m, 4H, $OCH_2CH_2OCH_3$), 3.35(s, 3H, OCH_3), 2.45(s, 3H, $PhCH_3$).

2-[(2-methoxyethoxy)methoxy]benzenemethanol (**6**)

To a mixture of 2-hydroxybenzyl alcohol (5.0 mg, 40.3 mmol), potassium carbonate (11.1 g, 80.6 mmol), and 18-crown-6 (5.35 mg, 20.1 mmol) in dry acetone (200 mL), 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate (12.15 g, 44.3 mmol) was added dropwise at 0℃. This solution was refluxed for 48h and allowed to room tempreture. After the mixture was filtered, it was extracted with CH_2Cl_2, washed with HCl aq and the organic layer was dried over anhydrous $MgSO_4$. The crude product was purified by silica-gel column chromatography to give **6** as a colorless viscous liquid. Yield: 66.2% (6.0 g). Rf = 0.31 (ethyl acetate / hexane = 1 / 1). ^{1}H-NMR (400MHz, $CDCl_3$, TMS): δ = 7.23(m, 2H, Ph*H*), 6.90(m, 2H, Ph*H*), 4.65(d, 2H, *J* = 5.0 Hz, $PhCH_2OH$), 4.18(t, 2H, $PhOCH_2CH_2$), 3.83-3.54(m, 6H, $CH_2CH_2OCH_2CH_2OCH_3$), 3.36(s, 3H, OCH_3), 3.33(t, 1H, *J* = 5.0 Hz, CH_2OH).

1-(bromomethyl)-2-(2-(2-methoxyethoxy)ethoxy)benzene (**7**)

To a mixture of **6** (5.71 g, 25.2 mmol) dissolved in CH_2Cl_2 (200 mL), Triphenylphosphine (10.0 g, 38.2 mmol) and CBr_4(14.2 g, 42.9 mmol) was dded dropwise at 0℃. This solution was stirred at this tempreture for 1h and add the saturated $NaCO_3$ aq to stop the reaction. This mixture was extracted with CH_2Cl_2, washed with saturated $NaCO_3$ aq and the organic layer was dried over anhydrous $MgSO_4$. The crude product was purified by silica-gel column chromatography to give **7** as as a colorless viscous liquid. Yield: 86.5% (6.3 g). Rf = 0.5 (ethyl acetate / hexane = 3 / 1). ^{1}H-NMR (400MHz, $CDCl_3$, TMS): δ = 7.28(m, 2H, $\mathrm{Ph}\mathit{H}$), 6.88(m, 2H, $\mathrm{Ph}\mathit{H}$), 4.57(s, 2H, $\mathrm{PhC}\mathit{H}_2\mathrm{Br}$), 4.19(t, 2H, $\mathrm{PhOC}\mathit{H}_2\mathrm{CH}_2$), 3.90-3.54(m, 6H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{OCH}_3$), 3.37(s, 3H, $\mathrm{OC}\mathit{H}_3$).

(5-ethylnyl-2-((2-(2-(2-methoxyethoxy)ethoxy)benzyl)oxy)-1,3-phenylene)dimethanol (**EO**)

To a mixture of 2,6-bis(acetoxymethyl)-4-ethylphenol (1.10 g, 6.17 mmol), potassium carbonate (1.71 g, 12.3 mmol), and 18-crown-6 (1.79 g, 6.79 mmol) in dry acetone (33 mL), 1-(bromomethyl)-2-(2-(2-methoxyethoxy)ethoxy)benzene (1.96 g, 6.79 mmol) was added dropwise at 0℃. This solution was refluxed for 40h and then allowed to room tempreture. After the mixture was filtered, it was extracted with CH_2Cl_2, washed with HCl aq and the organic layer was dried over anhydrous $MgSO_4$. The crude product was purified by silica-gel column chromatography to give the monomer EO as a white solid. Yield: 65.0 % (1.5 g). Rf = 0.17 (ethyl acetate / hexane = 1 / 1). ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = 7.53(s, 2H, $\mathrm{C{\equiv}CPh}\mathit{H}$), 7.45-7.30(m, 2H, *H*PhOCH$_2$CH$_2$), 7.03-6.90(m, 2H, *H*PhOCH$_2$CH$_2$), 5.01(s, 2H, PhOC*H*$_2$Ph), 4.75(d, 4H, *J* = 5.0 Hz, PhC*H*$_2$OH), 4.19(t, 2H, PhOC*H*$_2$CH$_2$), 3.88-3.57(m, 6H, CH$_2$C*H*$_2$OC*H*$_2$C*H*$_2$OCH$_3$), 3.36(s, 3H, OC*H*$_3$), 3.03(s, 1H, *H*C≡C), 2.82(t, 2H, *J* = 5.0 Hz, PhCH$_2$O*H*). $C_{22}H_{26}O_6$(386.4): Cacld. C 68.38, H 6.78, O 24.84; found. C 68.41, H 6.83, O 24.76.

2.3.4 Synthesis of P-EO by helix-sense-selective polymerization (HSSP) of EO

A solution of [Rh(nbd)Cl]$_2$ (1.37 mg, 0.38 μmol) and (S)- or (R)-phenylethylamine (PEA) (153 μL, 1.2 mmol) in CHCl$_3$ (1 mL) was added to a solution of EO (100 mg, 0.26 mmol) in CHCl$_3$ (1.6 mL). The reaction solution was stirred at room temperature for 12h. The crude polymer was purified by reprecipitation of the CHCl$_3$ solution into a large amount of hexane/ethyl acetate = 2/3 and dried in vacuo to give a brownish red polymer. ^{1}H-NMR (400MHz, CDCl$_3$ / DMSO-d_6 = 60 / 40): δ = 7.28(d, 1H, *H*PhOCH$_2$CH$_2$O), 7.16(t, 1H, *H*PhOCH$_2$CH$_2$O), 6.81(m, 4H, HC=CPh*H* and *H*PhOCH$_2$CH$_2$O), 4.57-4.37(m, 6H, PhOC*H*$_2$Ph and PhC*H*$_2$OH), 3.97-3.49(m, 10H, OC*H*$_2$C*H*$_2$OC*H*$_2$C*H*$_2$OCH$_3$ and PhCH$_2$O*H*), 3.36(s, 3H, OC*H*$_3$).

2.3.5 Synthesis of T-EO by selective photocyclic aromatization (SCAT) of P-EO

The P-EO membrane (thickness 20 μm) was irradiated under nitrogen by visible light (400-500 nm, 2.54 mW/cm^2) for 2 weeks. The reaction was monitored by GPC detected by UV and CD. Visible light (400-500 nm) irradiation was carried out by using a 300 W of Xe lamp (Asahi Spectra, MAX-302 with vis mirror module) through a cutoff filter (Asahi Spectra, LUX400 ($\lambda > 400$ nm), XF541 ($\lambda < 510$ nm), and XF546 ($\lambda < 610$ nm). ^{1}H-NMR (400MHz, $CDCl_3$, TMS): $\delta = 7.11$(s, 3H, 3(Ph*H*)), 7.09(s, 6H, 3(Ph*H*)), 4.57 (s, 12H, 3($PhC\mathit{H}_2OH$)), 5.13(s,6H, 3($PhOC\mathit{H}_2Ph$)), 7.58-6.81(m, 12H, 3($\mathit{H}PhOCH_2CH_2O$)), 4.87(s, 6H, 3($PhCH_2O\mathit{H}$)), 4.20-3.42(m, 24H, $OC\mathit{H}_2C\mathit{H}_2O$ $C\mathit{H}_2C\mathit{H}_2$), 3.36(s, 9H, 3($OC\mathit{H}_3$)).

2.4 Results and discussion

A 1,3,5-trisubstituted benzene (T-EO: Scheme 2.1) which has six hydroxyl groups and three oligoethylene groups was synthesized successfully for the first time by selective photocyclic aromatization(SCAT) method we developed and reported recently.[3a] In addition, the conversion and selectivity were very high and the procedure was pretty simple, that is, only light irradiation to the corresponding polymer membrane. Four kinds of blend membranes containing T-EO was prepared by using the two methods. One was conventional method (Method I) using one solvent which can solve the base polymer and the additives and the other was newly-developed method (Method II) using two solvents which were miscible but have different solubilities for the base polymer and the additive (T-EO) and different boiling points.

2.4.1 Oxygen permeation through the PVA based polymer memnranes

Oxygen permeation behavior (Po_2 and $\alpha = Po_2 / PN_2$) through the resulting four kinds of blend membranes were measured. The results were shown in Table 2.1 and Figure 2.1.

As shown in Table 2.1, nos. 1 and 4 and Figure 2.1A, the α values of T-EO/PVA blend membranes（●) increased steeply from 1.71 to 3.88 without any drop in Po_2 when only 1.0 wt% of the cyclic trimer (T-EO) was added. On the other hand, by adding the same amount(1.0 wt%) of the corresponding polymer (P-EO) into the PVA membrane（■), the permselectivity showed almost no change. By increasing the content of T-EO from 1.0 to 10 wt% in T-EO/PVA blend membranes, the permselectivity had almost no change but the permeability decreased markedly (Figure 2.1A and Table 2.1).

In summary, the PVA-based blend membrane containing 1.0 wt% of T-EO had the best performance and the small amount of addition of T-EO to PVA was effective method on enhancing the permselectivity of the PVA membranes without any drop in Po_2.

2.4.2 Oxygen permeation through the poly(SPA) based polymer membranes

The T-EO (5.0 wt%)/poly(SPA) membranes（●) prepared by Method II we developed showed a higher permselectivity compared with the ones（■) having the same content of T-EO by Method I (Figure 2.1B and Table 2.1). The permselectivities of the membranes prepared by Method II increased more largely compared with those by Method I although the decreases in permeability

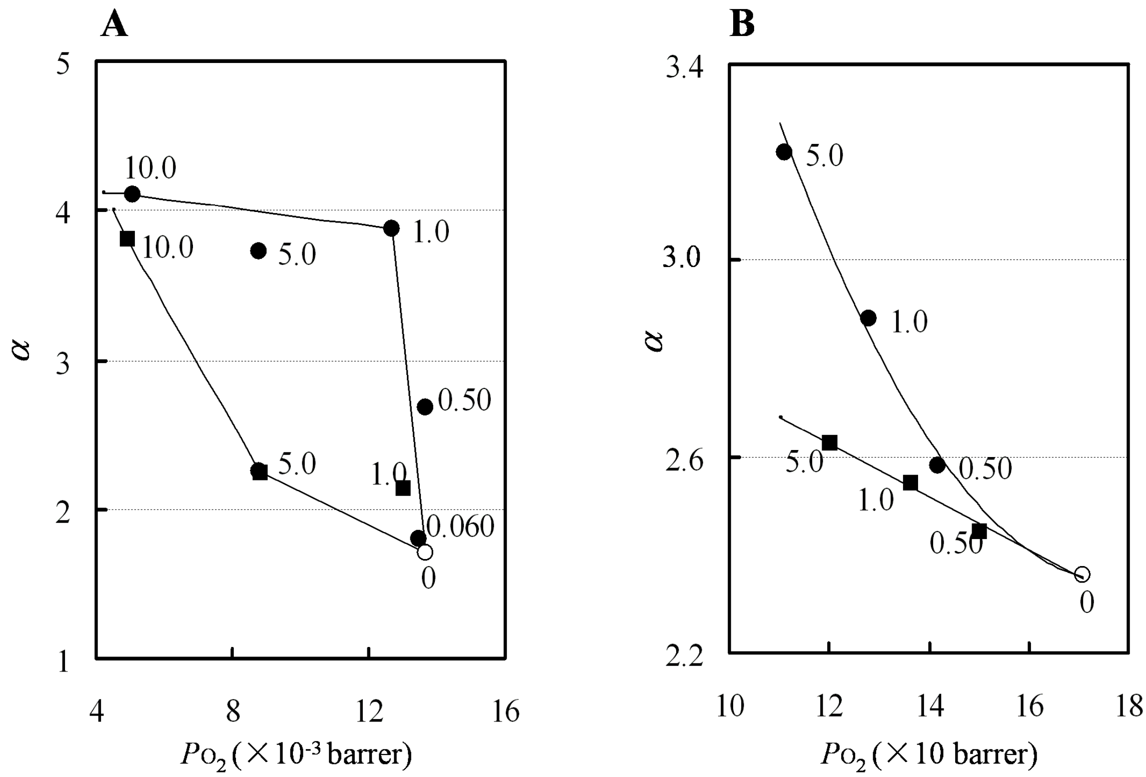


Figure 2.1 Relationship between the $P\mathrm{O}_2$ and α of the blend membranes (The numbers in the figure are the content of additives (wt%)). A: ●:T-EO/PVA blend membranes; ■:P-EO/PVA blend membranes. B: ■:T-EO/poly(SPA) blend membranes prepared by Method I; ●:T-EO/poly(SPA) blend membranes prepared by Method II (1 barrer = 10^{-10}cm^3(STP)·cm/cm^2·s·cmHg).

were almost the same (Figure 2.1B and the lower lines of Table 2.1). In summary, we measured oxygen permeation through the two kinds of T-EO/poly(SPA) blend membranes prepared by the two methods I and II. As a result, the membranes prepared by Method II showed a better performance on enhancing the permselectivity compared with the ones prepared by Method I.

Table 2.1. Oxygen permeation and contact angles of four kinds of blend membranes.

No.	T-EO[a] or P-EO	T-EO/PVA (Method I)			P-EO/PVA (Method I)		
		PO_2[b]	α[c]	θ[d]	PO_2[b]	α[c]	θ[d]
1	0	13.7	1.71	39.1	13.7	1.71	39.1
2	0.060	13.5	1.80	40.4	-	-	-
3	0.50	13.7	2.68	40.1	-	-	-
4	1.0	12.7	3.88	40.4	12.9	2.15	42.2
5	5.0	8.8	3.73	51.5	8.8	2.25	30.2
6	10	5.1	4.11	53.1	4.9	3.82	34.2
No.	T-EO[a]	T-EO/poly(SPA) (Method I)			T-EO/poly(SPA) (Method II)		
		PO_2[e]	α[c]	θ[d]	PO_2[e]	α[c]	θ[d]
7	0	171	2.36	106	171	2.36	106
8	0.50	150	2.45	105	142	2.58	100
9	1.0	136	2.55	107	128	2.88	95
10	5.0	120	2.63	104	111	3.22	87

[a] In wt%; [b]In $10^{-13}cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg$; [c]$\alpha = PO_2/PN_2$; [d]Contact angles of water droplets on the air surface of the blend membranes(°); [e]In $10^{-10}cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg$.

In conclusion, by comparing these four kinds of membranes above mentioned, we concludes that the PVA-based membrane containing 1.0 wt% T-EO on the surface was the best judging from the performance and the degree of the improvements.

2.4.3 Structure comfirmation of the surface modified membranes their effect on the permeation behavior

To obtain the reason for the effective improvement of the α values without large drops in *Po*$_2$ described above, we investigated their surfaces of the blend membranes by measuring contact angles (*θ*) of water droplets. The results are shown in Figure 2.2 and Table 2.1.

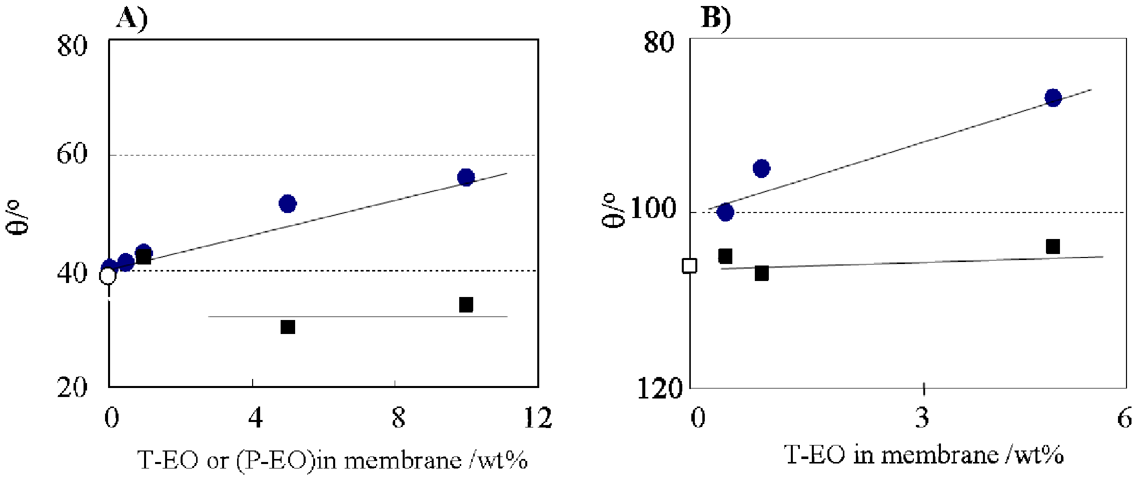


Figure 2.2 Plots of contact angles vs the content of additives in the blend membranes. A: ●:T-EO/PVA blend membranes; ■:P-EO/PVA blend membranes. B: ■:T-EO/poly(SPA) blend membranes prepared by Method I; ●:T-EO/poly(SPA) blend membranes prepared by Method II

Judging from the θ values in Figure 2.2A and the upper part of Table 2.1, nos.1-6), the surface of T-EO/PVA blend membranes (●) became more hydrophobic than the original pure polymer membrane (PVA) but the surface of P-EO/PVA blend membranes (■) did not become more hydrophobic. Therefore the surface of T-EO/PVA blend membranes were more effectively modified by the newly-synthesized additives (T-EO) than those of P-EO/PVA blend membranes. In addition, as described above, T-EO/PVA blend membranes showed much better performance of oxygen permselectivity

P-EO/PVA blend membranes (Figure 2.1A). Therefore, the effective improvement and good performance in T-EO/PVA blend membranes are thought to be caused by the effective surface-modification by T-EO.

In the case of addition of 5.0 wt% of T-EO or P-EO to PVA, they showed almost the same Po_2 but the former membrane showed about twice higher α than the latter as described above (Figure 2.1A) and simultaneously the θ value of the former membrane showed higher than that of the latter (Table 2.1, No. 5, and Figure 2.2A). Therefore, the modified surface can be one of the reasons for the effective enhancement of α. The difference effect between T-EO and P-EO may be caused by the difference of their molecular assemble structures on the surface. It may mean T-EO is a good 2D surface modifier. Especially in the case of addition of 1.0 wt% of T-EO to PVA, the blend membrane showed about twice higher α than the original pure PVA membrane with almost no drop in Po_2 (Figure 2.1A). It may also be caused by effective surface modification although no clear change in θ value was observed. It is thought to be that the surface was modified very effectively and no alternation of the inside or bulk structure of the blend membrane and as a result only α was increased and no drop in Po_2 was observed.

Judging from the θ values in Figure 2.2B and the lower part of Table 2.1, nos.7-10, the surface of T-EO/poly(SPA) blend membranes prepared by Method II which was developed in this study became more hydrophilic than the original pure polymer membrane (poly(SPA)) but the surface of T-EO/poly(SPA) blend membranes prepared by Method I (conventional method) did not become more hydrophilic. Therefore the surfaces of T-EO/poly(SPA) blend membranes prepared by Method II were more effectively modified by the newly-synthesized additives (T-EO) than those by Method I. It was unusual phenomena that the surfaces were modified by more hydrophilic additives by Method II. We have achieved such unusual modification by Method II. The reason for the success is not clear at present but we speculate the reason as follows: The point is the difference of the boiling points (bp) of the two solvent used. Since the more hydrophilic solvent (methanol) having a lower bp, which is evaporating first, has higher solubility for T-EO, which is more hydrophilic than poly(SPA), T-EO could be accumulated at the surface. As we described above, T-EO/poly(SPA) blend membranes prepared by Method II showed better performances of oxygen permselectivity than those by Method I (Figure 2.1B). Therefore, the effective improvement and good performance in oxygen permeation of T-EO/ poly(SPA) blend membranes prepared by Method II are thought to be caused by the effective surface-modification.

2.5 Conclutions

In conclusion, we reported the four kinds of blend membranes based on PVA or poly(SPA) containing the new amphiphilic cyclic trimer (T-EO), which was simply prepared in a high yield by SCAT reaction, we developed before, of the corresponding polymer (P-EO) or P-EO, that is, T-EO/PVA, T-EO/ PVA, and

T-EO/poly(SPA) membranes prepared by the conventional solvent casting method(Method I) and T-EO/ poly(SPA) membranes prepared by the new solvent casting method we developed(Method II). T-EO/PVA membranes prepared by Method I and T-EO/poly(SPA) membranes prepared by Method II showed better performance in oxygen permeation than P-EO/PVA membranes prepared by Method I and T-EO/poly(SPA) membranes prepared by Method I, respectively. Especially the 1.0wt% of T-EO containing PVA-based membranes showed the best result, because the α became twice higher than that of the original PVA membrane without any decrease in Po_2. The ideal improvement may be caused by effective surface modification by T-EO. Since T-EO has a planner part in its molecule, it can arrange in 2D manner on the surface. The 2D supramolecular surface may improve the performance. Further investigation about surface structures are now in progress.

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[1] a) J. Ahn, W. J. Chung, I. Pinnau, J. Song, N. Du, G. P. Robertson, M. D. Guiver, *J. Membr. Sci.* **2010**, *346*, 280. b) L. M. Robeson, *J. Memb. Sci.* **2008**, *320*, 390. c) T. Aoki, *Prog. Polym. Sci.* **1999**, *24*, 951. d) T. Aoki, T. Kaneko, M. Teraguchi, *Polymer* **2006**, *47*, 4867. e) C. H. Jung, J. E. Lee, S. H. Han, H. B. Park, Y. M. Lee, *J. Membr. Sci.* **2010**, *350*, 301. f) S. K. Sen, S. Banerjee, *J. Membr. Sci.* **2010**, *350*, 53. g) S. Thomas, I. Pinnau, N. Du, M. D. Guiver, *J. Membr. Sci.* **2009**, *333*, 125. h) J. Li, J. Wang, Y. Zang, T.

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Supporting information:

1. Characterization of the T-EO

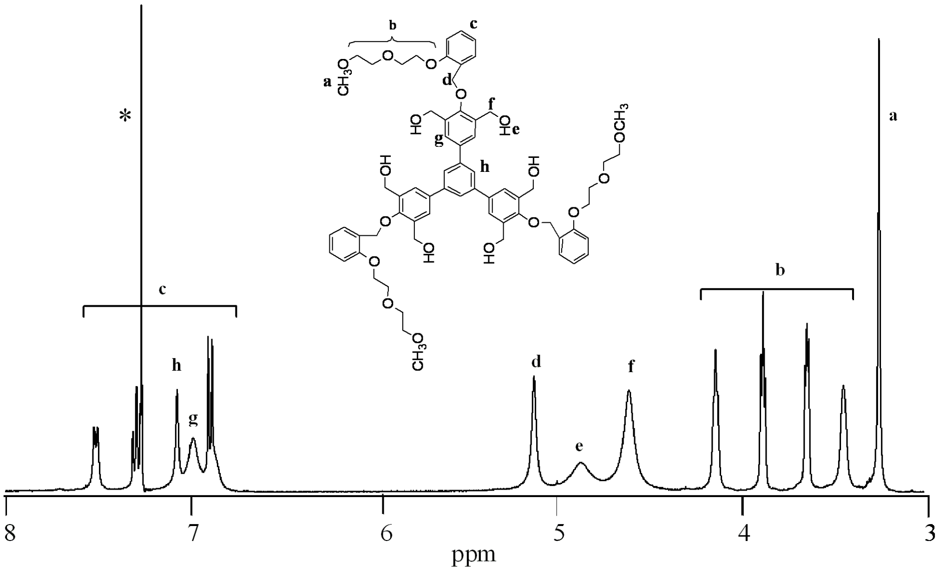


Figure S2.1 ^{1}H-NMR spectra of T-EO prepared by SCAT. (* : $CDCl_3$)

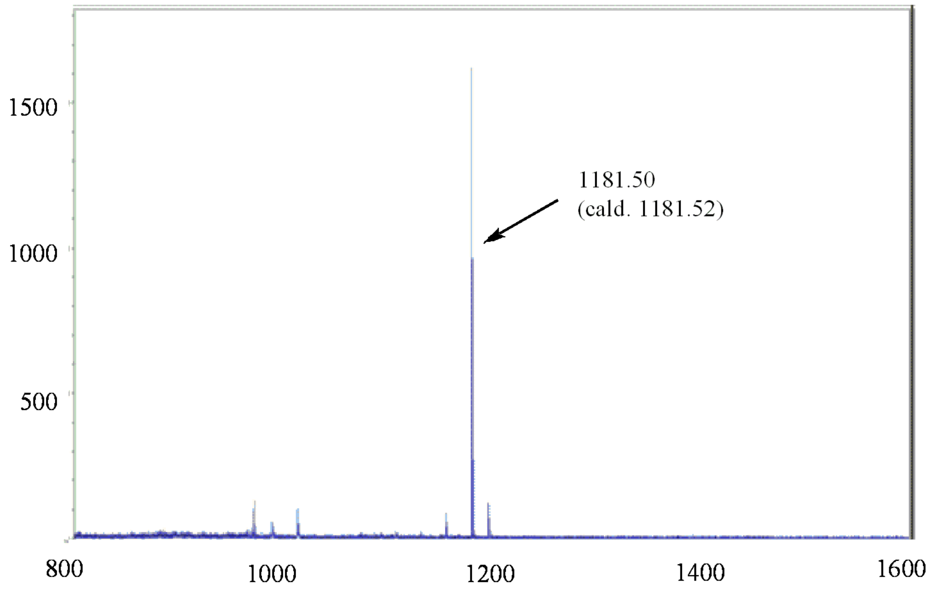


Figure S2.2 MALDI-TOF-MS of T-EO prepared by SCAT.

2. Preparation of membranes.

Method I(conventional method): A toluene solution of the polymer and

0.060-5.0 wt.-% of the additives was cast on a poly(tetrafluoroethylene) sheet. After the solvent was evaporated for 24h at r.t., the membrane was detached from the sheet and dried in vacuo for 24h at room tempreture.

Method II(newly developed method): A toluene solution of poly-(trimethylsilylphenylacetylene) (poly(SPA)) and methanol solution of T-EO was first blended together and then the solution was cast on a poly(tetrafluoroethylene) sheet. After the solvent was evaporated for 24h at r.t., the membrane was detached from the sheet and dried in vacuo for 24h at room tempreture.

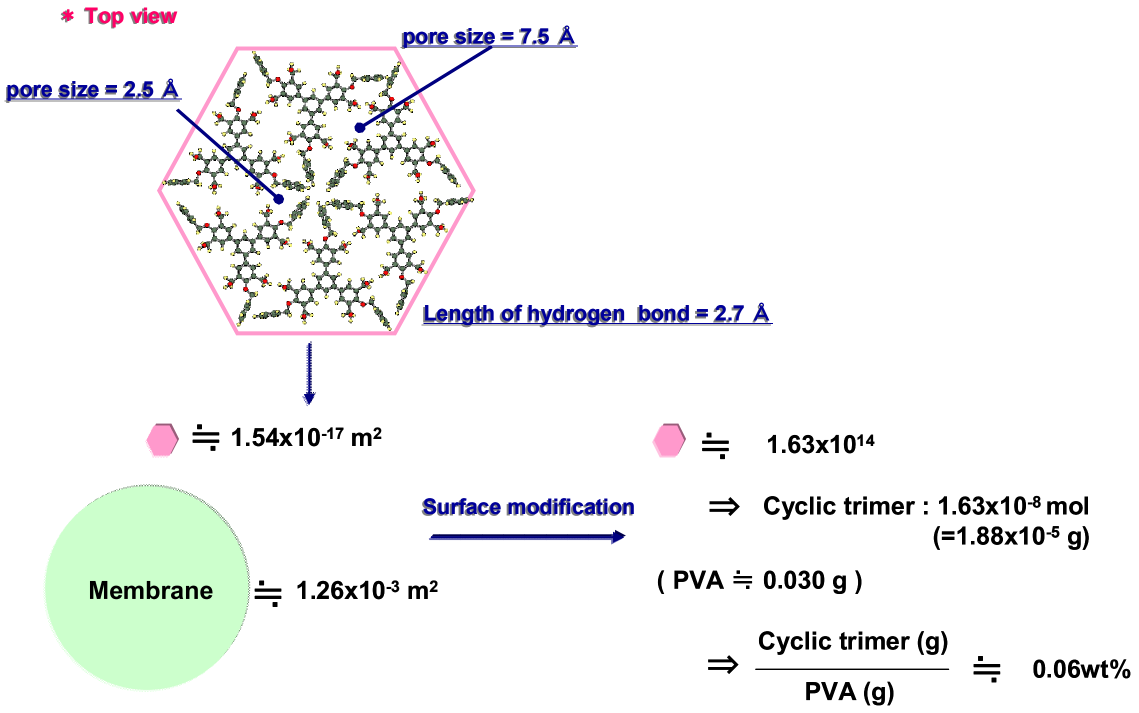


Figure S2.3 Ideal and possible 2D surface structure created by T-EO supramolecular assembly connected by hydrogen bonds and estimation of the minimum amounts of T-EO needed to form the 2D supramolecular assembly.

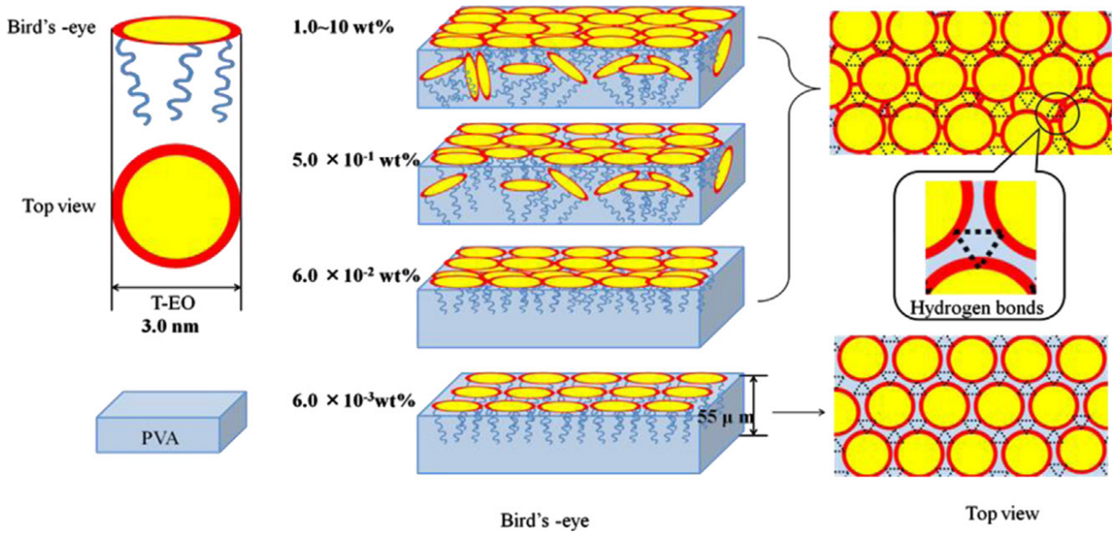
Chapter 3

Facile Synthesis of fFive 2D SurfaceModifiers by Highly Selective Photocyclic Aromatization and Efficient Enhancement of Oxygen Permselectivities of Three Polymer Membranes by Surface Modification Using a Small Amount of the 2D Surface Modifiers

3.1 Abstract

A facile synthesis of novel five 2D (planar) surface modifiers having a triphenylbenzene derivatives as a 2D structure has been achieved by the highly selective photocyclic aromatization reaction. Efficient enhancement of oxygen permselectivities through the three polymer membranes has been achieved by adding a small amount (<5.0 wt%) of the 2D surface modifiers. Among the five 2D surface modifiers, a modifier compound having oligoethylene oxide groups showed the best performance for the enhancement.

These improvements were thought to be caused mainly by improvement of the solution selectivity on the membrane surface where the 2D surface modifiers were accumulated.



Possible membrane structures of T-EO/PVA membranes having different amount of T-EO.

3.2 Introduction

Permselective membranes separating gases such as oxygen and nitrogen have many practical uses to solve environmental and energy problems. So, many studies have been reported on such membranes in the form of not only organic polymers but also inorganic compounds[1-25]. The requirements for oxygen permselective membranes are (1) a high permeability coefficient (Po_2 : $cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg$), (2) a high separation factor ($\alpha = Po_2 / P_{N_2}$), and (3) good membrane forming ability (high mechanical strength). However, it has proven difficult to realize all three requirements at the same time in almost all membrane materials reported. For example, membranes having higher Po_2 values had lower α values, and membranes having higher α values had lower Po_2 values, that is, Po_2 and α showed a tradeoff relationship[1-25]. Also membranes having higher Po_2 values tended to be too flexible and those having higher α values tended to be too brittle.

To solve the above problems, that is, to obtain materials that simultaneously satisfy the above three requirements, we reported surface modifications of conventional polymer membranes having enough mechanical strength by solvent casting of a mixture of small amounts of surface active polymers and the conventional base polymers[26-28]. It was an effective method to enhance α with a small decrease in Po_2, while resulting in no change to the good membrane forming abilities of the base polymers. Although similar reports have been made for nanofiltration of aqueous solution,[29-31] to the best of our knowledge, there have been no reports except for our group[26-28] on such methods of surface modifications of membranes for enhancing gas separation selectivities. However, the extent of enhancement of α was not enough. In this study, to improve the effectiveness of the surface modifiers, five kinds of 2D(= a planar structure) surface modifiers were designed (Chart 3.1). They have a π-conjugated planar (2D) part, hydroxyl groups, and hydrophilic or hydrophobic groups.

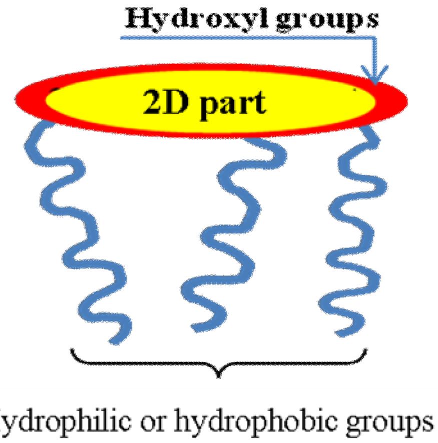
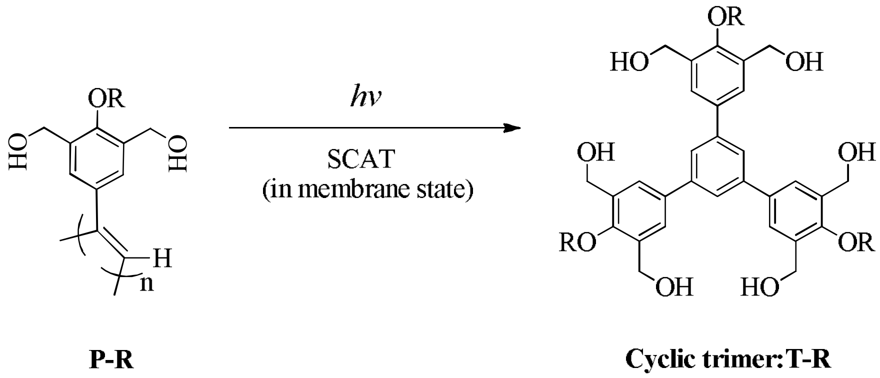


Chart 3.1 Molecular design of 2D surface modifiers.

We have reported recently a novel polymer reaction called SCAT (highly selective photocyclic aromatization reaction) (Scheme 3.1)[32]. It quantitatively gives 1,3,5-triphenylbenzene derivatives having six hydroxyl groups and any kinds of three substituents by a simple procedure (using only light irradiation) in high conversions and selectivity. In addition the reaction has good tolerance for many kinds of functional groups. These advantages of SCAT are very useful for the synthesis of 2D surface modifiers having different kinds of functional groups and therefore we selected SCAT as the synthetic route in this study. In this article, a facile synthesis of the 2D surface modifiers by the SCAT reaction and enhancement of by surface modification using the 2D surface modifiers are reported.



Scheme 3.1 Highly selective photocyclic aromatization(SCAT)

3.3 Experimental

3.3.1 Material

All the solvents except for tetrahydrofuran(THF) used for monomer synthesis and polymerization were distilled as usual. Dry THF (99.5% purity) purchased from Kanto chemistry was used. The polymerization initiator, $[Rh(nbd)Cl]_2$ (nbd = 2,5-norbornatiene) purchased from Aldrich Chemistry was used as received. Poly(vinyl alchohol)(PVA) purchased from Wako Pure Chemistry Industries, Ltd. was used as received. 1-Phenyl-2-*p*-(trimethylsilyl)phenylacetylene (DPA)[33] and *p*-(trimethylsilyl)phenylacetylene(SPA)[34] were synthesized and polymerized according to the literatures.

3.3.2 Synthesis of new 2D surface modifiers(T-R)(Chart 3.2)(Scheme 3.2)

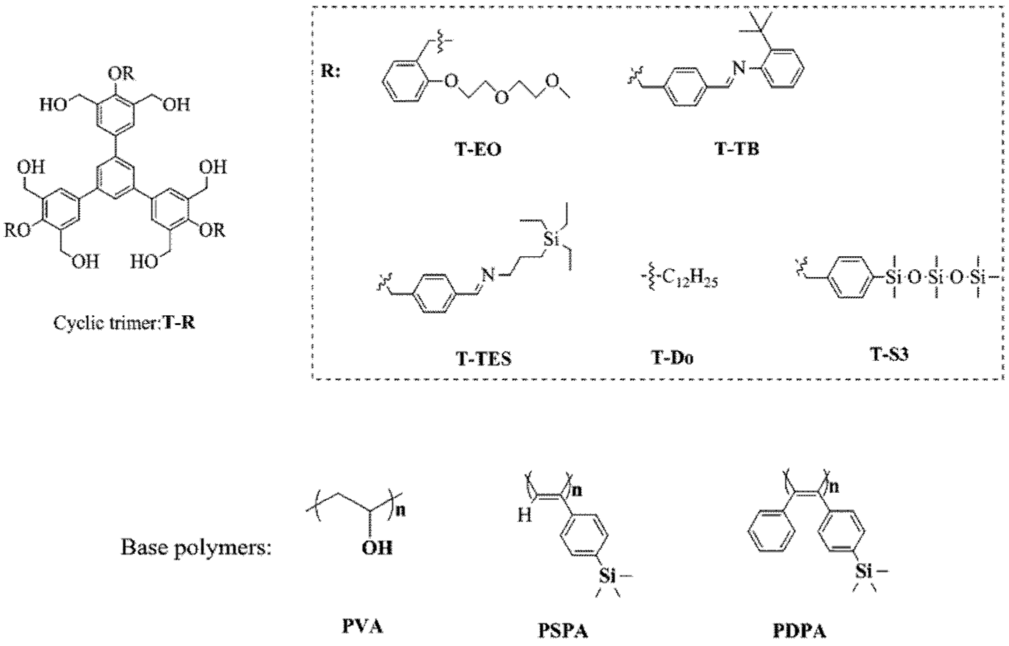
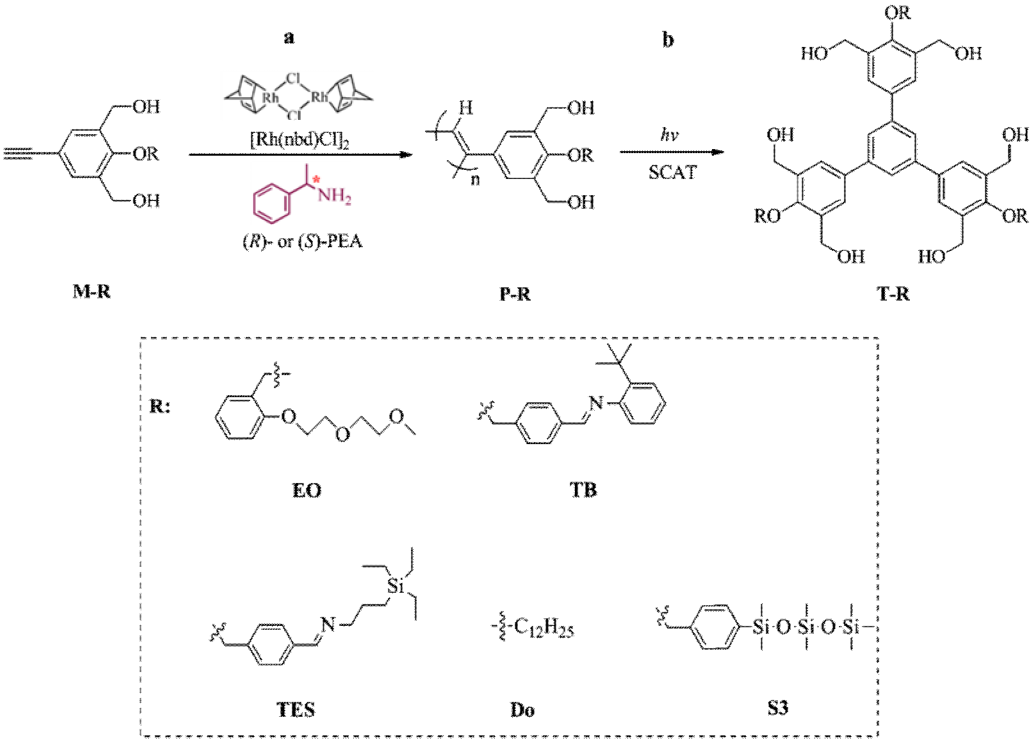


Chart 3.2 Chemical structures of the 2D surface modifiers and the base polymers.

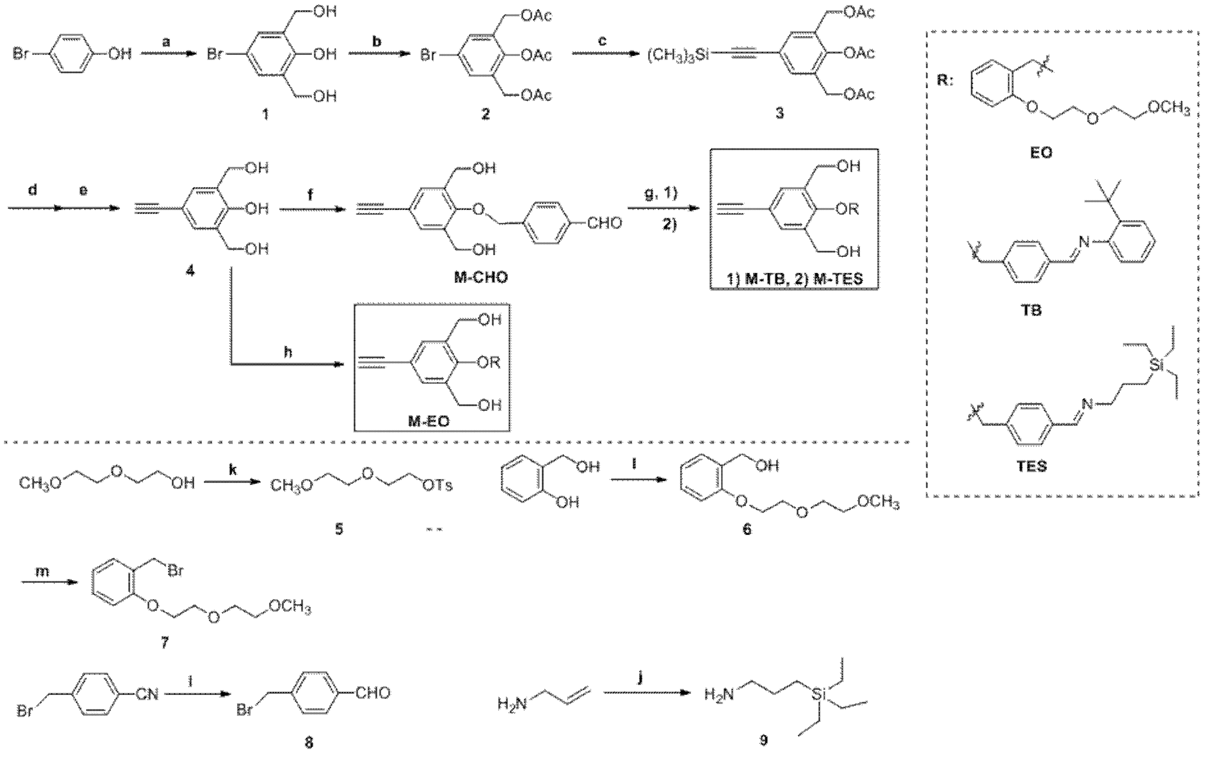


Scheme 3.2 Synthesis of the 2D surface modifiers by **a**) helix-sense-selective polymerization(HSSP) and **b**) highly selective photocyclic aromatization(SCAT).

3.3.2.1 Synthesis of M-EO, M-Do and M-S3 (Scheme 3.3)

(1) 3,5-bis(hydroxymethyl)-4-{2-(1,4,7-trioxaoctyl)phenylmethyl}oxy-1-phenylacetylene (**M-EO**) (Scheme 3.3)

According to the synthetic route shown in Scheme 3.3, **M-EO** was synthesized via compounds **1-7** in 8.1% as a total yield.(Chapter 2) All the following reaction procedures were conducted under dry nitrogen.



Scheme 3.3 Synthesis of the monomers(**M-R**). (a) HCHO, 2-propanol, and KOH; (b) Ac_2O and pyridine; (c) PPh_3, CuI, $PdCl_2(PPh_3)_2$, trimethylsilylacetylene, and Et_3N; (d) $LiAlH_4$, dry THF; (e) H_2O; (f) **8**, K_2CO_3, DMF; (g) 1): 2-*tert*-butylaniline, Al_2O_3, THF; 2): **9**, Al_2O_3, THF; (h) **7**, K_2CO_3, 18-crown-6, and acetone; (i) Dry CH_2Cl_2, DIBAL; (j) $(CH_3CH_2)_3SiH$, $H_2PtCl_6{\cdot}{}_6H_2O$, toluene; (k) NaH, *p*-toluenesulfonyl chloride, and dry THF; (l) **5**, K_2CO_3, 18-crown-6, and acetone; (m) CBr_4, PPh_3, and CH_2Cl_2;

(2) Synthesis of 3,5-bis(hydroxymethyl)-4-dodecyloxy-1-phenylacetylene (**M-Do**) (Scheme 3.3)[35]

M-Do was synthesized according to our previous paper[31]. ^{1}H NMR ($CDCl_3$, TMS): δ = 7.48(s, 2H, $(PhH)_2$), 4.70(d, 4H, J = 5.9 Hz, $(CH_2OH)_2$), 3.88(t, 2H, J = 6.6 Hz, OCH_2CH_2), 3.04(s, 1H, C≡CH), 2.11(t, 2H, J = 5.9 Hz, $(CH_2OH)_2$), 1.79(quint, 2H, J = 6.6 Hz, $OCH_2CH_2CH_2$), 1.50-1.20(m, 18H, $OC_2H_4(CH_2)_9CH_3$), 0.89(t, 3H, CH_2CH_3). IR (KBr): 3600-3100(OH), 3308(HC≡C), 3000-2800(CH), 2116(C≡C), 1200-1000(CO) cm^{-1}. Anal. Cacld for $C_{22}H_{34}O_3$: C, 76.70; H, 9.36; O, 13.94; Found: C, 76.65; H, 9.76; O, 13.68.

(3) Synthesis of 3,5-bis(hydroxymethyl)-4-{4'-(1-heptamethyltrisiloxanyl)benzyloxy}-1-phenylacetylene (**M-S3**) (Scheme 3.3)[37]

M-S3 was synthesized according to our previous paper[33].. ^{1}H NMR ($CDCl_3$, TMS): δ = 7.59 (d, 2H, J = 8.0 Hz, $PhOCH_2(PhH)_2$), 7.50(s, 2H, C≡C$(PhH)_2$), 7.40(d, 2H, J = 8.0 Hz, Si$(PhH)_2$), 4.96(s, 2H, $PhOCH_2$), 4.67(d, 4H, J = 6.0 Hz, $Ph(CH_2OH)_2$), 3.03(s, 1H, C≡CH), 1.96(t, 2H, J = 6.0 Hz, $(PhCH_2OH)_2$), 0.33(s, 6H, $PhSi(CH_3)_2$), 0.06(s, 9H, $Si(CH_3)_3$), 0.03(s, 6H, $OSi(CH_3)_2O$). IR (KBr): 3600-3100(OH), 3312(HC≡C), 2109(C≡C), 1258(SiC) cm^{-1}. Anal. Cacld for $C_{24}H_{36}O_5Si_3$: C, 58.97; H, 7.42; Found: C, 58.96; H, 7.49.

3.3.2.2 Synthesis of M-TB and M-TES (Scheme 3.3)

According to the synthetic route as shown in Scheme 3.3, **M-TB** and **M-TES** were synthesized via compounds **1-4, M-CHO, 8-9** in 12.0% as a total yield. All the following reaction procedures were conducted under dry nitrogen.

(1) Synthesis of 3,5-bis(hydroxymethyl)-4-{4’-(2’’-tert-butyl-1-iminomethyl)benzyloxy}-1-phenylacetylene (**M-TB**) (Scheme 3.3)[38]

4-Bromomethylbenzaldehyde(**8**) (Scheme 3.3)

4-bromomethylbenzonitrile (14.0 g, 71.4 mmol) was dissolved in dry CH_2Cl_2 (260 mL) and the solution was stirred at 0 ℃ for 20min. 1.0 M diisobutylaluminium hydride hexane solution (DIBAL) (70 mL, 70 mmol) was added dropwise to the solution at 0℃. The solution was stirred for 15min at 0℃ and then DIBAL solution (35 mL) was added dropwise again. The mixture was stirred for 15 min at 0℃ and for 30 min at 25℃. This reaction mixture was washed with 50% H_2SO_4 (150 mL) aq. solution to precipitate the aluminium salt. After the mixture was filtered, deionized water was added to the solution and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ for 1h. This mixture was filtered and concentrated to give **8** as a white solid. Yield: 56.3% (8.00 g). ^1H NMR ($CDCl_3$, TMS): $\delta = 10.0$ (s, 1H, PhCHO), 7.85 (d, 2H, J = 8.0 Hz, $BrCH_2(PhH)_2$), 7.54 (d, 2H, J = 8.0 Hz, $(HPh)_2CHO$), 4.50 (s, 2H, $BrCH_2Ph$).

3,5-Bis(hydroxymethyl)-4-(4’-formylbenzyloxy)phenylacetylene(**M-CHO**) (Scheme 3.3)

A mixture of **4** (3.79 g, 21.3 mmol), **8** (4.23 g, 21.3 mmol) and K_2CO_3 (8.80 g, 63.9 mmol) in DMF (107 mL) was stirred for 50 h at 70℃. After the mixture was filtered, the solvent was evaporated. The residue was washed with water and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ for 1h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **M-CHO** as a white solid. Rf = 0.70 ($CHCl_3$ / MeOH = 95 / 5 (v/v)). ^{1}H NMR ($CDCl_3$, TMS): δ = 10.0 (s, 1H, PhCHO), 7.94 (d , 2H, J = 8.0 Hz, $(HPh)_2CHO$), 7.63 (d , 2H, J = 8.0 Hz, $OCH_2(PhH)_2$), 7.54 (s, 2H, $HC\equiv C(PhH)_2$), 5.08 (s, 2H, $PhOCH_2Ph$), 4.69 (d, 4H, J = 6.0 Hz, $Ph(CH_2OH)_2$), 3.07 (s, 1H, $HC\equiv C$), 1.74 (t, 2H, J = 6.0 Hz, $Ph(CH_2OH)_2$).

3,5-Bis(hydroxymethyl)-4-{4'-(2''-tert-butyl-1-iminomethyl)benzyloxy}-1-phenyl-acetylene (**M-TB**) (Scheme 3.3)

A mixture of **M-CHO** (200 mg, 0.670 mmol), 2-tert-butylaniline (0.21 mL, 1.4 mmol) and Al_2O_3 (700 mg) in dry THF (7 mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed by evaporation to yield a white solid. The crude product was purified by recrystallization from chloroform/hexane(= 10 / 90 (v/v)) to give **M-TB** as a white solid. Yield: 70.0 % (200 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 8.36(s, 1H, PhCH=N), 7.90-6.81(m, 10H, PhH), 5.01(s, 2H, $PhOCH_2Ph$), 4.62(d, 4H, $Ph(CH_2OH)_2$), 3.38(s, 1H, $HC\equiv C$),1.43(s, 9H, $PhC(CH_3)_3$). IR (KBr): 3326 (OH), 3232 ($HC\equiv C$), 1646 (C=N) cm^{-1}. Anal. Cacld for $C_{28}H_{29}O_3N$: C, 78.66; H, 6.84; N, 3.28; Found: C, 77.68; H, 6.81; N, 3.28.

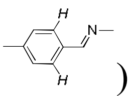
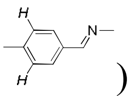
(2) Synthesis of 3,5-bis(hydroxymethyl)-4-[4'-{3-(triethylsilyl)propyliminomethyl}benzyloxy]-1-phenyl-acetylene (**M-TES**) (Scheme 3.3)[39]

3-(Triethylsilyl)propylamine (**9**) (Scheme 3.3)

$H_2PtCl_6 \cdot 6H_2O$ (26 mg, 50 μmol) and toluene (15 mL) were added to a flask and the mixture was stirred at 80℃ until $H_2PtCl_6 \cdot 6H_2O$ was dissolved completely. Triethylsilane (8.00 mL, 50.2 mmol) and allylamine (4.20 mL, 55.2 mmol) were added dropwise to the solution at 40℃ separately and this reaction solution was stirred at 85℃ for 120h. The solvent was removed by evaporation and the crude product was purified by vacuum distillation at 54℃ (250 Pa) to give **9** as a colorless liquid. Yield: 67.7% (5.89 g). ^{1}H NMR ($CDCl_3$, TMS): δ = 2.65 (t, 2H, J = 7.0 Hz, NH_2CH_2), 1.42 (m, 2H, $NH_2CH_2CH_2CH_2$), 1.27(br, 2H, CH_2NH_2), 0.92 (t, 9H, J = 8.0 Hz, $Si(CH_2CH_3)_3$), 0.59 (t, 2H, J = 8.0 Hz, $NCH_2CH_2CH_2Si$), 0.49 (q, 6H, J = 8.0 Hz, $Si(CH_2CH_3)_3$).

3,5-Bis(hydroxymethyl)-4-[4'-{3-(triethylsilyl)propyliminomethyl}benzyloxy]-1-phenylac-etylene (**M-TES**) (Scheme 3.3)

A mixture of **M-CHO** (500 mg, 1.68 mmol), **9** (586 mg, 3.36 mmol) and Al_2O_3 (10.0 g) in dry THF (16 mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed by evaporation to yield a white solid. The crude product was purified by recrystallization in chloroform / hexane(= 5 / 95 (v/v)) to give **M-TES** as a white solid. Yield: 56.5% (428 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 8.27 (s, 1H, PhCH=N), 7.76 (d, 2H, J = 8 Hz,

), 7.50 (s, 2H, C≡CPhH), 7.45 (d, 2H, J = 8 Hz, ), 4.99 (s, 2H, PhOCH$_2$Ph), 4.65 (d, 4H, J = 6.0 Hz, Ph(CH$_2$OH)$_2$), 3.59 (t, 2H, J = 7.0 Hz, NCH$_2$CH$_2$), 3.04 (s, 1H, HC≡C), 1.90 (t, 2H, J = 6.0 Hz, Ph(CH$_2$OH)$_2$), 1.68 (m, 2H, NCH$_2$CH$_2$CH$_2$), 0.91 (t, 9H, J = 8.0 Hz, Si(CH$_2$CH$_3$)$_3$), 0.53 (t, 2H, J = 8.0 Hz, NCH$_2$CH$_2$CH$_2$Si), 0.49 (q, 6H, J = 8.0 Hz, Si(CH$_2$CH$_3$)$_3$). IR (KBr): 3322 (OH), 3233 (HC≡C), 1643 (C=N) cm^{-1}. Anal. Cacld for $C_{27}H_{37}O_3NSi$: C, 71.80; H, 8.26; N, 3.10; Found: C, 71.74; H, 8.17; N, 3.10.

3.3.2.3 Synthesis of the polymers (P-R) by helix-sense-selective polymerization (HSSP) of M-R (Scheme 3.2a)[35]

(1) Synthesis of **P-EO** by HSSP of **M-EO** (Chapter 2)

(2) Synthesis of **P-TB** by HSSP of **M-TB** (Scheme 3.2a)

A solution of [Rh(nbd)Cl]$_2$ (0.80 mg, 1.76 μmol) and (S)- or (R)-PEA (28.2μL, 220 μmol) in dry THF (0.44 mL) was added to a dry THF (0.44 mL) solution of **M-TB** (37.0 mg, 88.0 μmol). The reaction solution was stirred at room temperature for 24h. The crude polymer was purified by reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried in vacuo to give **P-TB** as a red solid in 57% yield. **Mw** = 7.9×10^7. ^{1}H NMR (CCl$_4$/DMSO-d$_6$ = 5/1(v/v), TMS): δ = 7.56-6.81(br, 10H, PhH), 5.93(br, cis proton in the main chain), 4.79(br, 2H, PhOCH$_2$Ph), 4.37(br, 4H, Ph(CH$_2$OH)$_2$), 1.51(br, 9H, C(CH$_3$)$_3$). IR (KBr): 3600-3100(OH), 3000-2800(CH), 1645 (C=N) cm^{-1}.

(3) Synthesis of **P-TES** by HSSP of **M-TES** (Scheme 3.2a)

The HSSP of **M-TES** was carried out similarly to that of **M-TB** to give **P-TES** as an orange solid in 98% yield. **Mw** = 3.0×10^5.^{1}H NMR(CCl_4/DMSO-d_6 = 5/1(v/v)): δ = 8.15 (br, 1H, PhCH=N), 7.58-6.92 (br, 6H, PhH), 5.91 (br, cis proton in the main chain), 4.75 (br, 2H, $PhOCH_2Ph$), 4.35 (br, 4H, $Ph(CH_2OH)_2$), 3.53 (br, 2H, NCH_2CH_2), 1.65 (br, 2H, $NCH_2CH_2CH_2$), 0.88 (br, 9H, $Si(CH_2CH_3)_3$), 0.51 (br, 2H, $NCH_2CH_2CH_2Si$), 0.47 (br, 6H, $Si(CH_2CH_3)_3$). IR (KBr): 3375 (OH), 1645 (C=N) cm^{-1}.

(4) Synthesis of **P-Do** by HSSP of **M-Do** (Scheme 3.2a)[35]

P-Do was synthesized from **M-Do** according to our previous paper in 36.5% yield. **Mw** = 2.5×10^6.^{1}H NMR ($CDCl_3$ / DMSO-d_6 = 55 / 45(v/v), TMS): δ = 6.77(s, 2H, $(PhH)_2$), 5.76(br, cis proton in the main chain), 4.61(s, 2H, $PhOCH_2$), 4.32(s, 4H, $Ph(CH_2OH)_2$), 3.55(br, 2H, $Ph(CH_2OH)_2$), 1.29-1.64(m, 20H, $OCH_2CH_2(CH_2)_9CH_3$), 0.89(b, 3H, CH_2CH_3). IR(KBr): 3700-3100(OH), 3000-2800(CH), 1200-1000(CO) cm^{-1}.

(5) Synthesis of **P-S3** by HSSP of **M-S3** (Scheme 3.2a)[36]

P-S3 was synthesized from **M-S3** according to our previous paper in 89% yield. **Mw** = 4.0×10^7. ^{1}H NMR (DMSO-d_6 / CCl_4 = 1 / 5, TMS): δ = 7.54-7.34(br, 6H, PhH), 5.89(br, cis proton in the main chain), 4.75(br, 2H, $PhOCH_2Ph$), 4.38(br, 4H, $(CH_2OH)2$), 0.34-0.04(br, 21H, ($-Si(CH_3)_3$ and ($-SiO(CH_3)_2-)_2$). IR(KBr): 3600-3100(OH), 1256(SiC), 1051 (SiO) cm^{-1}.

3.3.2.4 Synthesis of the 2D surface modifers(T-R) by highly selective photocyclic aromatization (SCAT) of P-R (Scheme 3.2b)[32]

The **P-R** membranes (thickness around 20 μm) were irradiated under nitrogen at 25℃ by visible light (400-500 nm, 2.54 mW/cm^2) for 2-4 weeks. The conversions and selectivities were determined by GPC detected by UV. Visible light (400-500 nm) irradiation was carried out by using a 300 W of Xe lamp (Asahi Spectra, MAX-302 with vis mirror module) through a cutoff filter (Asahi Spectra, LUX400 ($\lambda > 400$ nm), XF541 ($\lambda < 510$ nm), and XF546 ($\lambda <$ 610 nm).

3.3.3 Membrane preparation

The surface-modified membranes were prepared from the binary solution of the mixture consisting of small amounts(less than 5.0 wt%) of one of the 2D surface modifiers and one of the base polymers(see Chart 3.2) by two kinds of solvent casting methods(Method I and Method II) as shown in Scheme 3.4.

3.3.3.1 PVA-based membranes by Method I

A dimethyl sulfoxide(DMSO) solution(1.0 mL) of poly(vinyl alcohol)(PVA) (40 mg) and 0.060-10.0 wt% of one of the 2D surface modifiers was cast on a poly(tetrafluoroethylene) sheet. The solvent(DMSO) was evaporated in a reduced pressure (1.33×10^{-3} MPa) for 12h and then by heating at 50℃ at this pressure for 24h. The resulting membranes were allowed to stand for 8h at 25℃. Finally, the membranes were detached from the poly(tetrafluoroethylene) sheet and were annealed *in vacuo* at 30℃ for 24h.

3.3.3.2 PSPA-based and PDPA-based membranes by two methods (Methods I and II)

Method I (conventional method): A toluene solution(1.0 mL) of the base polymer(35 mg) and 0.060-5.0 wt% of the 2D surface modifier was cast on a poly(tetrafluoroethylene) sheet. After the solvent was evaporated for 24h at room temperature, the membrane was detached from the poly(tetrafluoroethylene) sheet and dried *in vacuo* for 24h at room temperature.

Method II (newly developed method): A toluene solution(1.0 mL) of the base polymer (50 mg) and chloroform solution(0.50 mL) of the 2D surface modifier (0.175 mg) were first blended together(In the case of T-EO, methanol was used instead of chloroform.) . And then the mixed solution was cast on a poly(tetrafluoroethylene) sheet. After the solvent was evaporated for 24h at room temperature, the membrane was detached from the sheet and dried *in vacuo* for 24h at room temperature.

3.3.4 Measurement of oxygen permselctivities

Oxygen and nitrogen permeability coefficients (PO_2 and PN_2: cm^3 (STP) $\cdot cm / cm^2 \cdot s \cdot cmHg$) of mixed gases of oxygen and nitrogen($O_2 / N_2 = 20 / 80$ (v/v)) were measured by gas chromatographic method using YANACO GTR-10. The P, the oxygen separation factors (α), the diffusion coefficients (D) and the solubility coefficients (S) were calculated by the following equations:

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

$$\alpha = P_{O_2} / P_{N_2}$$

$$D = l^2 / 6T$$

$$S = P / D$$

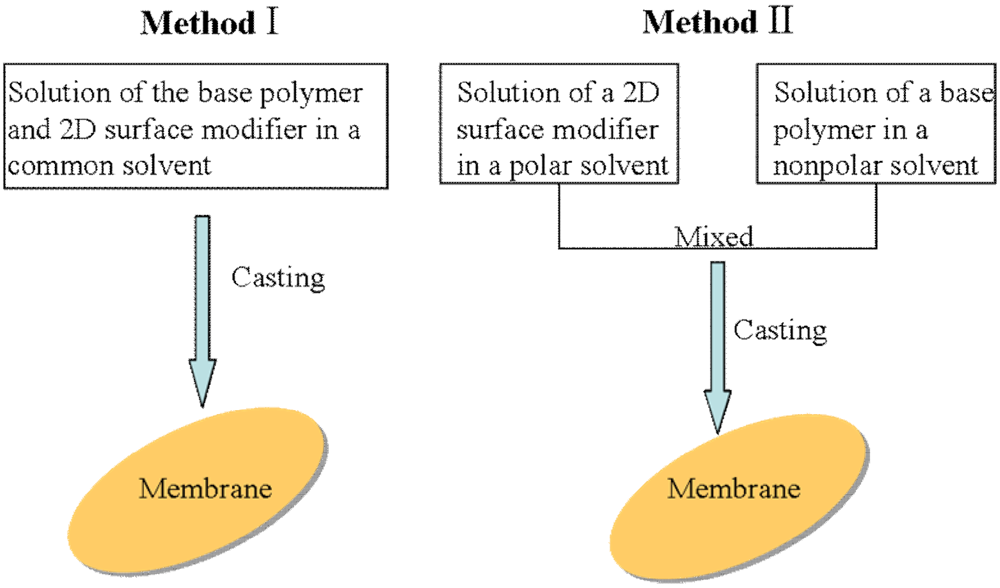
where Q, l, A, △p, t, and T are the amount of the permeated gas, the thickness of the membrane, the permeation area of the membrane, the pressure difference across the membrane, the permeation time and the time lag, respectively. The A and l of the membranes were 0.38-1.77cm^2 and 25-120 μm, respectively. Disc-type membranes were used. The △p was 1 atm and the measurement temperature was 25°C.

3.3.5 Characterization of membranes

ATR-FTIR(using ATR PR0450-S) and FT-IR spectra were recorded on a JASCO FTIR-4200 specrameter, contact angles of distilled water droplets on the air-side surface of the membranes were measured at 25℃ with a DM301, Kyowa Interface Science Co., LTD.

3.3.6 Apparatus

NMR spectra were recorded on a JEOL GSX 270 at 400 MHz for ^{1}H NMR and ^{13}C NMR. Average molecular weight (***Mw***) was estimated by gel permeation chromatography (tetrahydrofuran as an eluent, polystyrene calibration) using JASCO Liquid Chromatography instruments with PU 2080, DG 2080 53, CO 2060, UV 2070, CD 2095 and two polystyrene gel columns(Shodex KF 807L).



Scheme 3.4. Two preparation methods of surface-modified membranes (Method I: Casting a solution of the base polymer and 2D surface modifier in a common solvent; Method II: Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent).

3.4 Results and discussion

3.4.1 Molecular design and synthesis of new 2D surface modifiers

In this study, five kinds of 2D surface modifiers (Chart 3.2) were synthesized and used. All the compounds have a 1,3,5-trisubstituted benzene as a hydrophobic planar (2D) part, six hydroxyl groups, and three hydrophilic(**T-EO**) or hydrophobic(**T-TB**, **T-TES**, **TDo**, and **T-Si**) groups. All the 2D surface modifiers were synthesized by SCAT(Scheme 3.1)[28], which is our original method, of the corresponding polyphenylacetylenes according to Scheme 3.2. As a typical example, the 3D chemical structures of **T-EO** are shown in Chart 3.3. It has 1,3,5-trisubstituted benzene as a hydrophobic 2D part and three hydrophilic arms of an oligoethylene oxide which can function as an anchor segment in hydrophilic base polymer membranes such as poly(vinyl alcohol)(PVA). Chart 3.3 indicates an example of an ideal 2D supramolecular structure of six **T-EO** molecules on a membrane surface. It has some molecular-size pores which can recognize and separate gas molecules such as oxygen and nitrogen.

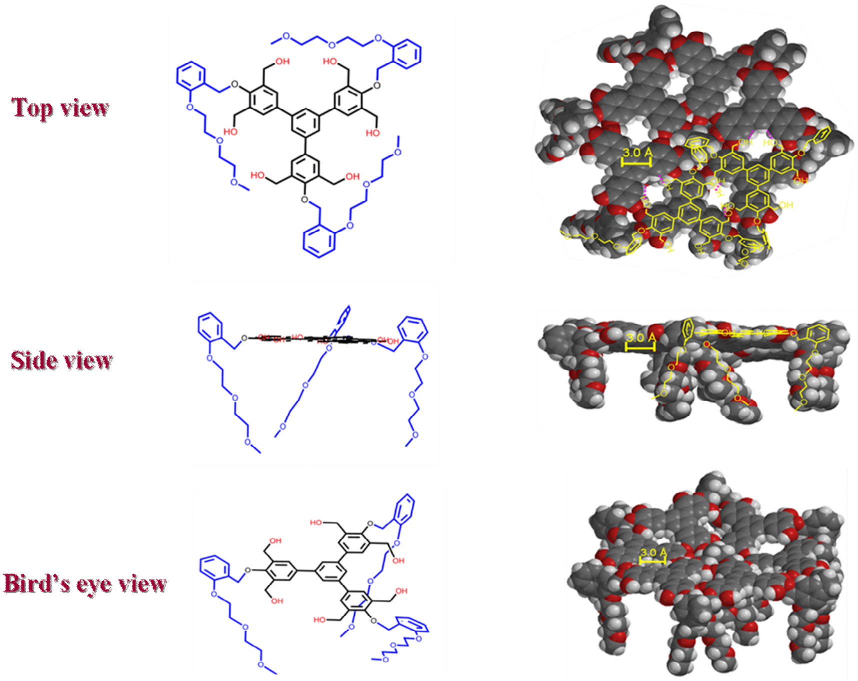


Chart 3.3 3D molecular structure of T-EO and possible 2D supramolecular structure of T-EO on the blend membrane surface.

In order to separate gas molecules more effectively, thinnest membranes without any defects are desired. In addition, no distribution of the additives inside the base membrane is thought to be better because such additives may change the original good performance of the base membranes. Therefore, the minimum amount of the 2D surface modifier (**T-EO**) needed for such a thinnest surface layer was calculated. As shown in Chart 3.4, the result of calculation showed very little amount (= 6.0×10^{-3} wt%) of **T-EO** is enough for making the ideal thin layer. Therefore we added small amounts of the additives in this study.

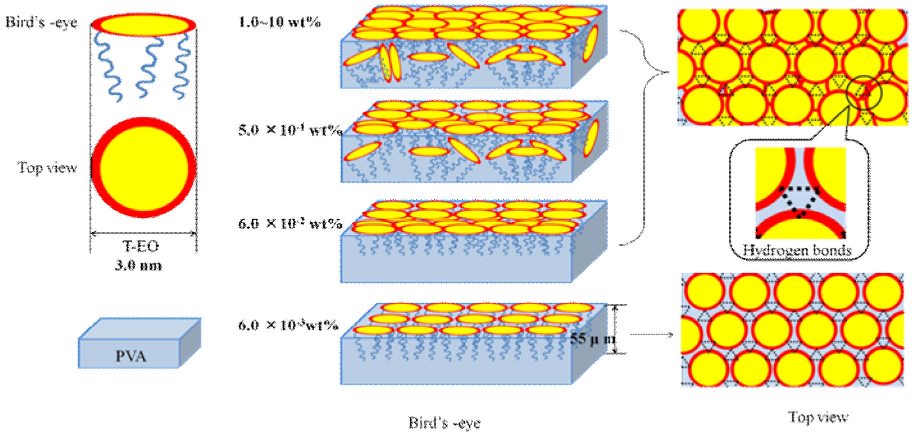


Chart 3.4 Possible membrane structure of **T-EO**/PVA membranes

3.4.2 New preparation method (Method II) of surface-modified membranes

The surface-modified membranes were prepared from the solution of the mixture consisting of small amounts(less than 5.0 wt%) of one of the 2D surface modifiers and one of the base polymers (see Chart 3.2) by two kinds of solvent casting methods as shown in Scheme 3.4. In Method I (a conventional method), a solution of the base polymer and 0.060-5.0 wt% of the 2D surface modifiers in a common solvent was cast on a poly(tetrafluoroethylene) sheet. In Method II (a new method), one solution of the base polymer in a non-polar solvent having a higher boiling point and anther solution of 0.060-5.0 wt% of the 2D surface modifiers in a polar solvent having a lower boiling point were prepared and then the two solutions were mixed and the binary solution was cast on a poly(tetrafluoroethylene) sheet. Because hydrophobic compounds tend to be concentrated at the surface when it was blended with a hydrophilic base polymer and the solution was cast in the air, in the case of this combination, i.e., a more hydrophobic additive and a more hydrophilic base polymer, the resulting membrane prepared by Method I (conventional method, see Scheme 3.4) forms more hydrophobic surface. Therefore, the combination of **T-EO** and PVA, i.e., a hydrophobic additive and a hydrophilic base polymer is suitable for Method I. As a fact, **T-EO** was accumulated at the surface of PVA judging from change in the contact angles (Table 3.1, nos. 1-6). However, in the case of the opposite combination, i.e., a more hydrophilic additive and a more hydrophobic base polymer like **T-EO** and poly(*p*-trimethylsilylphenylacetylene) (PSPA) were not suitable for Method I (Table 3.1, nos. 12-14). To overcome the problem, a new method, i.e., Method II (see Scheme 3.4) was designed and carried out. Methanol and toluene were used as a good solvent for **T-EO** and PSPA, respectively. As shown in Table 3.1, nos. 15-17, **T-EO** was successfully accumulated on the surface of PSPA membranes. Because the boiling point of methanol is lower than that of toluene, **T-EO** may be concentrated and precipitated at the surface first during the evaporation of the solvent after casting. By this new method, membranes whose surfaces were covered by more hydrophilic additives could be prepared easily.

3.4.3 Improvements of oxygen permselectivities by surface modification using the 2D surface modifiers

Table 3.1 Characterization of the surfaces of **T-EO** containing polymer membranes

No.[a)]	Additives [b)]	Content (wt%)	θ(°) [c)]
1	None(PVA)	0.0	39.1
2	**T-EO** (Method I)[d)]	0.06	40.4
3		0.50	40.1
4		1.0	40.4
5		5.0	51.5
6		10.0	53.1
7	**P-EO** (Method I)[d)]	1.0	42.2
8		5.0	30.2
9		10.0	34.2
10		100(=**P-EO**)	69.5
11	None(PSPA)	0.0	106
12	**T-EO** (Method I)[d)]	0.50	105
13		1.0	107
14		5.0	104
15	**T-EO** (Method II)[d)]	0.50	100
16		1.0	95
17		5.0	87

[a)] Nos.2-9: Prepared by Method I using PVA as a base polymer; nos.12-14: Prepared by Method I using PSPA as a base polymer; nos.15-17: Prepared by Method II using PSPA as a base polymer. [b)] For the code, see Chart 8.2; [c)] Advancing contact angles for water droplets on the air surface of the blend membranes; [d)] Method I: Casting a solution of the base polymer and 2D surface modifier in a common solvent; Method II: Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent.

3.4.3.1 Three kinds of membranes modified by the 2D surface modifier having oligo(ethylene oxides) (T-EO)

Figure 3.1 shows the results of oxygen permselectivity of **T-EO** containing polymer membranes based on PVA, PDPA[29], or PSPA[30]. In all the blend membranes, oxygen permselectivities were higher than that of pure membranes, PVA(○), PDPA(△), or PSPA(□) membranes, respectively. In the case of PVA-based membranes (Figure 3.1,●) when 1.0 wt% of **T-EO** was added, the permselectivity increased almost twice higher than that of the pure base polymer membrane, i.e., the PVA membrane without any drop of permeability. When 1.0 wt% of **P-EO** (the precursor polymer of **T-EO**, see Scheme 3.2) was added (Figure 3.1, ▼), the permselectivity was not improved and the permeability decreased. Therefore the small amount of **T-EO** may form a certain surface structure which enhanced the performance effectively. In particular, in the case of PDPA-based membranes (Figure 3.1, ▲), when a small amount(1.0 wt%) of **T-EO** was added, both the permselectivity and permeability increased simultaneously. In addition, the plots of **T-EO**/PDPA membranes(▲) are over the Robeson's boundary line[4] indicating a very excellent performance. It may be because **T-EO** may form an ideal surface structure. On the other hand, in the case of PSPA-based membranes (Figure 3.1, ■), when 5.0 wt% of **T-EO** was added, the permselectivity increased but permeability decreased a little. It may be because **T-EO** was present not only at the surface but also inside the membranes(See Chart 3.4).

3.4.3.2 Poly(*p*-trimethylsilyldiphenylacetylene)(PDPA)-based membranes modified by the four kinds of 2D surface modifiers

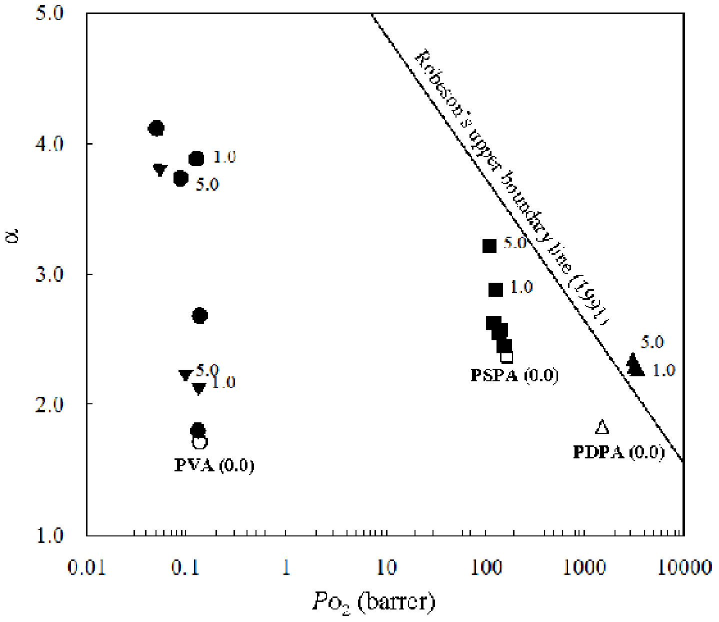


Figure 3.1. Oxygen permselectivity of T-EO containing polymer membranes (The numbers in the figure are the content of the additives(wt%)). ●: **T-EO**/PVA blend membranes prepared by Method I; ■:**T-EO**/PSPA blend membranes prepared by Method I and Method II; ▲: **T-EO**/PDPA blend membranes prepared by Method II; ▼: **P-EO**/PVA blend membranes prepared by Method I(1 barrer = 10^{-10} cm^3(STP)·cm/cm^2·s·cmHg; $\alpha = Po_2 / PN_2$).

Figure 3.2 shows oxygen permselectivity of PDPA-based polymer membranes modified by the four kinds of 2D surface modifiers. In all the blend membranes, oxygen permselectivities were higher than that of the pure PDPA membrane(○) although the permeability decreased except for **T-EO**(●). In particular, **T-TB**(■) enhanced the permselectivity most effectively among the four additives (**T-EO**(●), **T-TB**(■), **T-Do**(▼), and **T-S3**(◆)). Since the plots of **T-EO**/PDPA membranes(●) are over the Robeson's boundary line^4, they are very excellent performance.

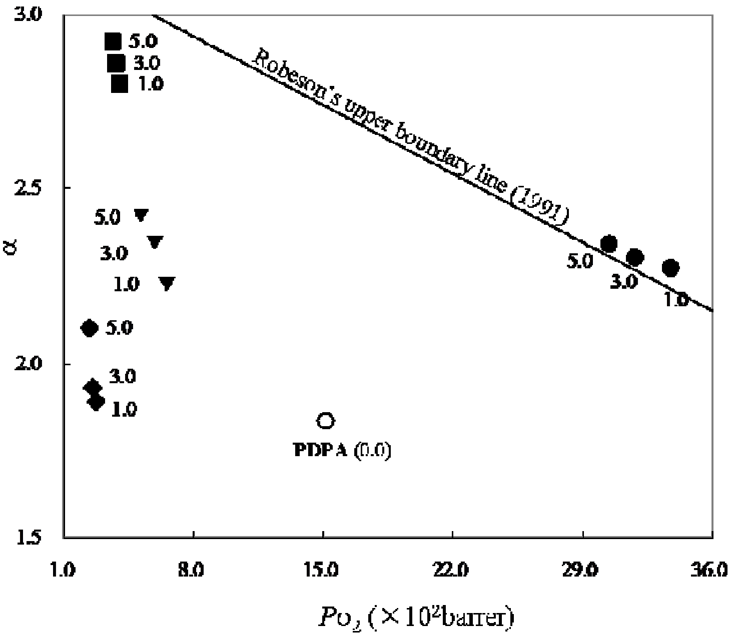


Figure 3.2. Oxygen permselectivity of PDPA-based polymer membranes(The numbers in the figure are the content of the additives(wt%)). ●:**T-EO**/PDPA blend membrane prepared by Method II; ■: **T-TB**/PDPA blend membranes prepared by Method II; ▼:**T-Do**/PDPA blend membranes prepared by Method II; ◆: **T-S3**/PDPA blend membranes prepared by Method II (1 barrer = 10^{-10}cm^3(STP)·cm/cm^2·s·cmHg; $\alpha = P_{O_2} / P_{N_2}$).

3.4.3.3 Poly(*p*-trimethylsilylphenylacetylene) (PSPA)-based membranes modified by the four kinds of 2D surface modifiers

Figure 3.3 shows oxygen permselectivity of **PSPA**-based polymer membranes. In all the blend membranes, oxygen permselectivities were higher than that of the pure PSPA membrane(○) although the permeability decreased. In particular, since the plot of a **T-TES**/PSPA membrane(▲) is closest to the Robeson's boundary line among the four additives, the performance is relatively good.

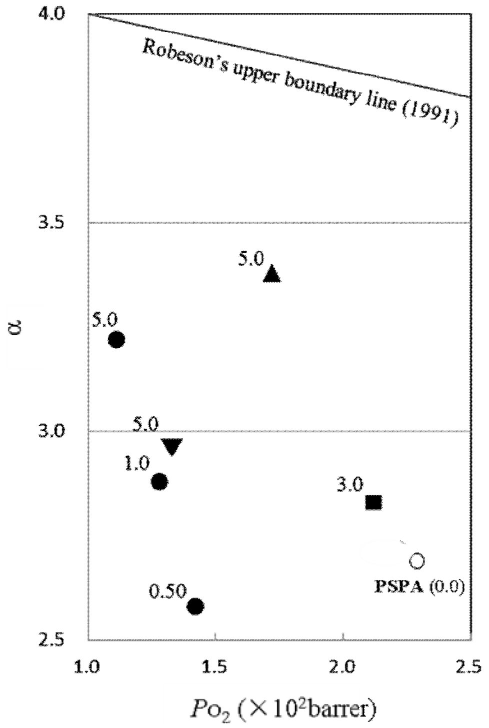


Figure 3.3. Oxygen permselectivity of PSPA-based polymer membranes(The numbers in the figure are the content of the additives (wt%)).●:**T-EO**/PSPA blend membranes prepared by Method II; ■:**T-TB**/PSPA blend membranes prepared by Method II; ▲:**T-TES**/PSPA blend membranes prepared by Method II; ▼:**T-Do**/PSPA blend membranes prepared by Method II (1 barrer = 10^{-10} $cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg$; $\alpha = Po_2 / PN_2$).

3.4.4.4 Summary of oxygen permselectivity through the surface-modified membranes

Figure 3.4 shows the results of oxygen permselectivity of all the blend membranes in this study together with other membranes (+) having excellent performances reported by other researchers[36-40]. All the oxygen permselectivities in this study were higher than that of the corresponding pure membrane, i.e., PVA(○), PDPA(△), or PSPA(□) membrane, respectively. In particular, **T-EO**/PDPA membranes(▲) and a **T-TES**/PSPA membrane(■) showed very good performances whose plots are over or close to the Robeson's upper boundary line[4]. Among the five additives(Chart 3.2), **T-EO** was the best to improve the performance of the original membranes (●, ▲). In summary, only small amounts (1.0-5.0 wt%) of the 2D modifiers were enough for the effective improvement of oxygen permselectivities.

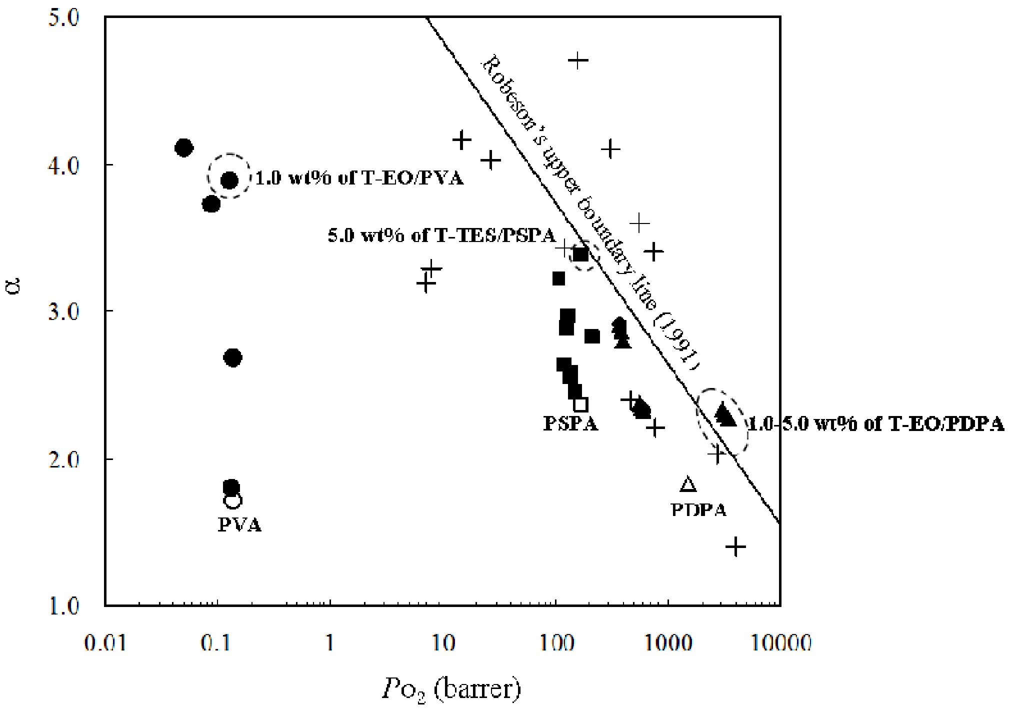


Figure 3.4. Oxygen permselectivity of all the surface-modified polymer membranes in this study(●: PVA-based polymer membranes; ■:PSPA-based polymer membranes; ▲: PDPA-based polymer membranes; +: from ref.[36]-[40].(1 barrer = $10^{-10}cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg$; $\alpha = Po_2 / PN_2$).

3.4.4 Reasons of the improvements of oxygen permselectivities

3.4.4.1 Structures of the blend membranes

To know structures of the membrane surface, contact angles of water droplets and ATR-IR on the membrane surface were measured. The results are listed in Tables 3.1-3.3. Table 3.1 shows the values of contact angles of water droplets on the surface of **T-EO** containing blend polymer membranes whose permselectivities have been shown in Figure 3.1. As shown in Table 3.1, nos.

1-6, judging from the contact angles, **T-EO** was accumulated at the surface in the **T-EO**/PVA membranes prepared by Method I whose performances were improved efficiently. On the other hand, since the **P-EO**/PVA membranes prepared by Method I whose performances were not improved efficiently showed almost no change in the contact angles, **P-EO** was not accumulated at the surface (Table 3.1, nos. 7-9).

In the case of the **T-EO**/PSPA membranes prepared by Method II whose performances were improved efficiently, judging from the contact angles, **T-EO** was found to be accumulated at the surface (Table 3.1, nos. 15-17). On the other hand, since the **T-EO**/PSPA membranes prepared by Method I whose performances were not improved efficiently showed almost no change in the contact angles, **T-EO** was not accumulated at the surface (Table 3.1, nos. 12-14).

Table 3.2 shows the values of contact angles of water droplets and ATR-IR at the surface of the PDPA-based polymer blend membranes prepared by Method II whose performances were improved efficiently. The θ values show all the additives were present at the surfaces because the surface became more hydrophilic. In addition, since the ratios(A_S) of absorbance(A_{3450}) for OH to that(A_{1250}) for $SiCH_3$ of the surface in the infrared spectra were much higher than those of the bulk(A_B), in other words, A_S values were much higher than A_B values(i.e., $R= A_S / A_B > 1.0$), the accumulation of the additives were confirmed. Table 3.3 shows the values of contact angles of water droplets at the surface of the PSPA-based polymer blend membranes prepared by Method II whose performances were improved efficiently. The θ values show all the additives were present at the surfaces because the surface became more hydrophilic similarly to those of the PDPA-based membranes prepared by Method II.

In summary, it was found that all the additives were accumulated at the surface in all the blend membranes containing the 2D surface modifiers. The possible supramolecular structure of **T-EO** at the surface of the **T-EO**/PVA membrane is shown in Chart 3.4. The three hydrophilic oligoethylene oxide groups in **T-EO** can work as anchors. In the case of the **T-EO**/PDPA and the

Table 3.2 Characterization of the surfaces of PDPA-based polymer membranes [a]

No.	Additives [b]	Content (wt%)	θ(°) [c]	A_S [d] ($\times 10^{-1}$)	A_B [e] ($\times 10^{-2}$)	R [f]
1	None	0.0	103	-	-	-
2	**T-EO**	1.0	93.5	7.03	7.10	9.90
3		3.0	92.2	7.58	8.64	8.77
4		5.0	89.6	7.73	9.73	7.94
5	**T-TB**	1.0	96.1	3.03	9.22	3.28
6		3.0	93.2	4.42	9.35	4.72
7		5.0	92.5	5.59	16.0	3.49
8	**T-Do**	1.0	90.7	5.00	6.71	7.45
9		3.0	85.1	5.14	7.83	6.56
10		5.0	83.9	5.40	12.8	4.21
11	**T-S3**	1.0	93.1	3.22	8.80	3.65
12		3.0	89.9	4.01	9.91	4.04
13		5.0	86.8	4.10	11.8	3.47

[a] Prepared by Method II using PDPA as a base polymer (Method II : Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent); [b] For the code, see Chart 3.2; [c] Advancing contact angles for water droplets on the air surface of the blend membranes; [d] $A_S = A_{3450} / A_{1250}$ of ATR-FTIR; [e] $A_B = A_{3450} / A_{1250}$ of FTIR; [f] $R = A_S / A_B$.

Table 3.3 Characterization of the surfaces of PSPA-based polymer membranes [a)]

No.	Additives [b)]	Contents (wt%)	θ(°) [c)]
1	None	0.0	106
2	T-EO	0.50	100
3		1.0	95.0
4		5.0	87.0
5	**T-TB**	3.0	97.9
6	**T-TES**	5.0	96.5
7	**T-Do**	5.0	97.1

[a)] Prepared by Method II using PSPA as a base polymer(Method II : Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent); [b)]For the code, see Chart 3.2; [c)]Advancing contact angles for water droplets on the air surface of the blend membranes.

T-EO/PSPA membranes, the three oligoethylene oxide groups in **T-EO** can not work as anchors. Instead, the hydrophobic part, i.e., the benzene derivatives may have interaction with the hydrophobic substrate polymers.

In order to estimate stability of the modified surface, aging effects of the contact angles were measured. Table 3.4 shows aging effects of the contact angles on the PDPA-based polymer membranes. Since almost no change in the contact angles was observed, it was found that the surface layer was stable.

3.4.4.2 Reason of the improvements of oxygen permselectivities

As described above, in all the blend membranes containing the 2D surface modifiers, the oxygen permselectivities were higher than the corresponding pure base polymer membranes and the additives were accumulated at the surface. Therefore, the surface layer must play an important role. To discuss the reason of the enhancement, diffusion coefficients(*D*) were estimated by the time lag methods and then solution coefficients (*S*) were calculated from $P = D \times S$. The results are listed in Tables 3.5-3.7. Table 3.5 shows the values of *P*, *D*, and

Table 3.4. Aging effects of the contact angles of the surfaces of PDPA-based polymer membranes[a)]

No.	Additives [b)]	Content (wt%)	θ (°) [c)]	
			Original	3 months
1	None	0.0	103	96.3
2	**T-EO**	1.0	93.5	94.6
3		3.0	92.2	94.0
4		5.0	89.6	93.2
5	**T-TB**	1.0	96.1	96.4
6		3.0	93.2	93.8
7		5.0	92.5	92.6
8	**T-Do**	1.0	90.7	91.7
9		3.0	85.1	85.7
10		5.0	83.9	84.1
11	**T-S3**	1.0	93.1	93.7
12		3.0	89.9	90.4
13		5.0	86.8	89.5

[a)] Prepared by Method II using PDPA as a base polymer (Method II : Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent); [b)] For the code, see Chart 3.2; [c)] Advancing contact angles for water droplets on the air surface of the blend membranes just after the membrane fabrication and 3 months after the membrane fabrication under air.

S of oxygen and nitrogen and their ratios, i.e., P_{O_2} / P_{N_2} ($= \alpha$), D_{O_2} / D_{N_2}, and S_{O_2} / S_{N_2} through the **T-EO** containing blend polymer membranes. As shown in Table 3.5, nos. 1-6, in the **T-EO**/PVA membranes, the enhancements of α values were found to be mainly caused by those of S_{O_2} / S_{N_2} and the decreases of Po_2 values were found to be caused by those of Do_2. The extent of increase of α and S_{O_2}/S_{N_2} values in 1.0 or 5.0 wt% of **T-EO**/PVA membranes were higher than those in 1.0 or 5.0 wt% of **P-EO**/PVA membranes (Table 3.5, nos. 4,5 and 7,8). Therefore, **T-EO** was more effective than **P-EO** for enhancing the performances because **T-EO** could show a better surface layer. In the case of the **T-EO**/PSPA membranes prepared by Method II (Table 3.5, nos. 15-17), increase of α values were found to be caused by those of S_{O_2}/S_{N_2} similarly to those in **T-EO**/PVA. On the other hand, in **T-EO**/PSPA prepared by Method I showed almost no effects on enhancing S_{O_2}/S_{N_2} (Table 3.5, nos. 12-14). Therefore, the surface thin layers produced by the 2D additives were effective for enhancing S_{O_2}/S_{N_2} Tables 3.6 and 3.7 show the values of *P*, *D*, and *S* of oxygen and nitrogen and their ratios, i.e., P_{O_2}/P_{N_2} (=α), D_{O_2}/D_{N_2}, and S_{O_2}/S_{N_2} through the PDPA- and PSPA-based blend polymer membranes, respectively. All the enhancements of α were found to be caused by those of S_{O_2}/S_{N_2}.

Table 3.5 Oxygen permselectivity of the **T-EO** containing polymer membranes

No.[a)]	Additives [b)]	Content (wt%)	PO_2 ($\times10^{-2}$barrer) [c)]	DO_2 [d)] ($\times10^{-2}$)	SO_2[e)]	PO_2/PN_2	DO_2/DN_2	SO_2/SN_2
1	None(PVA)	0.0	13.7	9.41	1.45	1.71	1.21	1.42
2	**T-EO** (Method I)[f)]	0.06	13.5	10.91	1.24	1.80	1.11	1.62
3		0.50	13.7	8.05	1.70	2.68	1.12	2.39
4		1.0	12.7	8.02	1.58	3.88	1.11	3.49
5		5.0	8.8	5.64	1.57	3.73	1.01	3.68
6		10.0	5.1	3.22	1.59	4.11	0.93	4.44
7	**P-EO** (Method I)[f)]	1.0	12.9	7.68	1.68	2.15	1.08	1.99
8		5.0	8.8	5.83	1.51	2.25	1.12	2.00
9		10.0	4.9	3.33	1.47	3.82	1.14	3.35
10		100(**P-EO**)	136	13.4	10.1	1.19	1.00	1.18

No.[a)]	Additives [b)]	Content (wt%)	PO_2 (barrer)[c)]	DO_2 [d)]	SO_2[e)]	PO_2/PN_2	DO_2/DN_2	SO_2/SN_2
11	None(PSPA)	0.0	171	3.35	51.1	2.36	0.95	2.48
12	**T-EO** (Method I)[f)]	0.50	150	2.95	50.8	2.45	0.98	2.51
13		1.0	136	2.60	52.4	2.55	1.04	2.45
14		5.0	120	2.32	51.8	2.63	1.02	2.58
15	**T-EO** (Method II)[f)]	0.50	142	3.25	43.7	2.58	0.97	2.66
16		1.0	128	3.10	41.3	2.88	1.02	2.82
17		5.0	111	2.98	37.2	3.22	1.06	3.16

[a)] Nos.2-9: Prepared by Method I using PVA as a base polymer; no.10: a pure **P-EO** membrane; nos.12-14: Prepared by Method I using PSPA as a base polymer; nos.15-17: Prepared by Method II using PSPA as a base polymer; [b)] For the code, see Chart 3.2; [c)] 1 barrer = 10^{-10}cm^3(STP)·cm·cm^{-2}·s^{-1}·cmHg^{-1}; [d)] In 10^{-7}cm^2·s^{-1}; [e)] In 10^{-3} cm^3(STP) ·cm^{-3}·cmHg^{-1}; [f)] Method I: Casting a solution of the base polymer and 2D surface modifier in a common solvent; Method II: Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent.

Table 3.6 Oxygen permselectivity of the PDPA-based polymer membranes [a)]

No.	Additives [b)]	Content (wt%)	$P\mathrm{O_2}$ [c)] (barrer)	$D\mathrm{O_2}$ [d)]	$S\mathrm{O_2}$ [e)]	$P\mathrm{O_2}/P\mathrm{N_2}$	$D\mathrm{O_2}/D\mathrm{N_2}$	$S\mathrm{O_2}/S\mathrm{N_2}$
1	None	0.0	1520	0.488	311	1.83	1.78	1.03
2	**T-EO**	1.0	3380	0.112	3030	2.27	1.36	1.67
3		3.0	3190	0.098	3230	2.30	1.26	1.83
4		5.0	3055	0.087	3440	2.34	1.17	2.00
5	**T-TB**	1.0	404	0.252	160	2.80	1.43	1.96
6		3.0	385	0.249	155	2.86	1.38	2.07
7		5.0	366	0.243	151	2.92	1.31	2.24
8	**T-Do**	1.0	604	0.275	219	2.32	1.48	1.57
9		3.0	577	0.312	186	2.35	1.43	1.64
10		5.0	549	0.361	152	2.38	1.36	1.75
11	**T-S3**	1.0	278	0.0375	742	1.89	1.40	1.35
12		3.0	256	0.0378	678	1.93	1.40	1.37
13		5.0	236	0.0371	636	2.10	1.38	1.50

[a)] Prepared by Method II using PDPA as a base polymer(Method II : Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent.); [b)] For the code, see Chart 3.2; [c)] 1 barrer = 10^{-10} $\mathrm{cm^3(STP)\cdot cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}}$; [d)] In $10^{-6}\mathrm{cm^{-2}\cdot s^{-1}}$; [e)] In 10^{-3} $\mathrm{cm^3(STP)\cdot cm^{-3}\cdot cmHg^{-1}}$.

Table 4.7 Oxygen permselectivity of the PSPA-based polymer membranes [a)]

No.	Additives [b)]	Contents (wt%)	$P\mathrm{O_2}$ [c)] (barrer)	$D\mathrm{O_2}$ [d)]	$S\mathrm{O_2}$ [e)]	$P\mathrm{O_2}/P\mathrm{N_2}$	$D\mathrm{O_2}/D\mathrm{N_2}$	$S\mathrm{O_2}/S\mathrm{N_2}$
1	None	0.0	229	3.02	76.0	2.69	1.41	1.91
2	**T-EO**	0.50	142	3.25	43.7	2.58	0.97	2.66
3		1.0	128	3.10	41.3	2.88	1.02	2.82
4		5.0	111	2.98	37.2	3.22	1.06	3.16
5	**T-TB**	3.0	212	3.86	55.0	2.83	0.98	2.90
6	**T-TES**	5.0	172	---	---	3.38	---	---
7	**T-Do**	5.0	132	0.981	135	2.96	1.17	2.54

[a)] Prepared by Method II using PSPA as a base polymer(Method II : Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent.); [b)] For the code, see Chart 3.2; [c)] 1 barrer = $10^{-10}\mathrm{cm^3(STP)\cdot cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}}$; [d)] In 10^{-7} $\mathrm{cm^2\cdot s^{-1}}$; [e)] In 10^{-3} $\mathrm{cm^3(STP)\cdot cm^{-3}\cdot cmHg^{-1}}$.

3.5 Conclutions

In this article, a facile synthesis of five 2D surface modifiers including two new compounds are reported by the SCAT(highly selective photocyclic aromatization) reaction and effective enhancement of α ($=Po_2 / PN_2$) through the three polymer membranes are reported by adding a small amount of the 2D surface modifiers. Among the five 2D surface modifiers, **T-EO** showed the best performance for the enhancement. The α values in **T-EO**/PVA increased with no decrease in Po_2 and the α and Po_2 values in **T-EO**/PDPA increased simultaneously. These improvements were thought to be caused mainly by improvement of the solution selectivity on the membrane surface where the 2D surface modifiers were accumulated. In all the blend membranes, **T-EO**/PDPA, **T-TB**/PDPA, and **T-TES**/PSPA membranes showed good performances since the plots in the Po_2 -α graph were close to the upper boundary line by Robeson[4].

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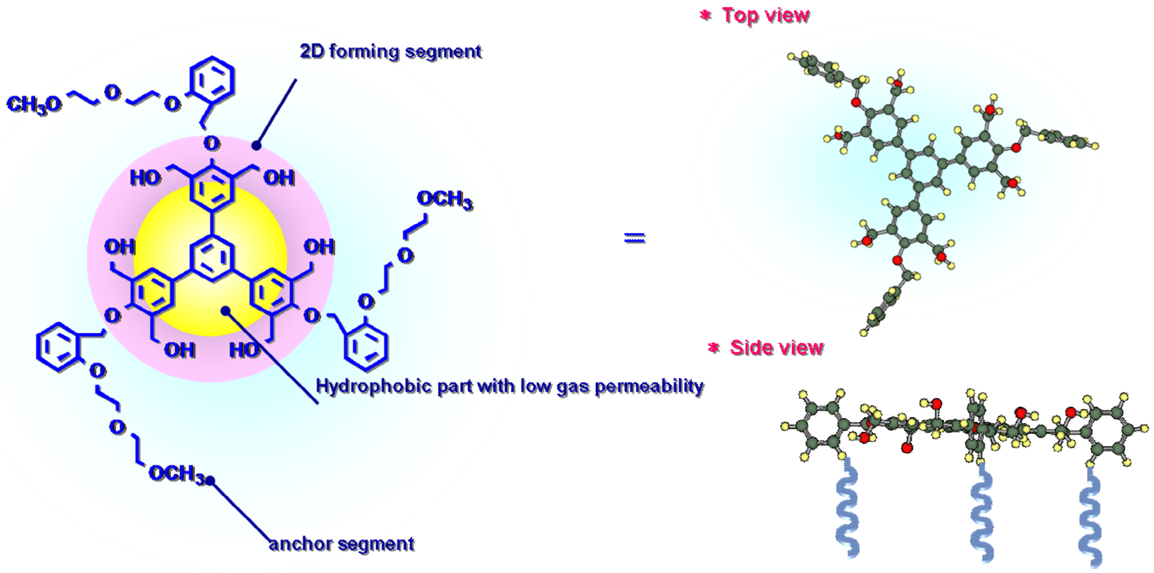
Conclusions of Part Ⅱ

A facile synthesis of novel five 2D (planar) surface modifiers having a triphenylbenzene derivatives as a 2D structure has been achieved by the highly selective photocyclic aromatization reaction. Efficient enhancement of oxygen permselectivities through the three polymer membranes has been achieved by adding a small amount (<5.0 wt%) of the 2D surface modifiers. Among the five 2D surface modifiers, a modifier compound having oligoethylene oxide groups showed the best performance for the enhancement.

These improvements were thought to be caused mainly by improvement of the solution selectivity on the membrane surface where the 2D surface modifiers were accumulated.



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List of Publications and Presentations

Papers

1. Jianjun Wang, Toshiki Aoki*, Lijia Liu, Takeshi Namikoshi, Masahiro Teraguchi and Takashi Kaneko, Facile Synthesis of an Amphiphilic 1,3,5-Trisubstituted Benzene as a Novel Surface Modifier by Selective Photocyclic Aromatization and Efficient Improvement of Oxygen Permselectivity by the Addition of the Surface Modifier, *Chem.Lett.* **2013***, 42*, 1090-1092.

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Review

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