

One-pot synthesis of poly (hyperbranched acetylene-type macromonomer) by simultaneous polymerization of two different modes of polymerizations for gas permselective membranes

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# 博 士 論 文

**One-pot synthesis of poly(hyperbranched acetylene-type  
macromonomer) by simultaneous polymerization of two  
different modes of polymerizations for gas permselective  
membranes**

異種様式同時重合法によるポリ(アセチレン型ハイ  
パーブランチマクロモノマー)の合成と気体分離膜  
としての性能

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## Contents

Abstract .....	8
Chapter 1: Introduction .....	10
1.1 Overview of gas separation membrane.....	11
1.2 Dendrimer.....	14
1.3 Hyperbranched polymers .....	14
1.4 Simultaneous polymerization.....	16
1.5 Aims of this thesis .....	19
References and Notes .....	22
Chapter 2: One-pot synthesis of novel poly(hyperbranched macromonomer) by simultaneous polymerization of two different modes of polymerizations i.e., addition polymerization and polyaddition of one monomer by using one catalyst for gas permselective membranes .....	28
Abstract .....	29
2.1 Introduction .....	30
2.2 Experimental part .....	32
2.2.1 Materials.....	32
2.2.2 Measurements.....	32
2.2.3 Synthetic procedures and characterization of monomer (1).....	34
2.3 Results and discussion.....	41
2.3.1 Discovery of one-pot synthesis of a new type of polymer, poly(hyperbranched macromonomer) by the simultaneous	

polymerization of two different types of polymerizations, <i>i.e.</i> , addition polymerization and polyaddition of one new monomer by using one catalyst .....	41
2.3.2 Advantage of the one-pot simultaneous synthetic route to the new type of polymer, poly(hyperbranched macromonomer) and the comparison of the structures of the resulting polymers prepared by the other two-step methods .....	52
2.3.3 Control of the ratio of polyaddition and addition polymerization in the simultaneous polymerization of 1 by changing amine cocatalysts.....	56
2.3.4 Good gas separation properties of membranes containing poly (hyperbranched macromonomer).....	57
2.4 Conclusion.....	59
References and Notes .....	60
Chapter 3: One-pot synthesis poly $\alpha$ ps(hyperbranched macromonomer) by simultaneous polymerization of two different modes of polymerizations <i>i.e.</i> , addition polymerization and polyaddition of 3,5-bis-[4-dimethylsilylphenyl]phenylacetylene (DHSPPA, 2) by using one catalyst for gas permselective membranes .....	62
Abstract .....	63
3.1 Introduction .....	64
3.2 Experimental part .....	66

3.2.1 Materials.....	66
3.2.2 Measurements.....	66
3.3 Results and discussion.....	74
3.3.1 Advantage of the one-pot simultaneous synthetic route to the new type of polymer, poly(hyperbranched macromonomer).....	74
3.3.2 Good gas separation properties of membranes containing poly (hyperbranched macromonomer)(polyaps(2)).....	75
3.4 Conclusions .....	78
References and Notes .....	79
Chapter 4: One-pot synthesis polyaps(hyperbranched macromonomer) by simultaneous polymerization of two different modes of polymerizations i.e., addition polymerization and polyaddition of <i>m</i> -bis[dimethylsilyl]phenylacetylene (DHSPA 3) by using one catalyst for gas permselective membranes .....	80
Abstract .....	81
4.1 Introduction .....	83
4.2 Experimental part .....	85
4.2.1 Materials.....	85
4.2.2 Measurements.....	86
4.2.3 Synthetic procedures and characterization of monomer (3) All the following reaction procedures were conducted under dry nitrogen.....	86

4.2.4 Membrane preparation. ....	92
4.3 Results and discussion.....	93
4.3.1 Advantage of the one-pot simultaneous synthetic route to the new type of polyaps(3) and the comparison of the structures of the resulting polymers prepared by the other two-step methods .....	93
4.3.2 Control of the ratio of polyaddition and addition polymerization in the simultaneous polymerization of 3 by changing amine cocatalysts.....	97
4.3.3 Gas separation properties of membranes containing poly(3) .....	100
4.4 Conclusions .....	105
References and Notes .....	106
Chapter 5: One-pot synthesis polyaps(hyperbranched macromonomer) by simultaneous polymerization of two different modes of polymerizations i.e., addition polymerization and polyaddition of <i>p</i> -dimethylsilylphenylacetylene(HSPA 4) by using one catalyst for gas permselective membranes .....	110
Abstract .....	111
5.1 Introduction .....	112
5.2 Experimental part .....	113
5.2.1 Materials.....	113
5.2.2 Measurements.....	114

5.2.3 Synthetic procedures and characterization of monomer (4).	114
5.3 Results and discussion.....	117
5.3.1 Advantage of the one-pot simultaneous synthetic route to the new type of poly(4) and the comparison of the structures of the resulting polymers prepared by the other two-step methods .....	117
5.3.2 Control of the ratio of polyaddition and addition polymerization in the simultaneous polymerization of 4 by changing amine cocatalysts.....	119
5.3.3 Copolymerization and gas separation properties of membranes containing poly(4).....	122
5.4 Conclusions .....	129
References and Notes .....	130
Chapter 6: Enhanced gas permselectivity of copoly(hyperbranched macromonomer) synthesized by one-pot simultaneous copolymerization of dimethylsilyl-containing phenylacetylenes .....	131
Abstract .....	132
6.1 Introduction .....	133
6.2 Experimental part.....	135
6.2.1 Materials.....	135
6.2.2 Measurements.....	135
6.2.3.1 Simutaneous addition polymerization and polyaddition of	

1 and 5 (Synthesis of copoly(1/5)) <sup>3</sup> .....	136
6.2.3.2 Addition polymerization of 1 and 5 (Synthesis of copoly(1/5)).....	136
6.3 Results and discussion.....	138
6.3.1 Simultaneous addition polymerization and polyaddition of 1, 3 or 4 with 5 (Synthesis of copoly(1/5, copoly(3/5), copoly(4/5))) <sup>3</sup> .....	141
6.3.2 Copolymerization and gas separation properties of membranes containing poly(4).....	144
6.4 Conclusions .....	150
References and Notes .....	151
Chapter 7: Conclusions .....	153
Acknowledgement.....	154



## Abstract

Simultaneous polymerization of the two different types of polymerizations, *i.e.*, addition polymerization and polyaddition of one new monomer(**1**) having one terminal triple bond and two Si-H groups has been achieved by using  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / various amines. To our

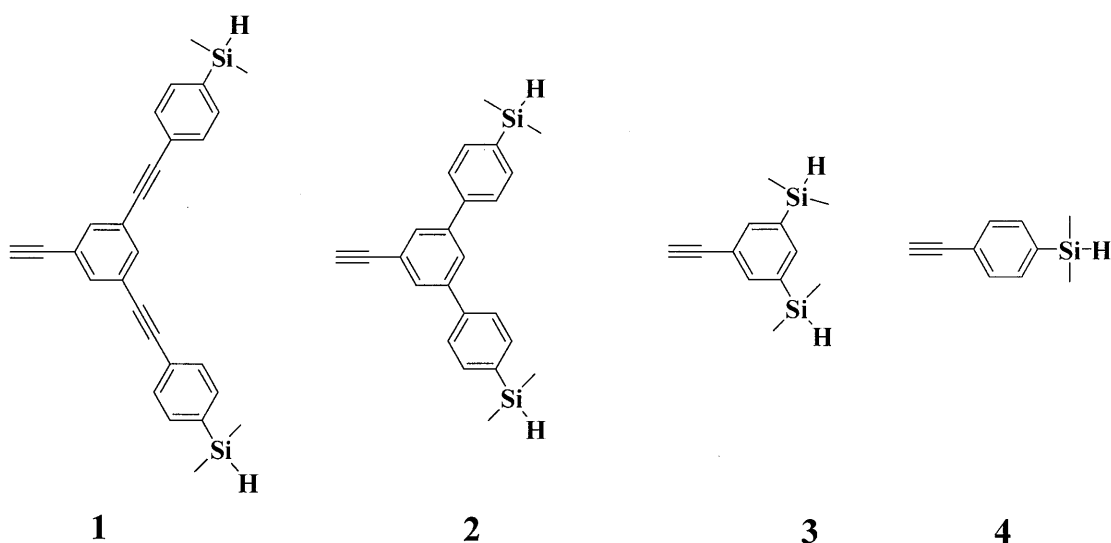


Chart 1

knowledge, this is the first example of such simultaneous polymerization of one monomer. In addition, the ratio of the two polymerizations could be controlled by changing amine cocatalyst. By this polymerization method, one-pot synthesis of poly(hyperbranched acetylene-type macromonomer) from **1** was realized. In addition monomer **2**, **3**, **4** (see chart 1) having one terminal triple bond and one or two Si-H groups have been polymerized by  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / various amines. To the best of our knowledge, this is the first synthesis of such complex polymers.

Membranes from the poly(hyperbranched acetylene-type macromonomer) had both the advantages of poly(phenylacetylene)s and poly(dendron). Some of them showed the highest performance as oxygen or carbon dioxide permselective membranes among the all membranes reported. In summary, a new complex polymer, poly(hyperbranched acetylene-type macromonomer) showing good performance as gas separation membranes were synthesized very easily by the one-pot simultaneous polymerization method.

## **Chapter 1: Introduction**

## 1.1 Overview of gas separation membrane

In the last two decades significant improvements in the performance of polymeric membranes for gas separation have been made<sup>1-6</sup>, and our understanding of the relationships among the structure, permeability and selectivity of polymeric membranes has been greatly advanced<sup>2,3</sup>. Newer polymeric membrane materials such as polyimides (PI) and cross-linked polyethylene glycol (PEG) have been continuously developed. Some polymeric membranes have already been used in industry. Polymeric membranes tend to be more economical than other membranes because of their ability to be easily spun into hollow fibers or spiral-wound modules due to their flexibility and solution processability<sup>1</sup>.

Membranes of polymeric material have been recognized in a number of separation processes of gas, liquid and mixed phases<sup>7,8</sup>. The basic principle of gas separation by polymeric membranes is the solution diffusion mechanism. In this model, the transport of a gas mixture component through the polymer matrix occurs under a gas phase partial pressure gradient (or chemical potential gradient) of that component across the membrane. The diffusion consists of three steps: (a) adsorption at the surface and dissolution into the polymer in the high pressure face of the membrane, (b) diffusion across the membrane thickness to the lower pressure side and (c) desorption of the gas and vaporization into

the gas phase.

Polyacetylenes with bulky spherical substituents show extremely high gas permeability. This is because the combination of their stiff main chain composed of alternating double bonds 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 permeability of their membranes has been investigated.<sup>9-12</sup> The incorporation of functional groups into poly(substituted acetylene)s is of great interest in the various fields due to their potential applications as polymer light-emitting devices, sensors, enantioselective materials, and separation membranes for specific gases.

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

Adsorption processes for gas separation applications<sup>13-16</sup>. Naturally, strong interest exists in the area of preparation of new membrane with higher separation efficiency. This means that both the permeability

coefficient and the selectivity should be as large as possible. Only glassy polymers combine sufficiently high permeability and selectivity needed for consideration as next generation gas separation membrane materials. 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<sup>17,18</sup>. Former studies of structure-property relationships on gas transport behavior in glassy polymers indicate important rules for the design of improved membrane materials. The increase in gas permeability while keeping selectivity is induced by the chemical structure changes which hinder packing of relatively rigid main chain. Furthermore, improved permselectivity without a loss of permeability, results from the chemical structure changes which reduce the rotational mobility around the flexible linkage in the polymer main chain if intersegmental packing is not significantly affected<sup>14,16</sup>. Because the introduction of bulky moieties to the main chain leads to both the reduction of the rotational mobility and the prohibition of intersegmental packing, the bulky moieties are considered effective in improving membrane performance. The phenylfluorene based cardo polymers show high thermal stability, high solubility, low refractive index, high optical transparency and low dielectric constant, because of the relatively high free volume<sup>19-21</sup>. In recent years, polymers containing fluorene moieties have been interesting

because of their potential applications as photoelectronic materials <sup>22,23</sup>. These polymers are also interesting for gas separation application. In fact, the improved gas transport properties of several cardo polymers were reported<sup>24-26</sup>. The bulky fluorene moiety in a diphenylfluorene based cardo polymers protrudes vertically from the polymer main chain. This chemical structure of four phenyl rings connected to a quaternary carbon leads to severe rotational hindrance of the phenyl groups. Thus, the stiff, bulky cardo moiety must hinder the packing and reduce the rotational mobility of main chain. Therefore, the diphenylfluorene cardo moiety is supposed to have the potential of improving the gas transport properties. Polysulfone <sup>27, 28</sup>, polycarbonates <sup>28</sup>, polyacrylates<sup>29</sup>, poly(ether ketone)s<sup>30</sup>, poly(arylene ether)s<sup>31</sup> and poly(arylene ether ketone)<sup>32</sup> derived from 4,4'-(9-fluorenylidene)bisphenol have been synthesized and their gas transport properties have been reported. It has been observed that polyimides are the most attractive candidates for gas separation membranes as they show high gas selectivity for different gas pair (CO<sub>2</sub>/CH<sub>4</sub>, H<sub>2</sub>/CH<sub>4</sub>, O<sub>2</sub>/N<sub>2</sub> etc.) along with a number of outstanding properties such as excellent thermal and thermo-oxidative stability, solvent resistance, fire retardance, mechanical and electrical properties <sup>32-35</sup>.

## 1.2 Dendrimer

Dendrimers are highly branched regular three-dimensional monodisperse

macromolecules with a branch occurring at each monomer unit. Large dendrimers adopt a globular shape. They are characterized by the presence of a large number of functional groups on the surface which results in solubility, viscosity, and thermal behaviors different from those of more classical polymers. They are also characterized by the presence of internal cavities which can be functionalized and by a core that does or does not bear functional groups. The synthesis of dendrimers is more closely related to organic chemistry rather than traditional polymer synthesis regarding with the requirement for a number of synthetic processes and procedures including repeating purification and exact characterization. Two different synthetic strategies, a divergent<sup>1-3</sup> and a convergent growth approach<sup>36</sup> are generally employed to construct dendritic frameworks. In both step-by-step synthetic approaches quantitative coupling reactions are required to construct high generation dendrimers. A host of dendrimers have been presented in the literatures: polyamidoamine (PAMAM), poly(propyl imine)(DAB-dendr-NH<sub>2</sub>), polyethers, polyesters, poly(ester amides), poly(ether amides), polyalkanes, polyphenylenes, poly(phenylacetylenes), polysilanes, phosphorus dendrimers and others<sup>37-42</sup>. Among them highly branched polymers like dendrimers have received much attention because of their regular structures. Dendrimers have highly regulated branched structures but generally they have two problems. One is synthesis of the polymers



needs many steps and results in very low yields because they were prepared not by polymerization but by multi-step organic reactions. The other problem is their low ability for fabrication because of no entanglement. Poly(dendron macromonomer) was a valuable polymer having regulated structures and better membrane forming ability than dendrimers. However it had still the two problems as described above. (1) Multi-step synthetic route(low yield) and (2) Low membrane forming ability. They were prepared more easily by one polymerization of  $AB_2$  type monomers in higher yields. To solve the second problem, we reported a new type of branched polymers, that is, poly(dendron macromonomer) which was a highly branched polymer having a linear rigid backbone prepared by addition polymerization of the acetylene group in the macromonomer having regularly branched dendritic structure<sup>11</sup> In addition, the resulting polymer showed good performance of gas permselectivity due to their regulated branched structures.

### **1.3 Hyperbranched polymers**

Hyperbranched polymers are highly branched macromolecules with three-dimensional dendritic architecture. Due to their unique physical and chemical properties and potential applications in various fields from drug-delivery to coatings, interest in hyperbranched polymers is growing

rapidly. A vast variety of highly branched polymer structures has been reported since their theoretical treatment in the middle of the 20th century.<sup>43, 44</sup> Especially in the last 20 years,<sup>45, 46</sup> very strong synthetic activity emerged on macromolecules that can be classified as “hyperbranched” (hb).<sup>47</sup> This term now not only covers the “classical” products based on Flory’s AB<sub>x</sub> approach<sup>2</sup> but is extended to various highly branched structures including those prepared by the A<sub>2</sub> B<sub>y</sub> monomer combination;<sup>44,48,49,50</sup> those prepared by self-condensing vinyl polymerization (SCVP),<sup>51</sup> ring-opening multibranching polymerization (ROMBP) or self-condensing ring-opening polymerization (SCROP), or proton transfer polymerization;<sup>52,53</sup> and those prepared by various copolymerizations and methodology combinations including self-assembly aspects, which lead to linear highly branched hybrids like dendronized polymers,<sup>54,55</sup> dendrigrafts,<sup>56,58</sup> and hb core star-branched structures<sup>59,60</sup> and nanocapsules.<sup>57,61</sup>

Hyperbranched polymers have similar structural properties compared with the dendrimers. Therefore, some research groups investigated the gas selectivity properties of membranes prepared from the hyperbranched polymers. For example, Suzuki et al., synthesized a novel hyperbranched material with 4,4’-(hexafluoroisopropylidene) diphtalilic anhydride (6FDA) and 1,3,5-tris(4-aminophenoxy)benzene (TAPOB) Fig. (19)<sup>62-64</sup>. They prepared a hybrid membrane with the 6FDA-TAPOB hyperbranched

material and silica. Compared with linear type polyimides, such as the novel 6FDA-TAPOB, hyperbranched polyimide had a better thermal stability and a higher fractional free volume. The prepared membrane exhibited considerably high gas solubility, resulting in high gas permeability (Table 2). It was shown that after incorporation of silica in the 6FDA-TAPOB-silica hybrids, both the diffusion and selectivity increased with the increasing content of the silica in the hybrids. In addition, the properties of oxidiphthallic anhydride (ODPA)-TAPOB hyperbranched membrane and the corresponding silica hybrid membrane were investigated in the same group and the result is similar to that of above-mentioned hyperbranched membrane <sup>65</sup>. Hyperbranched neopentyltetraethylene diamine was used to prepare membrane for carbon dioxide separation by Wang et al. <sup>66</sup>. Such membrane was prepared by casting the solution, which consists of dendritic neopentyltetraethylene diamine and polyvinyl alcohol, onto the polysulphone membrane or polyethersulphone membrane matrix. Compared to traditional gas separation membrane without the dendritic polymer, the new membrane had better permselectivity, higher stability and compression resistance.

#### **1.4 Simultaneous polymerization**

All synthetic polymers such as polystyrenes, acrylic polymers, polyesters, polyamides, and so forth, which heavily support our modern life, are obtained by either a chain- or step-growth polymerization. <sup>67,68</sup>

These two classes of polymerizations are mechanistically completely different and proceed via their characteristic profiles of polymer chain propagation to produce the polymers with their unique structures. In the chain-growth mechanism, polymer chains grow via reactions of the growing chain end with monomers, while in the step-growth counterpart, the chain gradually propagates via reactions among the functional chain-end groups of the monomer, oligomers, and finally polymers. The former representatives are radical polymerizations of vinyl monomers, which produce C-C bond main-chain polymers, whereas the latter includes polycondensation for polyesters and polyaddition for polyurethane, mostly containing heteroatoms in the main chains. If one could simultaneously perform both the chain- and step-growth polymerizations, the accessible polymer structures and properties could be widely varied.

### **1.5 Aims of this thesis**

Four monomers of phenylacetylenes structure (**HDENPA**, **DHSPPA**, **DHSPA**, **HSPA**) were designed and synthesized as shown in Chart 1,

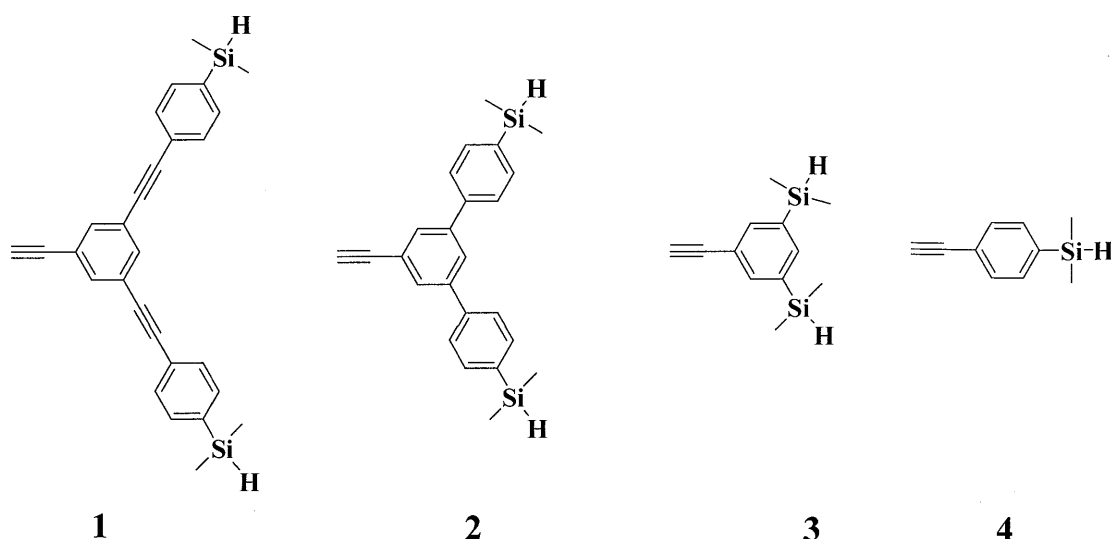
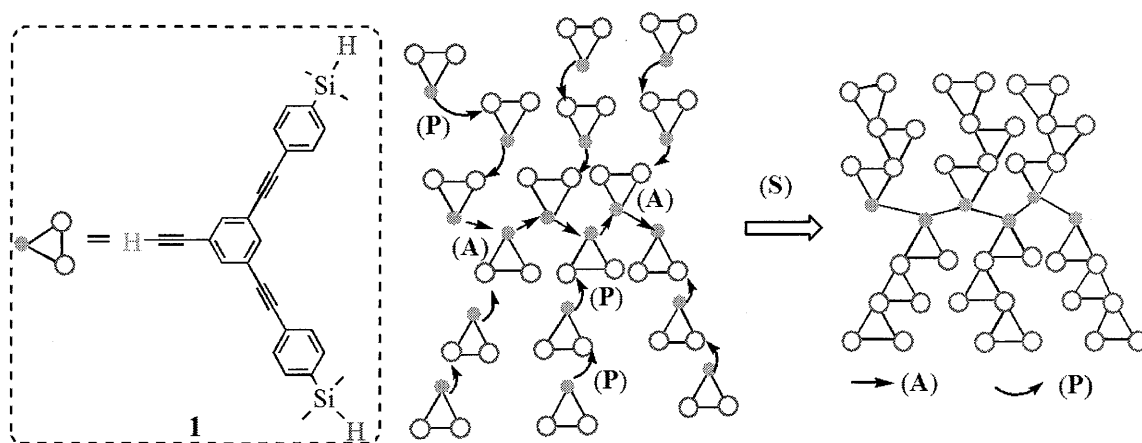


Chart 1. Chemical structures of the monomers

(HDENPA(1), DHSPPA(2), DHSPA(3), HSPA(4))

Simultaneous polymerization of the two different types of polymerizations, *i.e.*, addition polymerization and polyaddition of one monomer having one terminal triple bond and two Si-H groups has been achieved by using  $[\text{Rh}(\text{norbornadiene}(\text{=nbd}))\text{Cl}]_2$  / various amines.(Scheme 1-1) To our



**Scheme 1-1** Synthesis of polyaps(hyperbranched acetylene-type macromonomer) by simultaneous polymerization knowledge, this is the first example of such simultaneous polymerization of one monomer. In

addition, the ratio of the two polymerizations could be controlled by changing amine cocatalyst. By this polymerization method, one-pot synthesis of poly(hyperbranched acetylene-type macromonomer) from **1** was realized. To the best of our knowledge, this is the first synthesis of such complex polymers. Membranes from the poly(hyperbranched acetylene-type macromonomer) had both the advantages of poly(phenylacetylene)s and poly(dendron).

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**Chapter 2: One-pot synthesis of novel poly(hyperbranched acetylene-type macromonomer) by simultaneous polymerization of two different modes of polymerizations, *i.e.*, addition polymerization and polyaddition of one monomer by using one catalyst for gas permselective membranes**

## Abstract

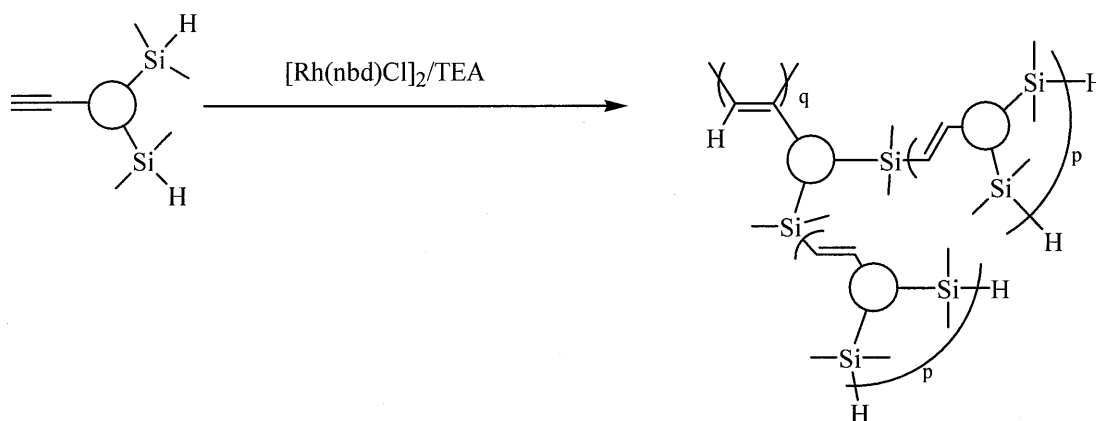
Simultaneous polymerization of the two different types of polymerizations, *i.e.*, addition polymerization and polyaddition of one new monomer(**1**) having one terminal triple bond and two Si-H groups has been achieved by using  $[\text{Rh}(\text{norbornadiene}(=\text{nbd}))\text{Cl}]_2$  / various amines. In addition, the ratio of the two polymerizations could be controlled by changing amine cocatalyst. By this polymerization method, one-pot synthesis of poly(hyperbranched acetylene-type macromonomer) from **1** was realized. To the best of our knowledge, this is the first synthesis of such complex polymers. Membranes from the poly(hyperbranched acetylene-type macromonomer) had both the advantages of poly(phenylacetylene)s and poly(dendron). Some of them showed the highest performance as oxygen permselective membranes among all the membranes reported. In summary, a new complex polymer, poly(hyperbranched acetylene-type macromonomer) showing good performance as gas separation membranes was synthesized very easily by the one-pot simultaneous polymerization method.

## 2.1 Introduction

Recently some kinds of new polymer molecules having unique structures have been reported. Among them highly branched polymers like dendrimers have received much attention because of their regular structures.<sup>1</sup> Dendrimers have highly regulated branched structures but generally they have two problems. One is synthesis of the polymers needs many steps and results in very low yields because they were prepared not by polymerization but by multi-step organic reactions. The other problem is their low ability for fabrication because of no entanglement.

To overcome the first problem, hyperbranched polymers have been reported.<sup>2</sup> They were prepared more easily by one polymerization of AB<sub>2</sub> type monomers in higher yields. To solve the second problem, we reported a new type of branched polymers, that is, poly(dendron macromonomer)(for example, polymers of **3**<sub>1-3</sub> in Chart 2-1) which was a highly branched polymer having a linear rigid backbone prepared by addition polymerization of the acetylene group in the macromonomer having regularly branched dendritic structure.<sup>3</sup> In addition, the resulting polymer showed good performance of gas permselectivity due to their regulated branched structures. Gas permselective membranes are very important and valuable because the necessity to remove impurities or purify mixtures of gases whose molecular sizes are very similar is enhancing because solving the recent environmental problems has been

focused on.<sup>4</sup> In general, tradeoff relationship between permeability and permselectivity is usually observed. To overcome this, more control of chemical structures of the side groups in the polymer used for permselective membranes are needed. Poly(dendron macromonomer) was a valuable polymer having regulated structures and better membrane forming ability than dendrimers. However it had still the two problems as described above. (1) Multi-step synthetic route(low yield) and (2) Low membrane forming ability.



polyaps(hyperbranched macromonomer)

In this study to overcome the two problems, we designed a new type of polymer, *i.e.*, poly (hyperbranched macromonomer). In addition, we propose its new synthetic method, *i.e.*, one-pot synthesis by simultaneous polymerization of two types of polymerization of one monomer. In other words, in this communication, we report a new complicated polymer and its very simple preparation method. The complex polymer could be synthesized by very easy one-pot procedure. In addition, we report



significantly better performance of gas permselectivities of the resulting polymer membranes which are on the Robeson's upper boundary line.<sup>4d</sup>

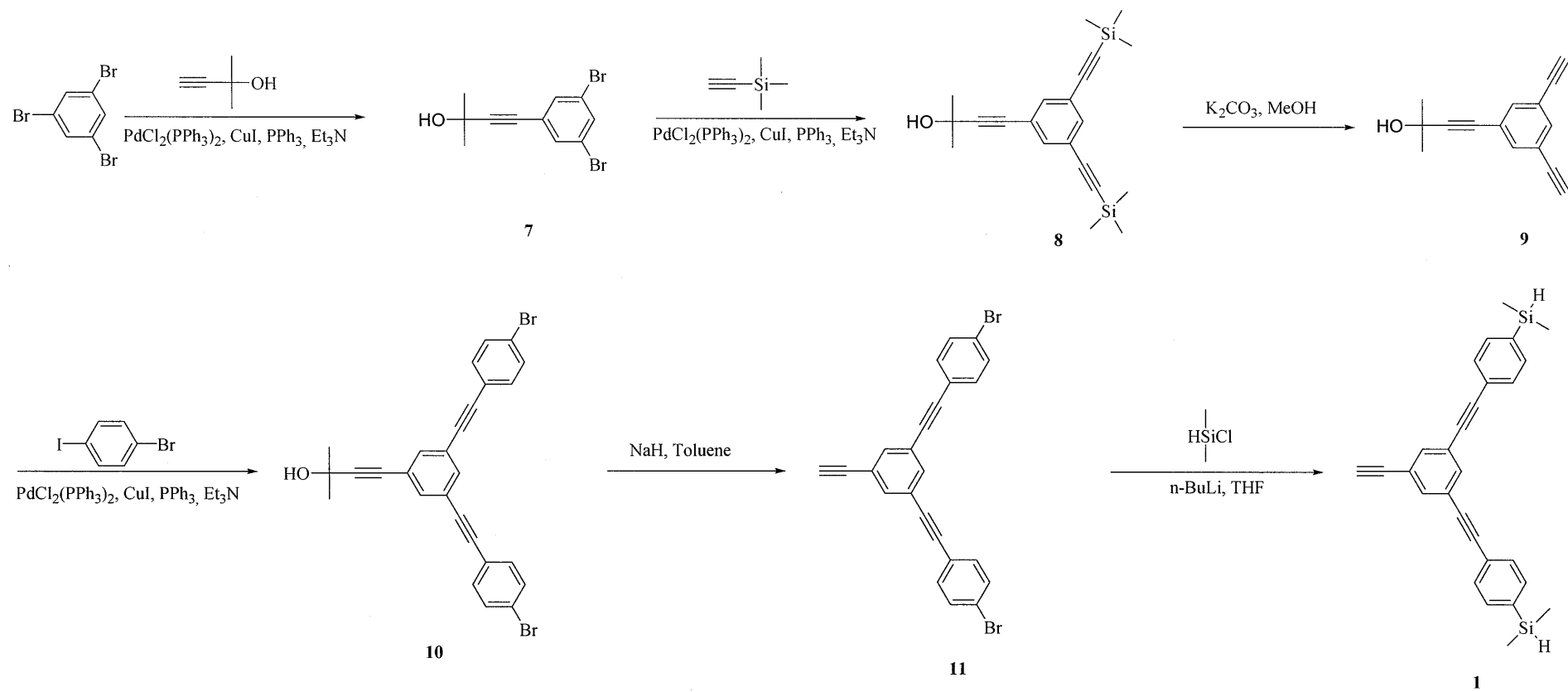
## 2.2 Experimental part

### 2.2.1 Materials.

All the solvents used for synthesis and polymerizations of the monomers were distilled as usual. The polymerization initiator,  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  (nbd = 2,5-norbornadiene) and amines purchased from Aldrich Chemical were used as received.

### 2.2.2 Measurements.

$^1\text{H}$  NMR (400 MHz) spectra were recorded on a VARIAN-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). The infrared spectra were recorded on FT/IR-4200 (JASCO). Oxygen, carbon dioxide, and nitrogen permeability coefficients ( $P_{\text{O}_2}$ ,  $P_{\text{CO}_2}$ , and  $P_{\text{N}_2}$ :  $\text{cm}^3(\text{STP})\text{cm}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{cmHg}^{-1}$ ) were measured by a gas chromatographic method at 25°C using YANACO GTR-10 according to Ref. (3e). The area of membrane was  $1.77\text{ cm}^2$ , and the initial feed gas pressure was 1 atm.

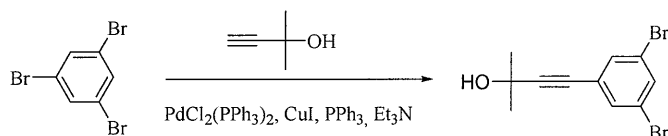


**Scheme 2- 2.** Synthetic route to the monomer (1)

### 2.2.3 Synthetic procedures and characterization of monomer (1)

All of the following reaction procedures were conducted under dry nitrogen. (Scheme 2-2)

#### 2.2.3.1 1-(3-Hydroxyl-3-methylbutynyl)-3,5-dibromobenzene(7).<sup>2</sup>



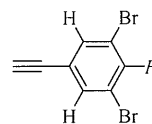
2-Methyl-3-butyn-2-ol (2.8 mL, 30 mmol) was added to 1,3,5-tribromobenzene (9.4 g, 30 mmol), bis(triphenylphosphine)palladium(II) chloride (0.14 g, 0.20 mmol), triphenylphosphine (0.24 g, 0.92 mmol) and copper(I) iodide (0.12 g, 0.63 mmol) in dry triethylamine (150 mL) under a nitrogen atmosphere. The solution was stirred for 16 h at 90°C to precipitate a white solid. The solid was filtered out, and the solvent of the filtrate was concentrated by evaporation. The crude product was purified by silica-gel column chromatography with ethyl acetate / hexane = 1/4 as an eluent to give **7**.  $R_f = 0.4$  (ethyl acetate / hexane = 1/4).

Appearance: yellow solid.

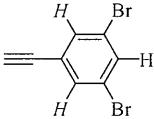
Weight: 6.0 g.

Yield: 63%.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS,  $\delta$ ): 7.60 (t, 1H,  $J = 1.5$  Hz,

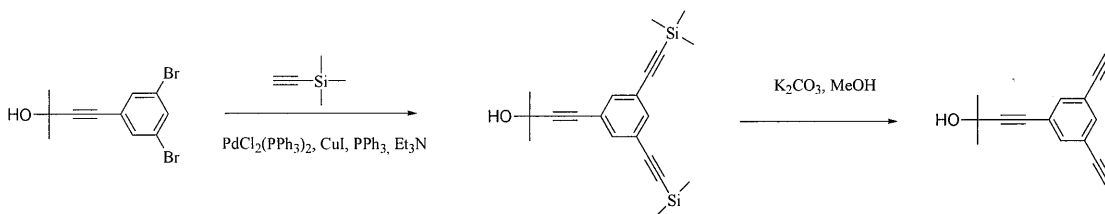


), 7.49 (d,

$2\text{H}, J = 1.5 \text{ Hz}$ , ,  $2.10 \text{ (s, 1H, -OH)}$ ,  $1.60 \text{ (s, 6H, -C(CH}_3)_2\text{)ppm}$ .  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , TMS,  $\delta$ ): 133.12, 122.22, 95.15, 94.09, 81.22, 65.59, 31.37ppm.

IR (KBr;  $\text{cm}^{-1}$ ): 3484 (OH), 2988 (C-H), 2356 ( $\text{C}\equiv\text{C}$ ).

### 2.2.3.2 1-(3-Hydroxyl-3-methylbutynyl)-3,5-diethynylbenzene(9).<sup>2</sup>



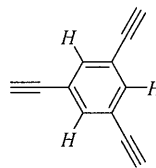
Trimethylsilylacetylene (3.5 mL, 38 mmol) was added to **7** (6.0 g, 19 mmol), bis(triphenylphosphine)palladium(II) chloride (0.26 g, 0.34 mmol), triphenylphosphine (90 mg, 0.34 mmol) and copper(I) iodide (60 mg, 0.34 mmol) in dry triethylamine (120 mL) under a nitrogen atmosphere. The solution was stirred for 24 h at  $90^\circ\text{C}$  to precipitate a white solid. The solid was filtered out. The solvent of the filtrate was concentrated by evaporation. The crude product of 1-(3-hydroxyl-3-methylbutynyl)-3,5-bis(trimethylsilylethynyl)benzene(**8**) was added slowly to  $\text{K}_2\text{CO}_3$  (2.5 g, 24 mmol) in methanol (40 mL). The mixture was stirred with a magnetic stirrer for 6 hours and 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%  $\text{HCl(aq)}$  and then water, and dried over anhydrous sodium sulfate. The

solvent of the filtrate was concentrated by evaporation, and the crude product was purified by silica-gel column chromatography with ethyl acetate / hexane = 1/4 as an eluent to give **9**.  $R_f = 0.25$  (ethyl acetate / hexane = 1/4).

Appearance: white solid.

Weight: 3.2 g.

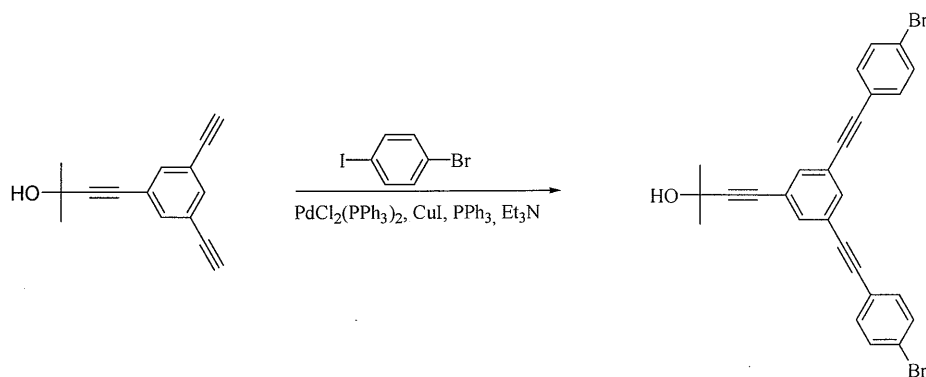
Yield: 81%.



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS,  $\delta$ ): 7.5 (s, 3H,  $\text{H}$ ), 3.1 (s, 2H,  $\text{HC}\equiv\text{C}$ ), 2.10 (s, 1H,  $-\text{OH}$ ), 1.60 (s, 6H,  $-\text{C}(\text{CH}_3)_2$ ),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 133.12, 122.22, 95.15, 94.09, 81.22, 65.59, 31.37 ppm.

IR (KBr;  $\text{cm}^{-1}$ ): 3484 ( $-\text{OH}$ ), 2988 (C-H), 2356 ( $\text{C}\equiv\text{C}$ ).

### 2.2.3.3 1-(3-Hydroxyl-3-methylbutynyl)-3,5-bis(4-bromophenyl-acetylene)benzene(10).<sup>2</sup>



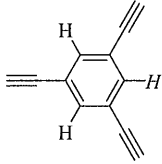
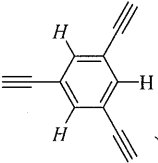
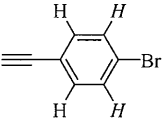
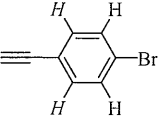
**9** (3.2 g, 15 mmol) was dissolved with dry triethylamine (40 mL). The

solution was added to bis(triphenylphosphine)palladium(II) chloride (260 mg, 0.34 mmol), copper(I) iodide (65 mg, 0.34 mmol), triphenylphosphine (90 mg, 0.34 mmol), 1-bromo-4-iodobenzene (10 g, 34 mmol) in dry triethylamine (80 mL) under a nitrogen atmosphere. The solution was stirred for 24 h at 90°C to precipitate a white solid. The solid was filtered out. The solvent of the filtrate was concentrated by evaporation. The crude product was purified by silica-gel column chromatography with chloroform as an eluent to give **10**.  $R_f = 0.4$  (chloroform)

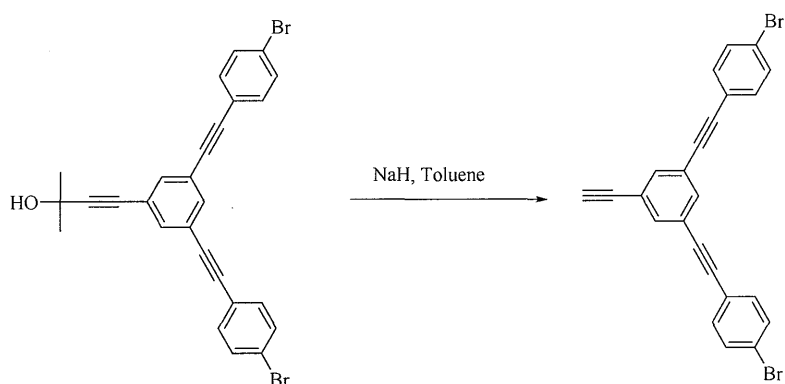
Appearance: yellow solid.

Weight: 4.0 g.

Yield: 52%.

$^1\text{H}$  NMR( $\text{CDCl}_3$ , TMS,  $\delta$ ): 7.60(t, 1H,  $J = 1.5$  Hz, , 7.54(d, 2H,  $J = 1.5$  Hz, , 7.51(d, 4H,  $J = 7.6$  Hz, , 7.38(d, 4H,  $J = 7.6$  Hz, , 2.00(s, 1H, -OH), 1.61(s, 6H, -C(CH<sub>3</sub>)<sub>2</sub>)ppm.

#### 2.2.3.4 3,5-Bis(4-bromophenylacetylene)-1-phenylacetylene(11).<sup>2</sup>



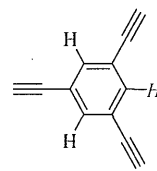
Sodium hydride (0.31 g, 7.1 mmol) was added to a toluene solution (126 mL) of **10** (3.7 g, 7.1 mmol). The mixture was heated to 90°C and stirred under a nitrogen flow for 2 h. It was allowed to room temperature slowly. The reaction mixture was filtered. The solvent of the filtrate was concentrated 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 **11**.  $R_f = 0.3$  (ethyl acetate / hexane = 1/20).

Appearance: yellow solid.

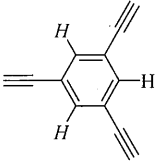
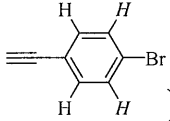
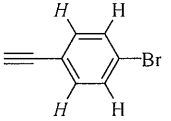
Weight: 2.4 g.

Yield: 72%.

$^1\text{H}$  NMR( $\text{CDCl}_3$ , TMS,  $\delta$ ): 7.65(s, 1H,  $J = 1.5$  Hz,

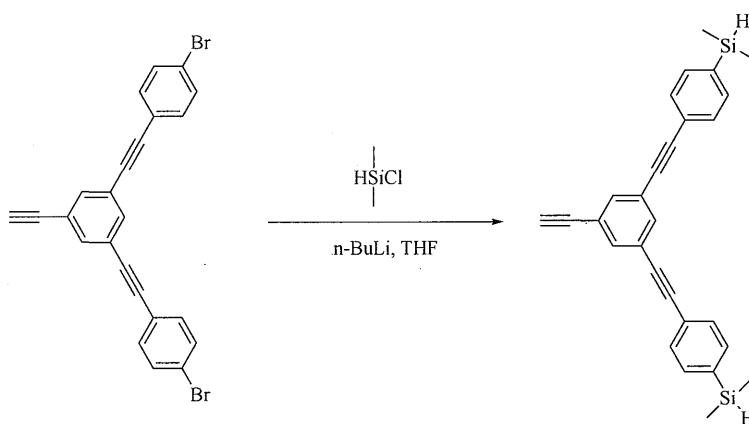


), 7.60(d,

$2\text{H}, J = 1.5 \text{ Hz}$ , ,  $7.50(\text{d}, 4\text{H}, J = 7.6 \text{ Hz}$  ,  $7.38(\text{d},$   
 $4\text{H}, J = 7.6 \text{ Hz}$  ,  $3.11(\text{s}, 1\text{H}, \text{HC}\equiv\text{C})\text{ppm}$ .

IR (KBr;  $\text{cm}^{-1}$ ): 3300(C-H), 2316 ( $\text{C}\equiv\text{C}$ ).

### 2.2.3.5 3,5-Bis(4-dimethylsilylphenylacetylene)phenylacetylene(1).<sup>3</sup>



A 200 mL round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen gas. **11** (1.6 g, 3.4 mmol) and dry THF (34 mL) were placed in the flask at  $-75^{\circ}\text{C}$ . At the same temperature, a hexane solution of *n*-butyllithium (6.4 mL, 10 mmol,  $C = 1.6 \text{ M}$  in hexane) was added dropwise, and the reaction mixture was stirred for 4 h at the same temperature,. A solution of dimethylchlorosilane (0.75 mL, 6.7 mmol) in dry THF (34 mL) was added dropwise, and it was allowed to warm to

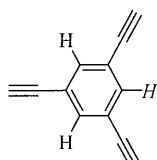
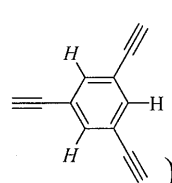
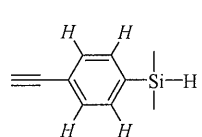


room temperature slowly and kept overnight at the same temperature. After excess water was added to the reaction mixture, the stirring was continued for 1 h. The mixture was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. Diethyl ether was evaporated, and the crude product was purified by flash column chromatography (Merck, silica gel 60; eluent, hexane) to give **1**.

Appearance: colorless liquid.

Weight: 0.74 g.

Yield: 52%.

<sup>1</sup>H NMR(CDCl<sub>3</sub>, TMS, δ): 7.68(t, 1H, *J* = 1.5 Hz, , 7.60(d, 2H, *J* = 1.5 Hz, , 7.50(m, 8H, , 4.42(heptet, 2H, *J* = 3.76 Hz -HSi(Me)<sub>2</sub>), 3.11(s, 1H, HC≡C), 0.37(d, 12H, *J* = 3.76Hz, -Si(CH<sub>3</sub>)<sub>2</sub>)ppm.

<sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ138.53, 134.68, 134.56, 133.95, 130.82, 124.00, 123.34, 122.84, 90.69, 88.14, 81.98, 78.34, -3.90ppm.

IR (KBr; cm<sup>-1</sup>): 3300, 2957, 2923, 2861, 2120, 1572, 1373, 1250, 1133, 880, 838, 763, 640

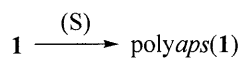
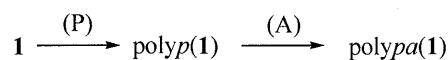
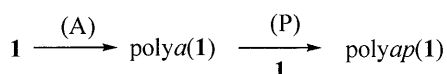
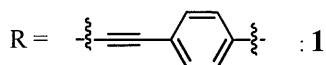
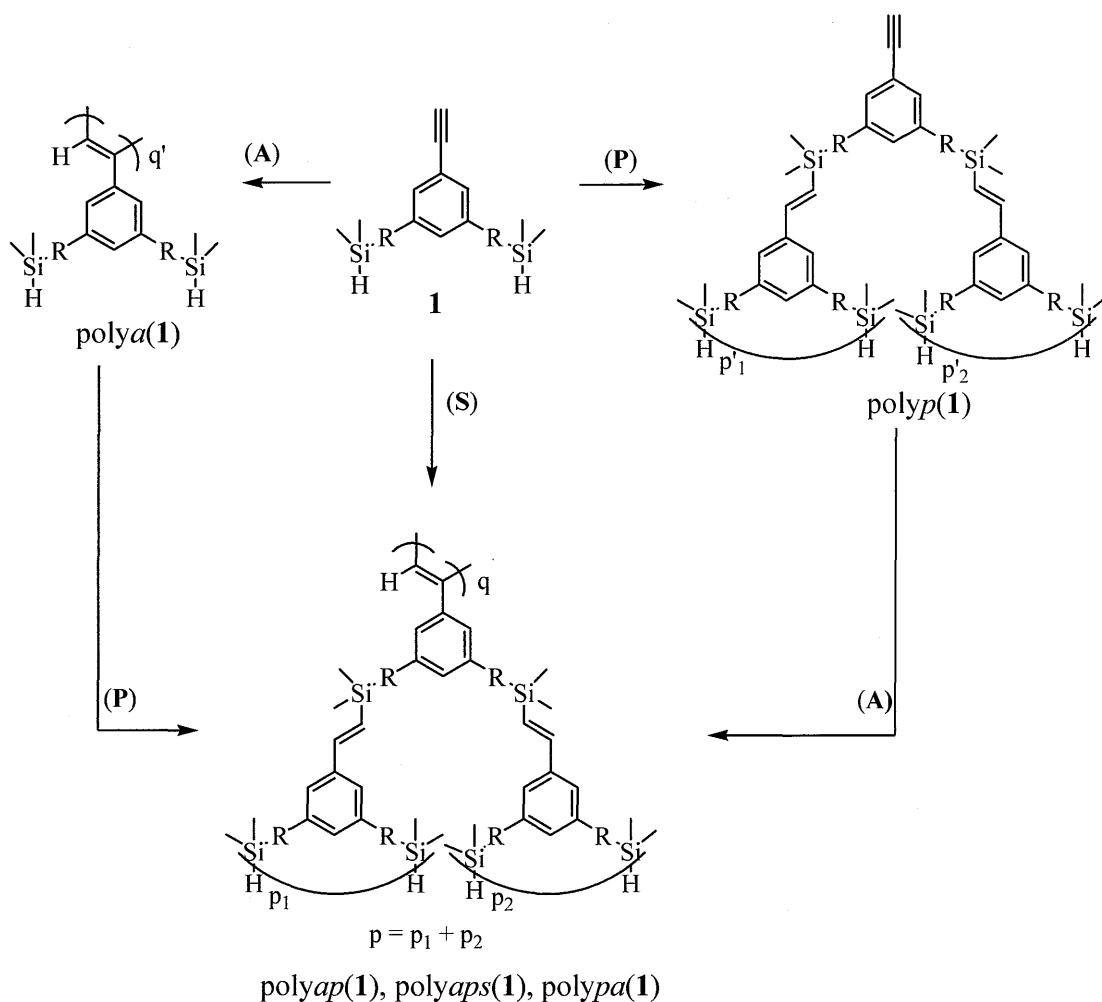
#### 2.2.4 Measurement of oxygen, carbon dioxide, and nitrogen permeability

Oxygen, carbon dioxide, and nitrogen permeability coefficients ( $PO_2$ ,  $PCO_2$ , and  $P_{N_2}$ :  $\text{cm}^3(\text{STP})\cdot\text{cm}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{cmHg}^{-1}$ ) were measured by a gas chromatographic method at 25°C using YANACO GTR-10 according to Ref. (3e). The area of membrane was 1.77  $\text{cm}^2$ , and the initial feed gas pressure was 1 atm.

## 2.3 Results and discussion

### 2.3.1 Discovery of one-pot synthesis of a new type of polymer, poly(hyperbranched acetylene-type macromonomer) by the simultaneous polymerization of two different types of polymerizations, *i.e.*, addition polymerization and polyaddition of one new monomer by using one catalyst

To begin with, we report discovery of one-pot synthesis of a new type of polymer, poly(hyperbranched acetylene-type macromonomer) by the simultaneous polymerization of two different types of polymerizations, *i.e.*, addition polymerization and polyaddition of one new monomer (**1** in Scheme 2-1) by using one catalyst. The new monomer **1** having one terminal triple bond and two Si-H groups via an ethynylene-phenylene spacer was synthesized (see Scheme 2-1) and polymerized with  $\text{RhCl}(\text{PPh}_3)_3$  / NaI or  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / various amines (see Chart 2-1) such as triethylamine (**TEA**), phenylethylamine (**PEA**), and so on. Table 1 shows the results of the polymerization of **1**



Scheme 2-1. Polymerization of **1**; (A): Addition polymerization by [Rh(nbd)Cl]<sub>2</sub> / phenylethylamine(PEA); (P): Polyaddition with RhCl(PPh<sub>3</sub>)<sub>3</sub> / NaI; (S): Simultaneous polymerization by [Rh(nbd)Cl]<sub>2</sub> / amine (**Ia**, **Ib**, **Ic**, and **TEA**)(see Chart 2-1).

and Figures 1 and 2 show the GPC and <sup>1</sup>H NMR of the resulting polymers, respectively. We defined and calculated some original values

( $p / q$ ,  $X(\%)$ ,  $G$ ,  $C(\%)$  and  $D(\%)$ ) in Table 1 to estimate the polymerizations and structures of the resulting polymers with  $^1\text{H}$  NMR. The values were defined as follows:  $p / q$ : the ratio of the degree of polyaddition( $p$ ) to the degree of addition polymerization( $q$ ),  $X(\%)$ : the ratio of the hyperbranched parts in the all polymer molecule,  $G$ : the average generation of the hyperbranched polymer parts,  $C(\%)$ : the ratio of unreacted dimethylsilyl groups( $P_{\text{H}}$ ) except for those at the position closest to the polyacetylene main chain( $Q_{\text{H}}$ ), and  $D(\%)$ : the content of silanol or siloxane formed by side reaction. They were calculated from the following equations:

$$p / q = B_{\text{Me}} / \{6A_{\text{H}}(\text{or } 6T_{\text{H}})\} \quad (1)$$

$$X(\%) = p / (p + q) \times 100 \quad (2)$$

$$G(\text{Average generation}) = \log\{(P_{\text{H}} + Q_{\text{H}}) / (A_{\text{H}}(\text{or } T_{\text{H}}))\} / \log 2 \quad (3)$$

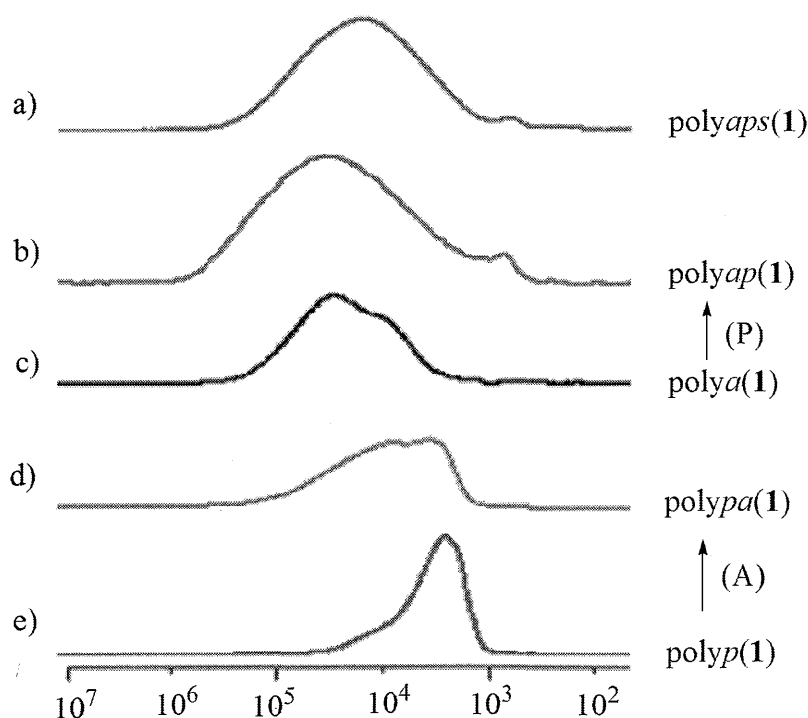
$$C(\%) = P_{\text{H}} / (P_{\text{H}} + Q_{\text{H}}) \times 100 \quad (4)$$

$$D(\%) = I_{\text{Me}} / (P_{\text{Me}} + Q_{\text{Me}} + B_{\text{Me}} + I_{\text{Me}}) \times 100 \quad (5)$$

where  $P_{\text{H}}$ ,  $Q_{\text{H}}$ ;  $P_{\text{Me}}$ ,  $Q_{\text{Me}}$ ,  $B_{\text{Me}}$ ;  $A_{\text{H}}$ ,  $T_{\text{H}}$ , and  $I_{\text{Me}}$  are integral values in  $^1\text{H}$  NMR (Figure 2). For the assignments see Figure 3.

When  $\text{RhCl}(\text{PPh}_3)_3 / \text{NaI}$  was used as a catalyst, **1** was polymerized only by hydrosilation between the terminal triple bond and the two Si-H groups in polyaddition mode ((**P**) in Scheme 1) to yield a hyperbranched acetylene type macromonomer (polyp(**1**) in Scheme 1, no.8 in Table 1

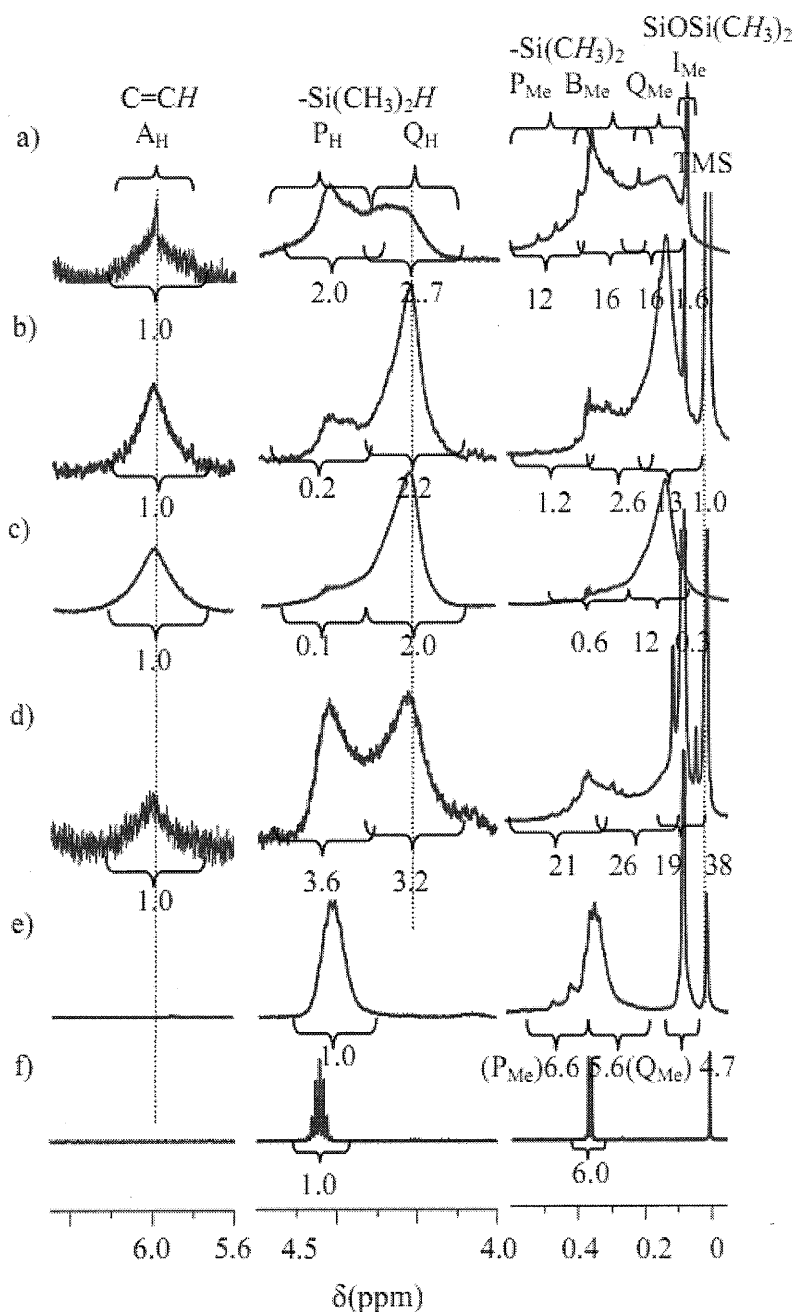
and Figure 2-1 and 2 e)) because **1** is an AB<sub>2</sub> type monomer. When at the terminal triple bonds in addition polymerization mode ((A) in Scheme 2-1) to yield poly $\alpha$ (**1**) as shown in Scheme 2-1 (no.6 in Table 2-1 and Figure 2-1 and 2 c)). On the other hand, when [Rh(nbd)Cl]<sub>2</sub> / TEA, 2-hydroxymethyl-2-aminoethanol(**Ia**), 2-ethyl-2-aminoethanol(**Ib**), or 1-cyclohexylethylamine(**Ic**) was used as a catalyst (For the structures, see Chart S1), **1** was polymerized simultaneously both in polyaddition mode and addition polymerization mode ((S) in Scheme 2-1, no.6 in Table 2-1 and Figure 2-1 and 2 c)) to yield poly $\alpha$ ps(**1**) as shown in Scheme 1 (nos.1-4 in Table 2-1, and Figures 2-1a) and 2 a)).



**Figure 2-1.** GPC of the polymers from **1**. a) poly $\alpha$ ps(**1**) (Table 2-1, No. 3); b) poly $\alpha$ p(**1**) (Table 2-1, No. 5); c) poly $\alpha$ (**1**) (Table 2-1, No.6); d)

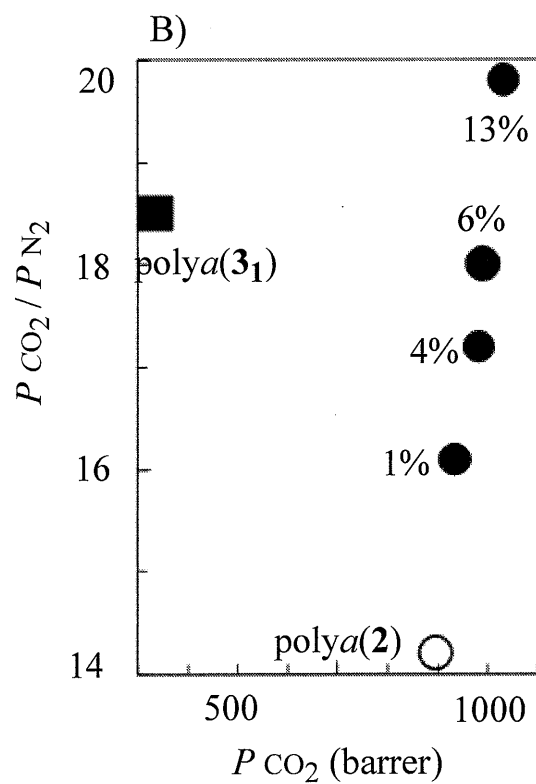
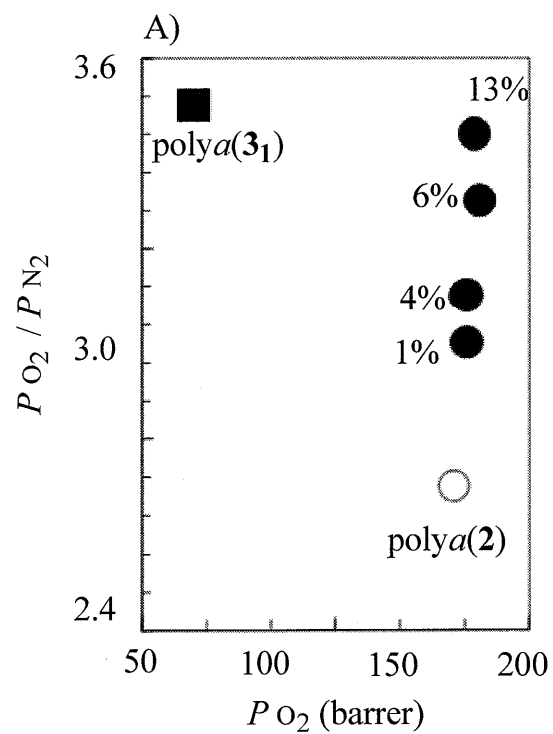
polypa(**1**) (Table 2-1, No. 7); e) polyp(**1**) (Table 2-1, No. 8). For (**A**) and (**P**), see Scheme 2-1.

The structure of polyaps(**1**), that is, poly(hyperbranched acetylene-type macromonomer) was confirmed by GPC (Figure 2-1) and  $^1\text{H}$  NMR (Figure 2-2) as follows: As model polymers for  $^1\text{H}$  NMR assignments, polya(**1**) (Figure 2-2 c)) and polyp(**1**) (Figure 2-2 e)) were used. They showed clear difference on the peaks assigned to the methyl and hydrogen in the dimethylsilyl groups (Figure 2-2). The  $^1\text{H}$  NMR for polyaps(**1**) (Figure 2-2 a)) had the both peaks assigned to polya(**1**) and polyp(**1**). Judging from the  $^1\text{H}$  NMR, it was confirmed that it contained both a polyacetylene main chain (the degree of the polymerization =  $q$  or  $q'$  in Scheme 2-1) and a hyperbranched side chains (the degree of the polymerization =  $p$  or  $p'$  in Scheme 2-1). In addition, since the GPC curve was unimodal, it was thought to be poly(hyperbranched acetylene-type macromonomer), not a mixture of the two types of



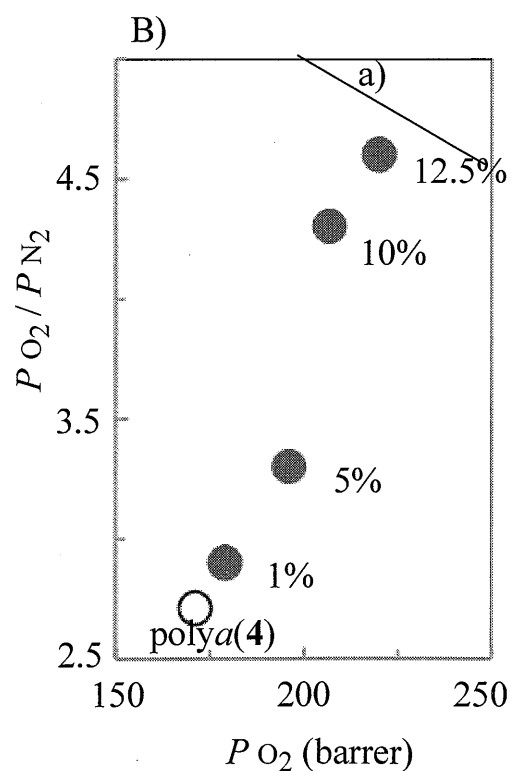
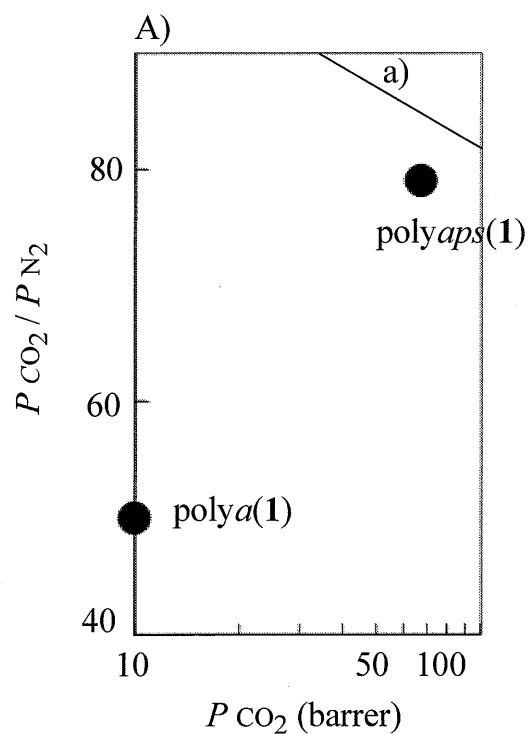
**Figure 2-2.**  $^1\text{H}$  NMR of the polymers from **1** and monomer **1**. a) polyaps(**1**) (Table 2-1, no. 3); b) polyap(**1**) (Table 2-1, no. 5); c) polya(**1**) (Table 2-1, no. 6); d) polypa(**1**) (Table 2-1, no. 7); e) polyp(**1**) (Table 2-1, no. 8); f) **1**. For the assignment to  $\text{A}_\text{H}$ ,  $\text{T}_\text{H}$ ,  $\text{B}_\text{Me}$ ,  $\text{P}_\text{H}$ ,  $\text{Q}_\text{H}$ ,  $\text{P}_\text{Me}$ ,  $\text{Q}_\text{Me}$  and  $\text{I}_\text{Me}$ , see Scheme 2-3.

polymers, polya(**1**) and polyp(**1**).



**Figure 2-3.** Plots of permselectivity versus permeability for A):  $O_2$  and B):  $CO_2$  through the poly(*aps*(1/4)) (13, 6, 4, 1, 0 mol%) membranes





**Figure 2-4.** Plots of permselectivity versus permeability for A):  $CO_2$  through the *polyα(1)* and *polyα(1)s(1)* membranes; B):  $O_2$  through the

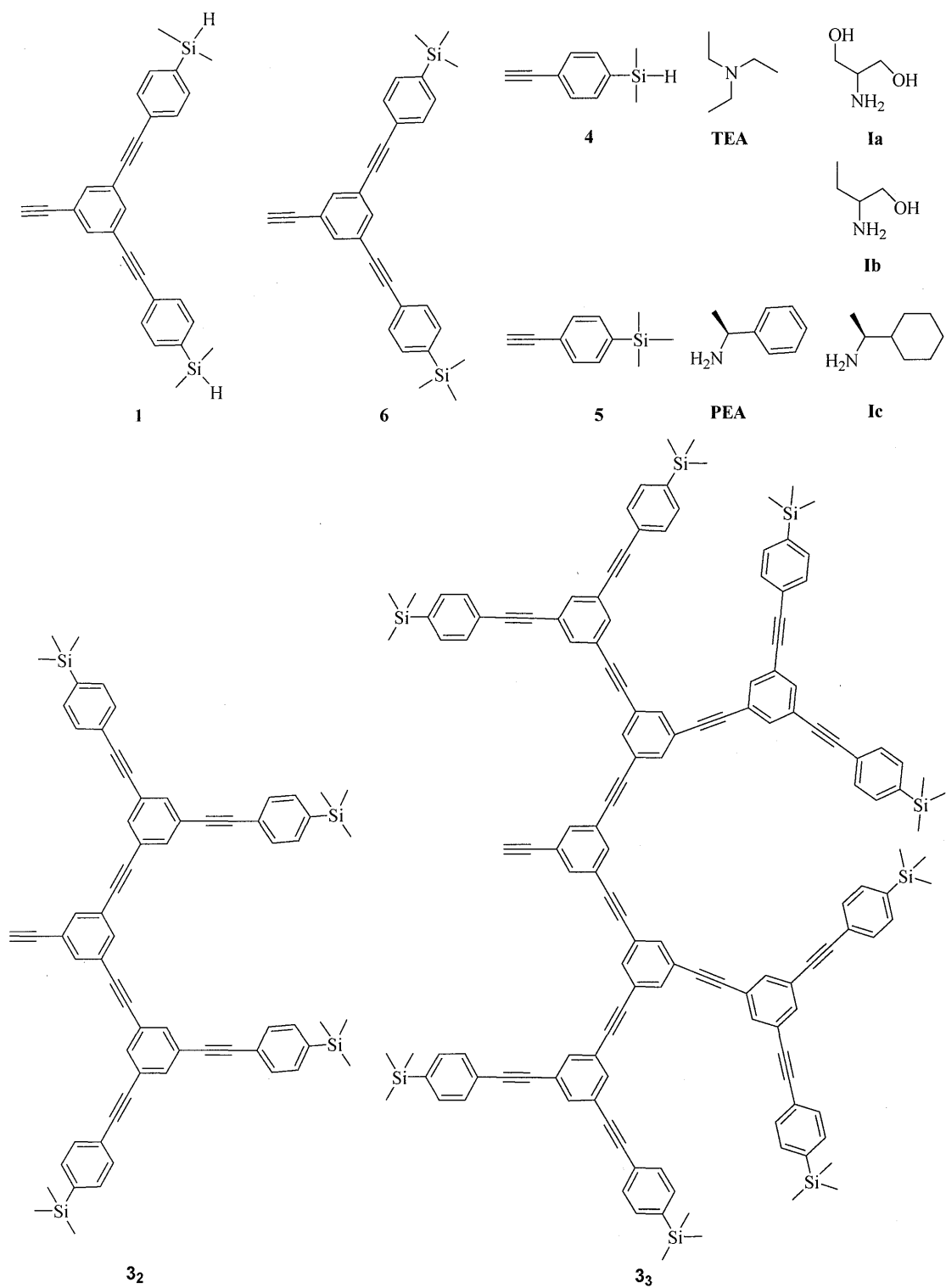
polyp(**1**) / poly(**5**) (12.5, 10, 5, 1, 0 mol%) membranes a): The upper boundary line from *ref.* 4d).

In summary, synthesis of a complex polymer, poly(hyperbranched acetylene-type macromonomer) by one-pot simultaneous polymerization of the two different types of polymerizations, *i.e.*, addition polymerization and polyaddition of one monomer(**1**) having one terminal triple bond and two Si-H groups has been achieved by using [Rh(nbd)Cl]<sub>2</sub> / various amines. To the best of our knowledge, the two findings, *i.e.*, synthesis of the new type of complex polymer, poly(hyperbranched acetylene-type macromonomer) and the simultaneous polymerization method of one monomer<sup>5</sup> by using one catalyst were the first examples.

**Table 2-2.** Gas permeabilities of membranes from homopolymers, copolymers, and blend polymers of **1**<sup>a</sup>

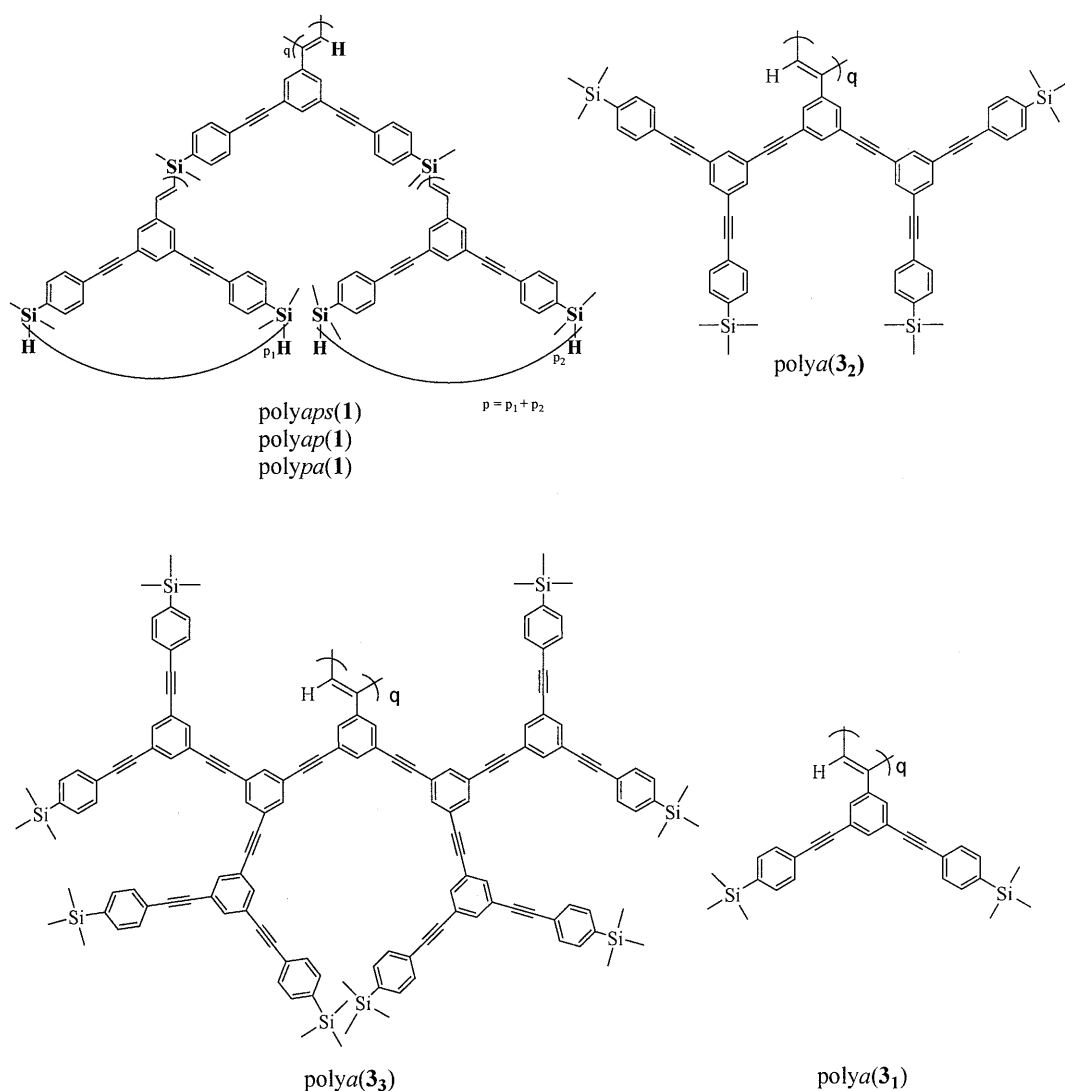
no. polymer <sup>b</sup>	feed ( <b>1</b> mol%)	composition <sup>c</sup> ( <b>1</b> unit mol%)	<i>Mn</i> <sup>d</sup> ( $\times 10^4$ )	<i>p</i> <sup>e</sup> / <i>q</i>	X(%) <sup>f</sup>	G <sup>g</sup>	<i>P</i> O <sub>2</sub> <sup>h</sup> (barrer)	<i>P</i> CO <sub>2</sub> <sup>h</sup> (barrer)	<i>P</i> N <sub>2</sub> <sup>h</sup> (barrer)	<i>P</i> O <sub>2</sub> <sup>h</sup> / <i>P</i> N <sub>2</sub>	<i>P</i> CO <sub>2</sub> <sup>h</sup> / <i>P</i> N <sub>2</sub>
1 poly( <b>1</b> ) <sup>i</sup>	100	100	— <sup>j</sup>	— <sup>j</sup>	— <sup>j</sup>	— <sup>j</sup>	—	10	0.20	—	49.9
2 polyaps( <b>1</b> )	100	100	— <sup>j</sup>	— <sup>j</sup>	— <sup>j</sup>	— <sup>j</sup>	—	67	0.80	—	79.0
3 poly( <b>3</b> <sub>1</sub> )	(100) <sup>k</sup>	(100) <sup>k</sup>	90	0	50	1.00	70	370	20.0	3.50	18.5
4 polyaps( <b>1/5</b> )	10	13	18	0.11	12	0.11	179	1030	52.0	3.44	19.8
5 polyaps( <b>1/5</b> )	10	6	16	0.06	6.0	0.07	181	990	54.8	3.30	18.0
6 polyaps( <b>1/5</b> )	5	4	19	0.04	4.0	0.04	176	980	57.1	3.08	17.2
7 polyaps( <b>1/5</b> )	1	1	18	0.01	1.0	0.01	176	934	58.7	3.00	16.1
8 poly( <b>5</b> )	0	0	21	0	0	0	171	895	63.1	2.71	14.2
9 <sup>l</sup> polyp( <b>1</b> )(12.5) <sup>m</sup>	—	—	0.3	4.4	100	2.80	220	—	47.8	4.60	—
10 <sup>l</sup> polyp( <b>1</b> )(10) <sup>m</sup>	—	—	—	—	—	—	207	—	48.1	4.30	—
11 <sup>l</sup> polyp( <b>1</b> )(5) <sup>m</sup>	—	—	—	—	—	—	196	—	59.4	3.30	—
12 <sup>l</sup> polyp( <b>1</b> )(1) <sup>m</sup>	—	—	—	—	—	—	179	—	61.7	2.90	—

<sup>a</sup> Reactions were carried out at room temperature for 12 h in toluene. [Monomer] = 0.01 mol/L, [Rh(nbd)Cl]<sub>2</sub> / **TEA** / [Monomer] = 1 / 250 / 250; <sup>b</sup> For the codes, see Scheme 2-1, and Chart 2-1; <sup>c</sup> By <sup>1</sup>H NMR; <sup>d</sup> Determined by GPC correlating polystyrene standard with THF eluent; <sup>e-g</sup> Determined by <sup>1</sup>H NMR. For the assignment for A<sub>H</sub>, T<sub>H</sub>, B<sub>Me</sub>, P<sub>H</sub>, Q<sub>H</sub>, see Scheme S3. <sup>e</sup> *p* / *q* = B<sub>Me</sub> / {6A<sub>H</sub>(or 6T<sub>H</sub>)}; <sup>f</sup> X(%) = *p* / (*p* + *q*) × 100; <sup>g</sup> G(Average generation) = log{(P<sub>H</sub> + Q<sub>H</sub>) / (A<sub>H</sub>(or T<sub>H</sub>))} / log 2; <sup>h</sup> Barrer: In 10<sup>-10</sup> cm<sup>3</sup>(STP)cm·cm<sup>-2</sup>·s<sup>-1</sup>·cmHg<sup>-1</sup>. <sup>i</sup> Catalyst by [Rh(nbd)Cl]<sub>2</sub> / **PEA** <sup>j</sup> Insoluble polymer membranes prepared by simultaneous membrane preparation and polymerization; <sup>k</sup> **3**<sub>1</sub> mol%; <sup>l</sup> Blend membranes of polyp(**1**) with poly(**5**); <sup>m</sup> The molar ratio(%) of polyp(**1**) in the blend membranes.



**Chart 2-1. Monomers and cocatalysts in this study**

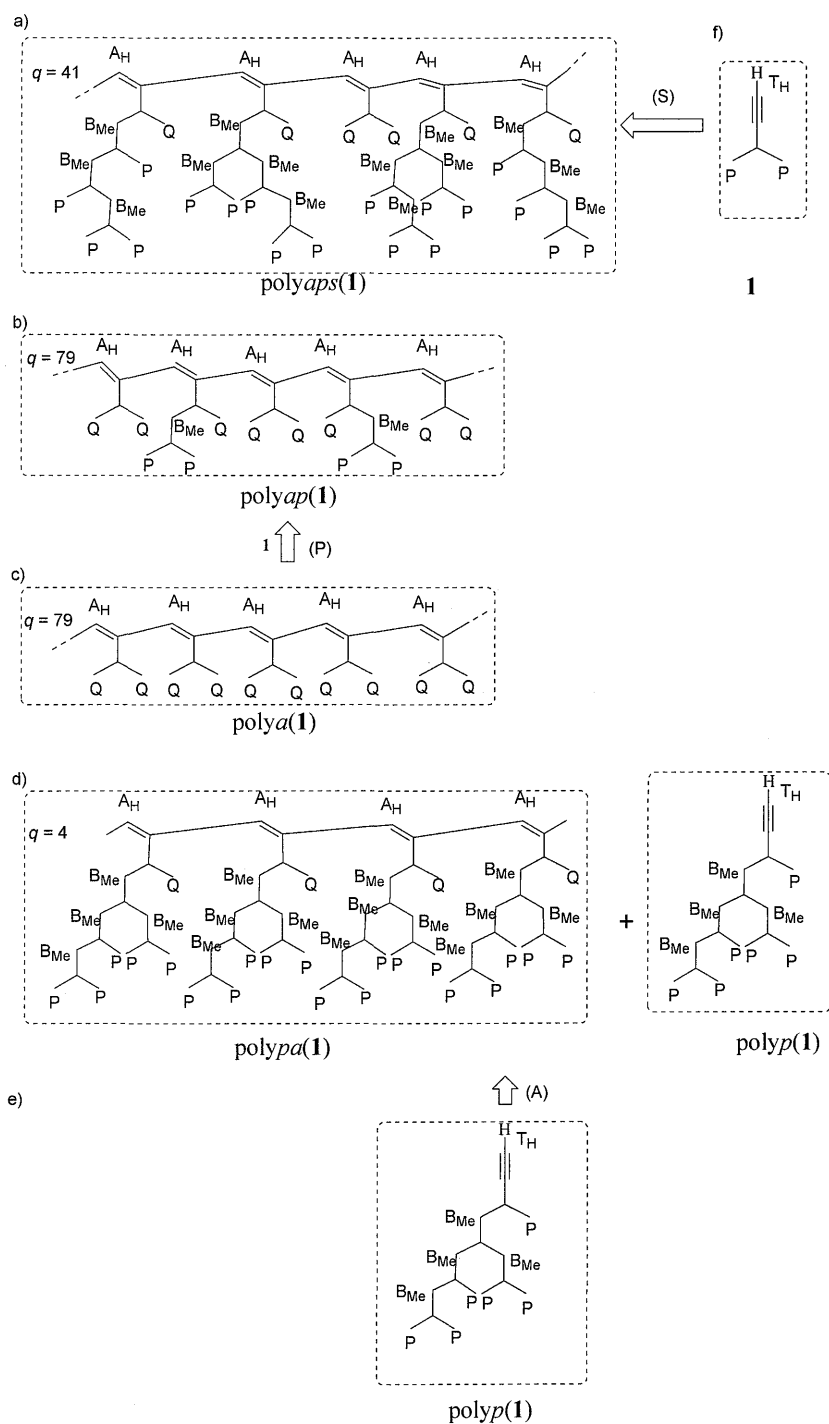
**2.3.2 Advantage of the one-pot simultaneous synthetic route to the new type of polymer, poly(hyperbranched acetylene-type macromonomer) and the comparison of the structures of the resulting polymers prepared by the two 2-step methods**



**Chart 2-2.** Poly(hyperbranched acetylene-type macromonomer) (1), and poly(dendron)s(3<sub>1-3</sub>)

To check the advantage of the one-pot simultaneous synthetic route to the new type of polymer, poly(hyperbranched acetylene-type macromonomer), we tried to synthesize polymers having structures

similar to polyaps(1) by two 2-step procedures (See Scheme 2-1, Scheme 2-2 and 2-3) yielding polyap(1) and polypa(1) having similar structure to polyaps(1). However

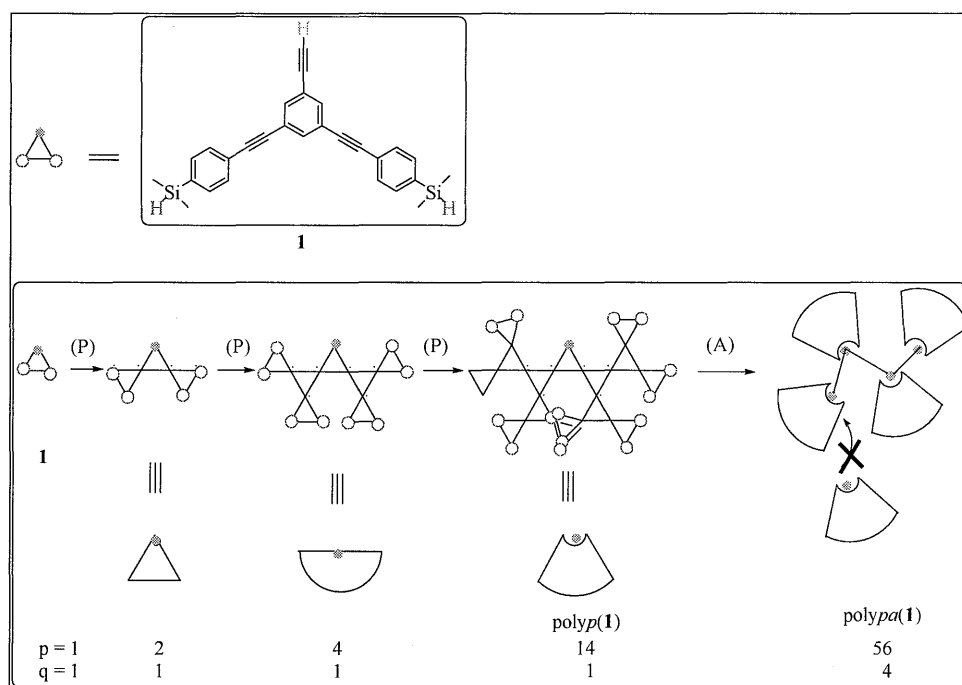


**Scheme 2-3.**  $^1\text{H}$  NMR assignments of the polymers from 1

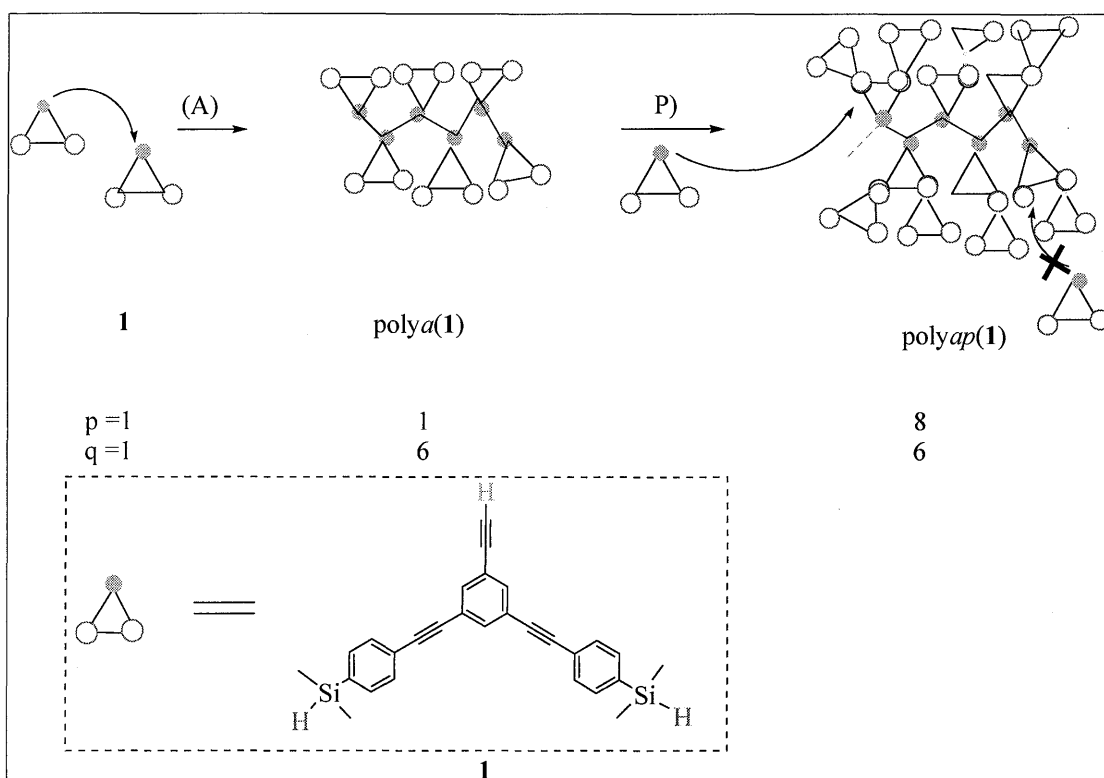
$\text{P}_{\text{Me}}$ :  $-\text{SiH}(\text{CH}_3)_2$  (60.34),  $\text{P}_{\text{H}}$ :  $-\text{SiH}(\text{CH}_3)_2$  (64.42);  $\text{B}_{\text{Me}}$ :  $-\text{C}=\text{Si}(\text{CH}_3)_2$  (60.21);  $\text{Q}_{\text{Me}}$ :  $-\text{SiH}(\text{CH}_3)_2$  (60.13),  $\text{Q}_{\text{H}}$ :  $-\text{SiH}(\text{CH}_3)_2$  (64.22);  $\text{A}_{\text{H}}$ :  $-\text{C}=\text{CH}$  (65.90);  $\text{T}_{\text{H}}$ :  $-\text{C}\equiv\text{CH}$  (63.11);  $\text{I}_{\text{Me}}$ :  $-\text{SiOSi}(\text{CH}_3)_2$  (60.07).

a)-f) Correspond to those in Figure 2-1 and Figure 2-2.

the structures of the resulting polymers,  $\text{polyap}(\mathbf{1})$  (Figures 2-1b) and 2-2 b) and Schemes 2-2b) and 2-3 b) ) obtained by polyaddition of  $\text{polya}(\mathbf{1})$  prepared by addition polymerization of  $\mathbf{1}$ , and  $\text{polypa}(\mathbf{1})$  (Figure 2-1 and 2 d) and Schemes 2-2d) and 2-3 d)) obtained by addition polymerization of  $\text{polyp}(\mathbf{1})$  prepared by polyaddition of  $\mathbf{1}$  were not complete compared with  $\text{polyaps}(\mathbf{1})$  by the one-pot simultaneous method. (The reason for the incompleteness of  $\text{polyap}(\mathbf{1})$  and  $\text{polypa}(\mathbf{1})$  was discussed in the Schemes 2-4 and 2-5)



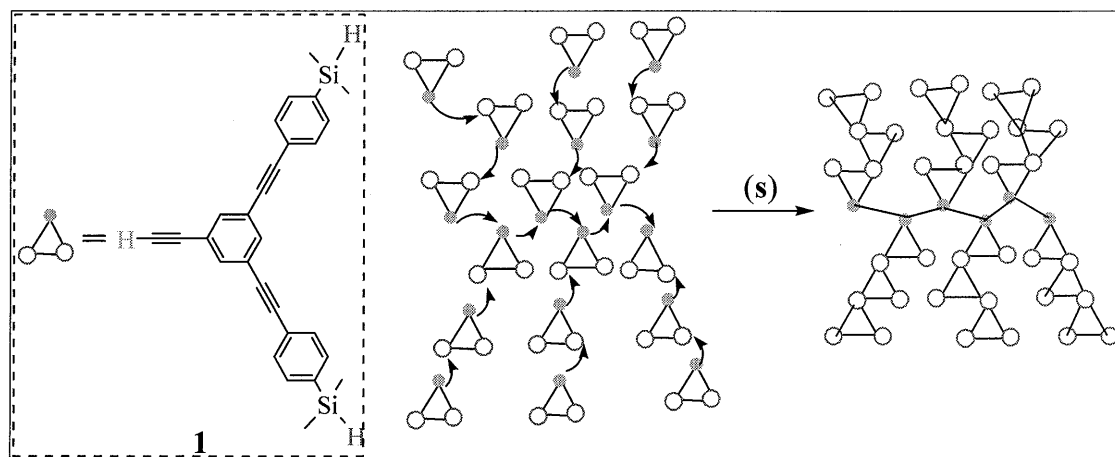
Scheme 2-4 Imaginative scheme of the formation of the structures of  $\text{polya}(\mathbf{1})$  from  $\mathbf{1}$  determined by  $^1\text{H}$  NMR.



Scheme 2-5. Imaginative scheme of the formation of the structures of polyap(1) from **1** determined by  $^1\text{H}$  NMR.

In conclusion, the simultaneous one-pot procedure we reported first here was found to be better one than the two 2-stepwise methods. The poly(hyperbranched acetylene-type macromonomer)(polyaps(**1**)) having both large degree of the polymerization of the addition polymerization( $q$ ) and the high degree of the branches( $p$ ) was synthesized by the simultaneous one-pot procedure for the first time. The reason why the simultaneous polymerization gave the best structures having the best balance of  $p$  and  $q$  were explained in Scheme 2-6

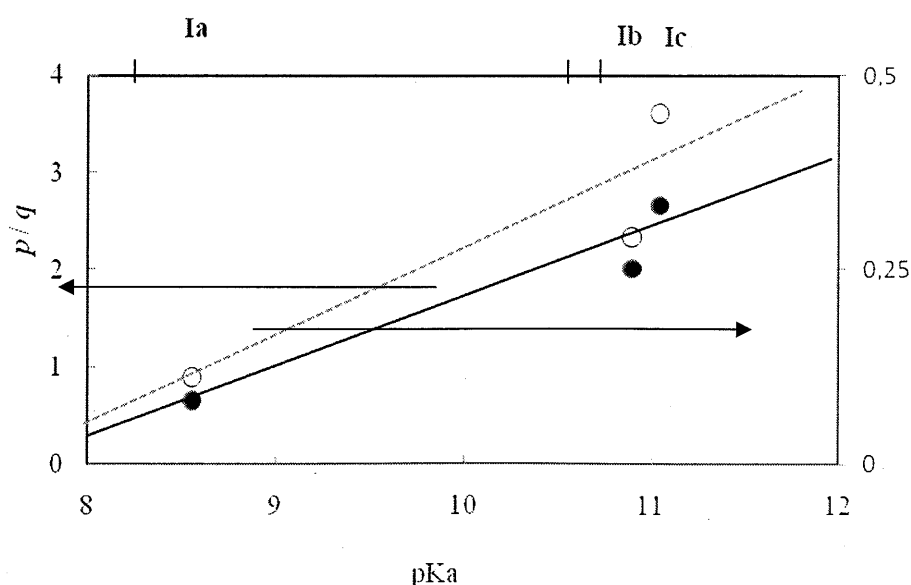




Scheme 2-6 Imaginative scheme of the formation of the structures of polyaps(1) from **1** determined by  $^1\text{H}$  NMR.

### 2.3.3 Control of the ratio of polyaddition and addition polymerization in the simultaneous polymerization of **1** by changing amine cocatalysts

The ratio of the two kinds of the polymerization *i.e.*, polyaddition and addition polymerization ( $= p / q$  or  $X(\%)$ ) in the simultaneous



**Figure 2-6.** The relationship between  $p / q$  and  $\text{pKa}$  ●: poly(**1**); ○: model

reaction (For **Ia**, **Ib**, and **Ic**, see Chart 2-1)

polymerization could be controlled by changing kinds of amines (Table 2-1, nos. 1- 4) having different substituents and pKa (Chart 2-1) used as a cocatalyst promoting addition polymerization. For example, when phenylethylamine(**PEA**) was used, only addition polymerization happened and almost no polyaddition occurred to give poly $a(1)$  ( no. 6 in Table 2-1). When triethylamine(**TEA**) was used, both addition polymerization and polyaddition occurred to give poly $aps(1)$  (no. 4 in Table 1). As shown in Table 2-1, nos.1-4, the ratios of the two degrees of the polymerizations were controlled by changing the cocatalyst. The values showing the ratio,  $p / q$ ,  $X(\%)$ ,  $G$  and  $C(\%)$  (For the definitions, see the SI-2(2).) were changed largely. The amine having higher pKa tended to produce poly $aps(1)$  having a higher  $p / q$  value, *i.e.*, higher degree of branches (See Figure 2-6).

#### **2.3.4 Good gas separation properties of membranes containing poly (hyperbranched acetylene-type macromonomer)**

Since the new types of polymers synthesized for the first time in this study had a unique branched structure having a linear rigid backbone, they were expected to show good properties as a gas permselective membrane materials due to the diffusion selectivity similarly to the case of poly(dendron) like poly $a(6)$  we previously reported<sup>3</sup> with good self membrane forming abilities.

The results of measurements of gas permeabilities through the polymer membranes are shown in Figures 2-3 and 2-4 and Table 2-2. The membranes of the poly(hyperbranched acetylene-type macromonomer / *p*-trimethylsilylphenylacetylene(**5**)) (poly $aps$ (**1/5**)) (nos.4-7 in Figure 2-3) showed higher permselectivity without decrease in permeability than membranes of the corresponding polymer (poly $a$ (**5**)) (no. 8 in Figure 2-3) without any branches. The permeabilities of poly(hyperbranched acetylene-type macromonomer / *p*-trimethylsilylphenylacetylene(**5**)) (poly $aps$ (**1/5**))(nos. 4 and 5 in Figure 2-3) increased without decrease in permselectivity than membranes of the corresponding dendronized polymer having regular branches (poly(**6**))(no.3 in Figure 2-3).

In addition, a homopolymer membrane (Figure 2-4A) and no. 2 in Table 2-2) by direct preparation during polymerization showed very good performance. The permselectivities were close and almost on the upper boundary line reported by Robeson <sup>4</sup>(Figure 2-4A)). The blend membranes of poly $p$ (**1**) with poly $a$ (**5**) (Figure 2-4B) and no. 9-12 in Table 2-4) also showed good performances. The permselectivities are close and almost on the upper boundary line as shown in Figure 2-4B). Therefore, the effectiveness of the hyperbranched structure on the permselectivities was proved.

## 2.4 Conclusion

1. A new complex polymer, polyaps(hyperbranched acetylene-type macromonomer) which has good performance for gas separation membranes was synthesized by simultaneous polymerization method of one monomer for the first time. The simultaneous one-pot procedure was found to be better one than the two 2-stepwise methods.

2. The ratio of the two kinds of the polymerization, *i.e.*, polyaddition and addition polymerization ( $= p / q$  or  $X(\%)$ ) in the simultaneous polymerization could be controlled by changing kinds of amines having different substituents and pKa used as a cocatalyst promoting addition polymerization.

3. Oxygen permselectivities through polyaps(1/5) membranes were improved with increase in  $p / q$ . Branched structure enhanced permselectivities in  $PO_2 / PN_2$  through polyaps(1/5) membranes.

## References and Notes

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**Chapter 3: One-pot synthesis poly $aps$ (hyperbranched acetylene-type macromonomer) by simultaneous polymerization of two different modes of polymerizations, *i.e.*, addition polymerization and polyaddition of 3,5-bis-(4-dimethylsilylphenyl)phenylacetylene (DHSPPA, 2) by using one catalyst for gas permselective membranes**

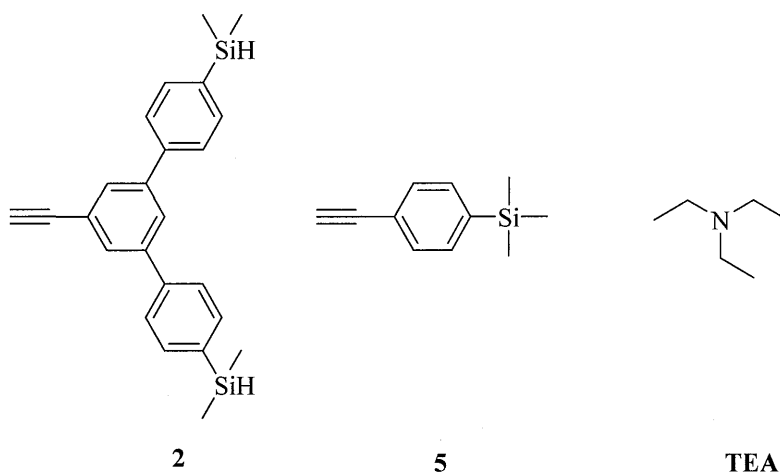
## Abstract

Simultaneous polymerization of the two different types of polymerizations, *i.e.*, addition polymerization and polyaddition of one monomer(**2**) having one terminal triple bond and two Si-H groups has been achieved by using  $[\text{Rh}(\text{norbornadiene}(= \text{ nbd}))\text{Cl}]_2$  / various amines. To our knowledge, this is the first example of such simultaneous polymerization of one monomer. In addition, the ratio of the two polymerizations could be controlled by changing amine cocatalyst. By this polymerization method, one-pot synthesis of poly(hyperbranched acetylene-type macromonomer) from **2** was realized. To the best of our knowledge, this is the first synthesis of such complex polymers. Membranes from the poly(hyperbranched acetylene-type macromonomer) had both the advantages of poly(phenylacetylene)s and poly(dendron). Some of them showed the highest performance as oxygen or carbon dioxide permselective membranes among all the membranes reported. In summary, a new complex polymer, poly(hyperbranched acetylene-type macromonomer) showing good performance as gas separation membranes was synthesized very easily by the one-pot simultaneous polymerization method.



### 3.1 Introduction

Recently some kinds of new polymer molecules having unique structures have been reported. Among them highly branched polymers like dendrimers have received much attention because of their regular structures.<sup>1</sup> Dendrimers have highly regulated branched structures but generally they have two problems. One is synthesis of the polymers needs many steps and results in very low yields because they were prepared not by polymerization but by multi-step organic reactions. The other problem is their low ability for fabrication because of no entanglement.



To overcome the first problem, hyperbranched polymers have been reported.<sup>2</sup> They were prepared more easily by one polymerization of AB<sub>2</sub> type monomers in higher yields. To solve the second problem, we reported a new type of branched polymers, that is, poly(dendron macromonomer)(for example, polymers of **3<sub>1-3</sub>**) which was a highly branched polymer having a linear rigid backbone prepared by addition

polymerization of the acetylene group in the macromonomer having regularly branched dendritic structure<sup>3</sup> In addition, the resulting polymer showed good performance of gas permselectivity due to their regulated branched structures. Gas permselective membranes are very important and valuable because the necessity to remove impurities or purify mixtures of gases whose molecular sizes are very similar is enhancing because solving the recent environmental problems has been focused on.<sup>4</sup> In general, tradeoff relationship between permeability and permselectivity is usually observed. To overcome this, more control of chemical structures of the side groups in the polymer used for permselective membranes are needed.

Poly(dendron macromonomer) was a valuable polymer having regulated structures and better membrane forming ability than dendrimers. However it had still the two problems as described above. (1) Multi-step synthetic route( low yield) and (2) Low membrane forming ability.

In this study to overcome the two problems, we designed a new type of polymer, *i.e.*, poly(hyperbranched acetylene-type macromonomer). In addition, we propose its new synthetic method, *i.e.*, one-pot synthesis by simultaneous polymerization of two types of polymerization of one monomer. In other words, in this communication, we report a new complicated polymer and its very simple preparation method. The complex polymer could be synthesized by very easy one-pot procedure. In addition, we report significantly better performance of gas

permselectivities of the resulting polymer membranes which are on the Robeson's upper boundary line.<sup>4d</sup>

## 3.2 Experimental part

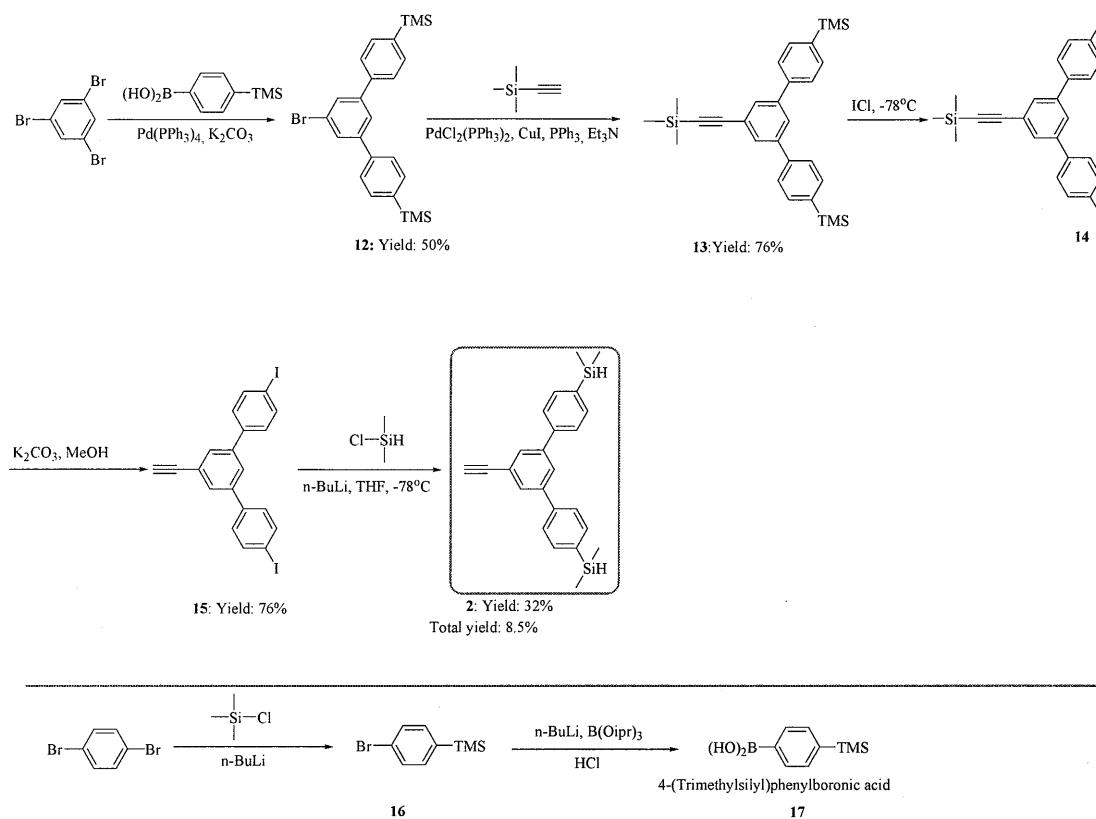
### 3.2.1 Materials.

All the solvents used for synthesis and polymerizations of the monomers were distilled as usual. The polymerization initiator,  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  (nbd = 2,5-norbornadiene) and amines purchased from Aldrich Chemical were used as received. According to the literature procedures, 3,5-bis(dimethylsilyl)phenylacetylene<sup>1</sup> (**1**, in Chart 3-1), was prepared.

### 3.2.2 Measurements.

<sup>1</sup>H NMR (400 MHz) spectra were recorded on a VARIAN-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). The infrared spectra were recorded on FT/IR-4200 (JASCO). Oxygen, carbon dioxide, and nitrogen permeability coefficients( $P_{\text{O}_2}$ ,  $P_{\text{CO}_2}$ , and  $P_{\text{N}_2}$ :  $\text{cm}^3(\text{STP})\text{cm}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{cmHg}^{-1}$ ) and the separation factor ( $P_{\text{O}_2}/P_{\text{N}_2}$  and  $P_{\text{CO}_2}/P_{\text{N}_2}$ ) were measured by a gas chromatographic method at 25°C using

YANACO GTR-10 according to Ref. (4). The area of membrane was 1.77 cm<sup>2</sup>, and the initial feed gas pressure was 1 atm.

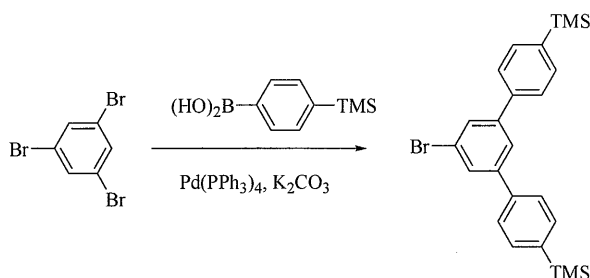


### 3.2.3 Synthetic procedures and characterization of monomer (2)

(Scheme S1). All the following reaction procedures were conducted under dry nitrogen.

#### 3.2.3.1 Preparation of 5-bromo-1,3-di(4-trimethylsilylphenyl)benzene,

12



A 100 mL Schlenk flask charged with 1,3,5-tribromobenzene (15.7 g, 50 mmol) and 4-trimethylsilylphenylboronic acid (4)(21.3 g, 110 mmol) was brought into a drybox and was combined with  $\text{Pd(PPh}_3)_4$  (2.89 g, 2.50 mmol). To the resulting mixture, aqueous  $\text{K}_2\text{CO}_3$  (2 M, 50 mL, degassed with nitrogen) and THF (100 mL) were syringed in under nitrogen. The reaction mixture was degassed again by three freeze pump thaw cycles and was then refluxed under nitrogen. After 24 h, the reaction mixture was poured into a mixture of  $\text{H}_2\text{O}$  and EtOAc. The aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the residue was passed through a silica gel column using hexanes as the eluent.

Appearance: white solid.

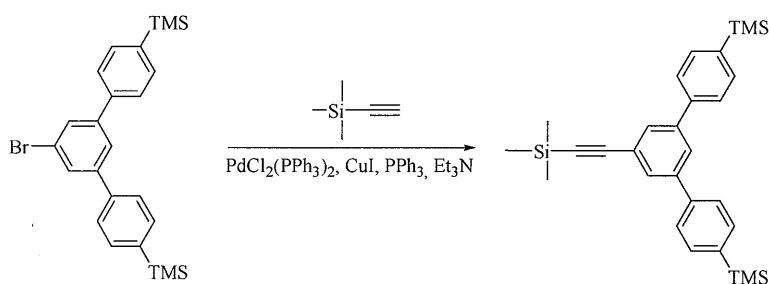
Weight: 22.6 g.

Yield: 50%.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS,  $\delta$ ): 7.76(s, 1H, -ArH), 7.69(s, 2H, -ArH), 7.63(m, 8H, -ArH), 0.40(s, 18H, -Si( $\text{CH}_3$ )<sub>3</sub>) ppm.

### 3.2.3.2 Preparation of 5-trimethylacetylene-1,3-di(4-trimethylsilyl-

### phenyl)benzene, 13



**12** (11.3 g, 25 mmol) was dissolved with dry triethylamine (160 mL). The solution was added to bis(triphenylphosphine)palladium(II) chloride (282 mg, 0.50 mmol), copper(I) iodide (96 mg, 0.50 mmol), triphenylphosphine (133 mg, 0.50 mmol), trimethylacetylene (120 mmol) under a nitrogen atmosphere. The solution was stirred for 24 h at 90 °C to precipitate a white solid. The solid was filtered out. The solvent of the filtrate was concentrated by evaporation. The crude product was purified by silica-gel column chromatography with chloroform as an eluent to give **13**.  $R_f = 0.4$  (chloroform)

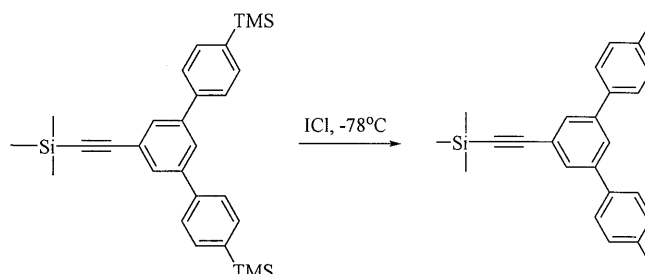
Appearance: white solid.

Weight: 8.9 g.

Yield: 76%.

$^1\text{H}$  NMR( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.6(m, 3H, -ArH), 7.5(m, 8H, -ArH), 0.40(s, 18H, -Si(CH<sub>3</sub>)<sub>3</sub>), 0.38(s, 9H, -Si(CH<sub>3</sub>)<sub>3</sub>).

### 3.2.3.3 Preparation of 5-trimethylacetylene-1,3-bis(4-iodophenyl)benzene, 14



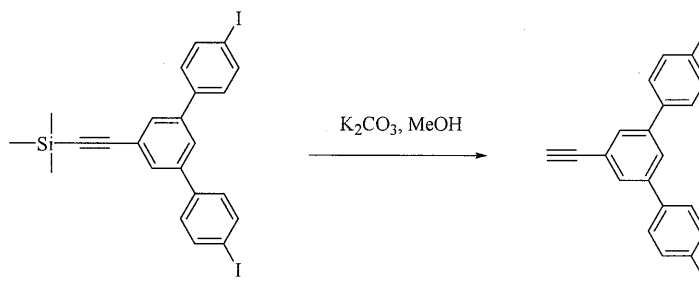
Appearance: yellow solid.

Weight: 1.64 g.

Yield: 15%.

$^1\text{H}$  NMR( $\text{CDCl}_3$ ,  $\delta$ , TMS): 7.8(d, 4H, -ArH), 7.7(s, 1H, -ArH), 7.6(s, 2H, -ArH), 7.4(m, 4H, -ArH), 0.38(s, 9H, -Si(CH $_3$ ) $_3$ ).ppm

#### 3.2.3.4 3,5-bis(4-iodo-phenyl)phenylacetylene, **15**



**14** was added slowly to  $\text{K}_2\text{CO}_3$  (0.64 g, 6.0 mmol) in methanol (40 mL).

The mixture was stirred with a magnetic stirrer for 6 hours and 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%  $\text{HCl}(\text{aq})$  and then water, and dried over anhydrous sodium sulfate. The solvent of the filtrate was concentrated by evaporation, and the crude product was purified by silica-gel column chromatography with ethyl acetate / hexane = 1 / 10 as an eluent to give **15**.  $R_f$  = 0.25(ethyl

acetate / hexane = 1/10).

Appearance: yellow solid.

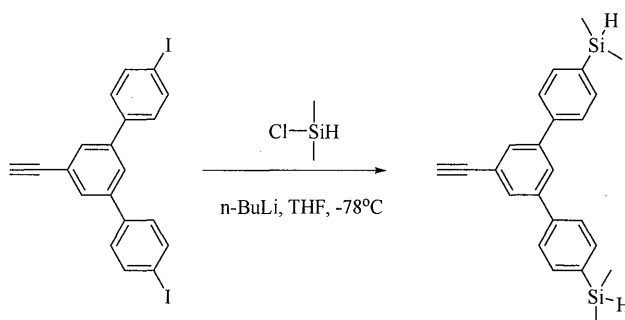
Weight: 1.1 g.

Yield: 76%.

$^1\text{H}$  NMR( $\text{CDCl}_3$ , 400 MHz, ppm): 7.64(t, 2H, -ArH), 7.60(d, 1H, -ArH), 7.57(d, 4H, -ArH), 7.40(d, 4H, -ArH), 3.11(s, 1H,  $\text{HC}\equiv\text{C}$ ).

### 3.2.3.5 3,5-bis-(4-dimethylsilylphenyl)phenylacetylene (DHSPPA,

2)



A 200 mL round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen gas. **15** (1.1 g, 2.8 mmol) and dry THF (34 mL) were placed in the flask at  $-75^\circ\text{C}$ . At the same temperature, a hexane solution of *n*-butyllithium (5.3 mL, 10 mmol,  $C = 1.6\text{ M}$  in hexane) was added dropwise, and the reaction mixture was stirred for 4 h. A solution of dimethylchlorosilane (0.63 mL, 6.7 mmol) in dry THF (34 mL) was added dropwise, and it was allowed to 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 flash column chromatography (Merck, silica gel 60; eluent, hexane) to give **2**.

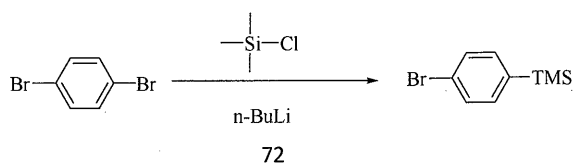
Appearance: colorless liquid

Weight: 125 mg.

Yield: 32%.

### 3.2.3.6 1-bromo-4-trimethylsilyl benzene

A 500 mL round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen gas. 1,4-dibromobenzene (23.6 g, 100 mmol) and dry diethyl ether (150 mL) were placed in the flask at 0 °C. At the same temperature, a hexane solution of *n*-butyllithium (63 mL, 100 mmol, C = 1.6 M in hexane) was added dropwise, and the reaction mixture was stirred for 2 h. A solution of trimethylchlorosilane (12 mL, 110 mmol) in dry diethyl ether (30 mL) was added dropwise, and it was allowed to warm to room temperature slowly and stirring for 1 h. 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 distillation under reduced pressure. (74 °C,  $5 \times 10^2$  Pa)



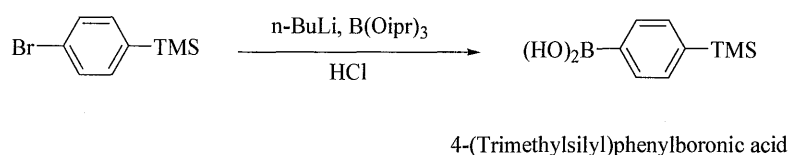
Appearance: colorless liquid

Weight: 14 g.

Yield: 72%.

$^1\text{H}$  NMR( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$ 0.29(s, 9H,  $-\text{Si}(\text{CH}_3)_3$ , 7.41, 7.52(4H,  $-\text{ArH}$ ).

### 3.2.3.7 Synthesis of 4-(trimethylsilyl)phenylboronic acid



*n*-Butyllithium (100 mol (63 ml, 1.60 M in hexanes)) was added dropwise to a stirred and cooled ( $-78^\circ\text{C}$ ) solution of 100 mol (22.9 g) of 1-bromo-4-trimethylsilyl benzene in anhydrous THF (100 mL) under an argon atmosphere. The reaction mixture was maintained under these conditions for a further 2.5 h. Trimethyl borate (0.12 mol, 2.5 g) in 20 ml THF was added dropwise to the mixture solution. The reaction mixture was allowed to warm to room temperature and was stirred for 1 h with hydrochloric acid (10%, 80 mL). The resulting mixture was extracted with diethyl ether ( $3 \times 80$  mL). The combined organic phases were washed with brine and dried over magnesium sulfate. The solvent was removed using a rotary evaporator. The raw product was recrystallized from petroleum ether to give a white powder product without further purification.

Appearance: white solid.

Weight: 2.0 g.

Yield: 76%.

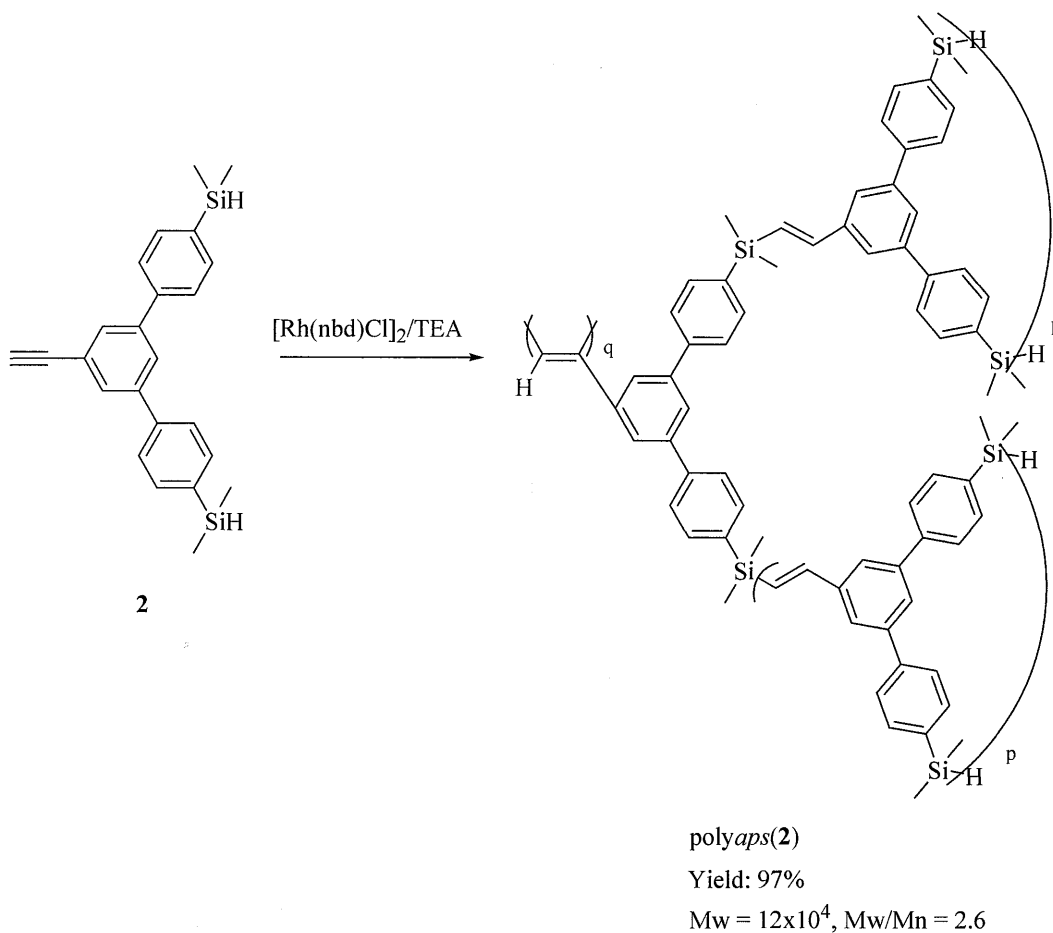
$^1\text{H}$  NMR( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$ 7.6(m, 2H, -ArH), 7.5(m, 2H, -ArH), ,  
0.38(s, 9H, -Si(CH<sub>3</sub>)<sub>3</sub>).

### 3.3 Results and discussion

#### 3.3.1 Advantage of the one-pot simultaneous synthetic route to the new type of polymer, poly(hyperbranched acetylene-type macromonomer)

To begin with, we report discovery of one-pot synthesis of a new type of polymer, poly(hyperbranched acetylene-type macromonomer) by the simultaneous polymerization of two different types of polymerizations, *i.e.*, addition polymerization and polyaddition of one monomer (**2** in Scheme 3-3) by using one catalyst .

The monomer **2** having one terminal triple bond and two Si-H groups via an phenylene spacer was synthesized (see Scheme 3-1) and polymerized with  $[\text{Rh}(\text{nbd})\text{Cl}]_2 / \text{TEA}$  (see Scheme 3-2)



Scheme 3-2

The results of the polymerization of **2**. show in Table 3-1

### 3.3.2 Good gas separation properties of membranes containing poly (hyperbranched macromonomer)(polyaps(2))

Since the new types of polymers synthesized for the first time in this study had a unique branched structure having a linear rigid backbone, they were expected to show good properties as a gas permselective membrane materials due to the diffusion selectivity similarly to the case of poly(dendron) like poly**a**(**6**) we previously reported<sup>3</sup> with good self membrane forming abilities.

The results of measurements of gas permeabilities through the polymer

membranes are shown in Figure 3-1. The membranes of the poly(hyperbranched acetylene-type macromonomer / poly(*p*-trimethylsilylphenyl-acetylene(**5**)) showed higher permselectivity than membranes of the corresponding polymer (polya(**5**)) without any branches.

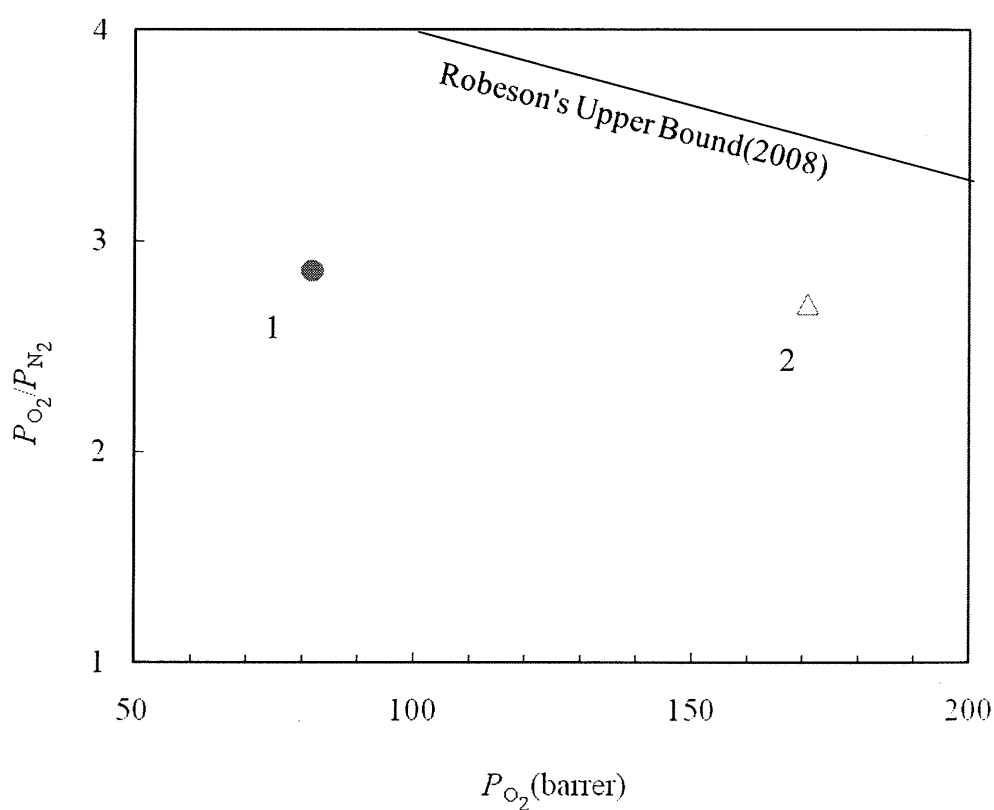


Figure 3-1. The relationship between permeability and permselectivity for  $O_2$  through the polyaps(**2**) (10mol%)/polya(**5**) blend membrane.

**Table 3-1.** Gas permeabilities of membranes from blend polymers of **2**<sup>a</sup>

no	polymer <sup>b</sup>	feed (2 mol%)	composition <sup>c</sup> (1unit mol%)	$M_n^d$ ( $\times 10^4$ )	$p^e$ /q	X(%) <sup>f</sup>	$P_{O_2}^g$ (barrer)	$P_{CO_2}^g$ (barrer)	$P_{N_2}^g$ (barrer)	$P_{O_2}^g$ / $P_{N_2}$	$P_{CO_2}^g$ / $P_{N_2}$
1	polyaps( <b>2</b> )	10	10	4.6	1.8	0.39	82	-	30	2.9	-
2	polya( <b>5</b> )		13	18	0.11	12	171	894	63	2.7	14.2

<sup>a</sup> Reactions were carried out at room temperature for 12 h in toluene. [Monomer] = 0.01 mol/L, [Rh(nbd)Cl]<sub>2</sub> / **TEA** / [Monomer] = 1 / 250 / 250; <sup>b</sup> For the codes, see Scheme 2-1, and Chart 2-1; <sup>c</sup> By <sup>1</sup>H NMR; <sup>d</sup> Determined by GPC correlating polystyrene standard with THF eluent; <sup>e-g</sup> Determined by <sup>1</sup>H NMR. For the assignment for A<sub>H</sub>, T<sub>H</sub>, B<sub>Me</sub>, P<sub>H</sub>, Q<sub>H</sub>, see Scheme S3. <sup>e</sup>  $p / q = B_{Me} / \{6A_H(\text{or } 6T_H)\}$ ; <sup>f</sup>  $X(\%) = p / (p + q) \times 100$ ; <sup>g</sup> Barrer: In  $10^{-10} \text{ cm}^3(\text{STP})\text{cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ .

### 3.4 Conclusions

1. poly*aps*(**2**) could be synthesized very easily and regulatedly by the one-pot simultaneous polymerization method for the first time.
2. Oxygen permselectivities through poly*aps*(**2**)(10mol%) /poly*a*(**5**) blend membrane was higher than poly*a*(**5**).

## References and Notes

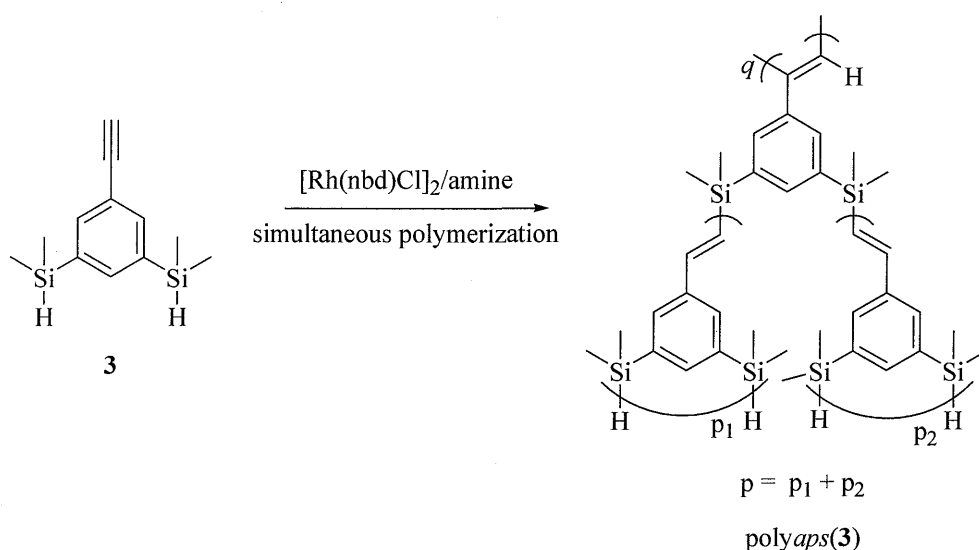
- 1 Yao K., et al., *J. Polymer Science: Part A: Polymer Chemistry*, **2010**, 48, 434–442.
- 2 Cheong-Jin Jang, Ja-Hyoung Ryu, Joon-Dong Lee, Deawon Sohn, and Myongsoo Lee, *Chem. Mater.*, **2004**, 16, 4226-4231.
- 3 Ja-Hyoung Ryu, Jinyoung Bae, and Myongsoo Lee *Macromolecules*, **2005**, 38, 2050-2052.
- 4 Liu-Zhu Gong, Qiao-Sheng Hu, and Lin Pu *J. Org. Chem.*, **2001**, 66, 2358-2367.
- 5 Isao Yamaguchi, Kazuyuki Goto, and Moriyuki Sato *Macromolecules*, **2009**, 42, 7836–7845.
- 6 Yonggang Wu, Xiaohui Hao, Junling Wu, Jia Jin, and Xinwu Ba *Macromolecules*, **2010**, 43, 731–738.
- 7 Yoo Y. S., et al., *J. Am. Chem. Soc.*, **2004**, 126, 6294-6300.
- 8 Lee M., et al., *Bull. Korean Chem. Soc.*, **2008**, 29, 1485.



**Chapter 4: One-pot synthesis polyaps(hyperbranched acetylene-type macromonomer) by simultaneous polymerization of two different modes of polymerizations, *i.e.*, addition polymerization and polyaddition of 3,5-bis(dimethylsilyl)phenylacetylene (DHSPA 3) by using one catalyst for gas permselective membranes**

## Abstract

Simultaneous polymerization of the two different types of polymerizations, *i.e.*, addition polymerization and polyaddition of one monomer(**3**) having one terminal triple bond and two Si-H groups has been achieved by using  $[\text{Rh}(\text{norbornadiene}(=\text{nbd}))\text{Cl}]_2$  / various amines. To our knowledge, this is the first example of such simultaneous polymerization of one monomer. In addition, the ratio of the two polymerizations could be controlled by changing amine cocatalyst. By this polymerization method, one-pot synthesis of poly(hyperbranched acetylene-type macromonomer) from **3** was realized.



To the best of our knowledge, this is the first synthesis of such complex polymers. Membranes from the  $\text{polyaps}(\mathbf{3})$  had both the advantages of poly(phenylacetylene)s and poly(dendron). Some of

them showed the highest performance as oxygen or carbon dioxide permselective membranes among all the membranes reported. In summary, a new complex polymer, poly(hyperbranched acetylene-type macromonomer) showing good performance as gas separation membranes was synthesized very easily by the one-pot simultaneous polymerization method.

## 4.1 Introduction

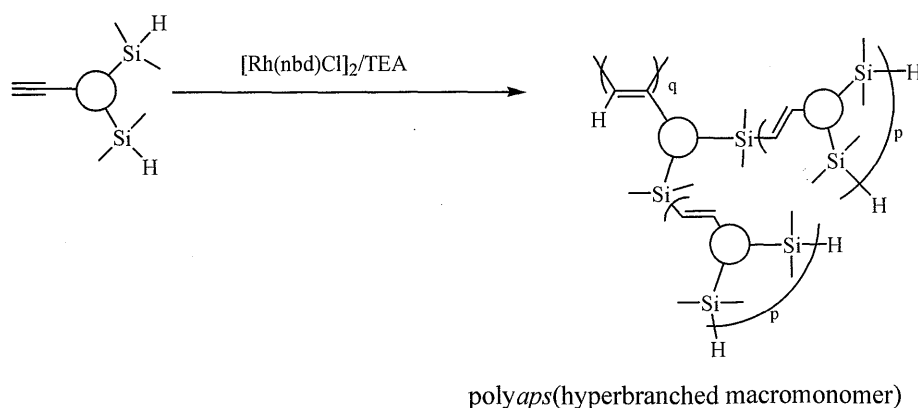
Recently some kinds of new polymer molecules having unique structures have been reported. Among them highly branched polymers like dendrimers have received much attention because of their regular structures.<sup>1</sup> Dendrimers have highly regulated branched structures but generally they have two problems. One is synthesis of the polymers needs many steps and results in very low yields because they were prepared not by polymerization but by multi-step organic reactions. The other problem is their low ability for fabrication because of no entanglement.

To overcome the first problem, hyperbranched polymers have been reported.<sup>2</sup> They were prepared more easily by one polymerization of  $AB_2$  type monomers in higher yields. To solve the second problem, we reported a new type of branched polymers, that is, poly(dendron macromonomer)(for example, polymers of **3**<sub>1-3</sub>) which was a highly branched polymer having a linear rigid backbone prepared by addition polymerization of the acetylene group in the macromonomer having regularly branched dendritic structure<sup>3</sup> In addition, the resulting polymer showed good performance of gas permselectivity due to their regulated branched structures. Gas permselective membranes are very important and valuable because the necessity to remove impurities or purify mixtures of gases whose molecular sizes are very similar is enhancing because solving

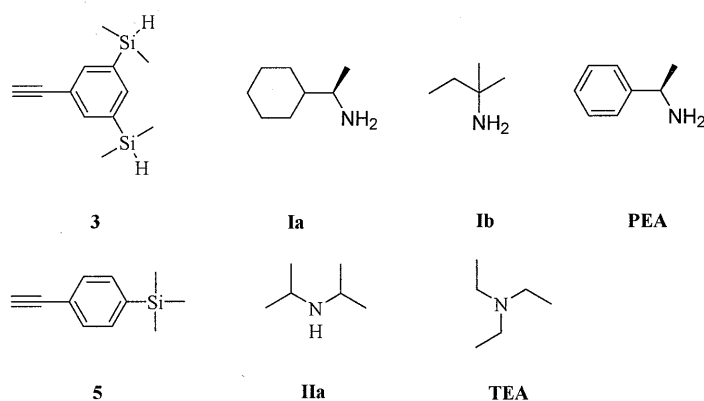
the recent environmental problems has been focused on.<sup>4</sup> In general, tradeoff relationship between permeability and permselectivity is usually observed. To overcome this, more control of chemical structures of the side groups in the polymer used for permselective membranes are needed.

Poly(dendron macromonomer) was a valuable polymer having regulated structures and better membrane forming ability than dendrimers. However it had still the two problems as described above. (1) Multi-step synthetic route (low yield) and (2) Low membrane forming ability.

In this study to overcome the two problems, we designed a new type of polymer, *i.e.*, poly(hyperbranched macromonomer). In addition, we propose its new synthetic method, *i.e.*, one-pot synthesis by simultaneous polymerization of two types of polymerization of one monomer. In other words, we report a new complicated polymer and its very simple preparation method. The complex polymer could be synthesized by very easy one-pot procedure. In addition, we report significantly better performance of gas permselectivities of the resulting copoly(1/5) membranes which are on the Robeson's upper boundary line.<sup>4d</sup>



the simultaneous one-pot procedure we reported here was found to be better one than the two 2-stepwise methods. The poly(hyperbranched acetylene-type macromonomer)(poly $aps(3)$ ) having both large degree of the polymerization of the addition polymerization( $q$ ) and the high degree of the branches( $p$ ) was synthesized by the simultaneous one-pot procedure for the first time. The ratio of the two kinds of the polymerization, *i.e.*, polyaddition and addition polymerization ( $= p / q$  or  $X(\%)$ ) in the simultaneous polymerization could be controlled by changing kinds of amines(Chart 4-1)



**Chart 4-1.** Monomers and cocatalysts in this study.

## 4.2 Experimental part

### 4.2.1 Materials.

All the solvents used for synthesis and polymerizations of the monomers were distilled as usual. The polymerization initiator,  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  (nbd = 2,5-norbornadiene) and amines purchased from Aldrich Chemical were

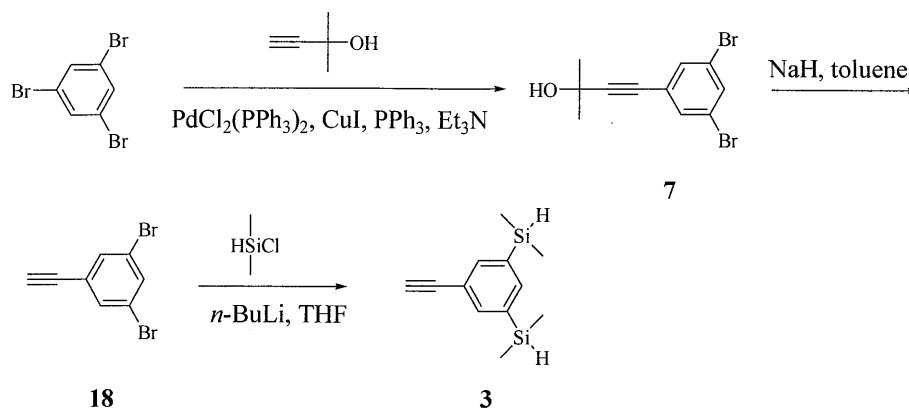
used as received. According to the literature procedures, 3,5-bis(dimethylsilyl)phenylacetylene<sup>1</sup> (**3**, in Chart 4-1), was prepared.

#### **4.2.2 Measurements.**

<sup>1</sup>H NMR (400 MHz) spectra were recorded on a VARIAN-400 spectrometer. The average molecular weights (*M<sub>n</sub>* and *M<sub>w</sub>*) 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, carbon dioxide, and nitrogen permeability coefficients (*P<sub>O<sub>2</sub></sub>*, *P<sub>CO<sub>2</sub></sub>*, and *P<sub>N<sub>2</sub></sub>*: cm<sup>3</sup>(STP)cm·cm<sup>-2</sup>·s<sup>-1</sup>·cmHg<sup>-1</sup>) and the separation factor (*P<sub>O<sub>2</sub></sub>* / *P<sub>N<sub>2</sub></sub>*, *P<sub>CO<sub>2</sub></sub>* / *P<sub>N<sub>2</sub></sub>*) were measured by a gas chromatographic method at 25°C using YANACO GTR-10 according to Ref. [4]. The area of membrane was 1.77 cm<sup>2</sup>, and the initial feed gas pressure was 1 atm.

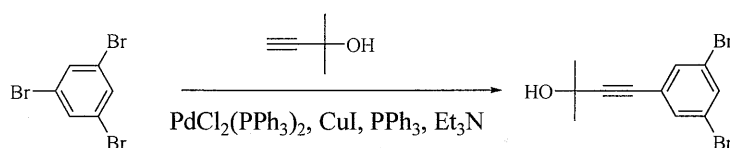
#### **4.2.3 Synthetic procedures and characterization of monomer (3)**

(Scheme 4-1). All the following reaction procedures were conducted under dry nitrogen.



**Scheme 4-1.** Synthesis route of **3**

#### 4.2.3.1 1-(3-Hydroxyl-3-methylbutynyl)-3,5-dibromobenzene(**7**).<sup>3</sup>

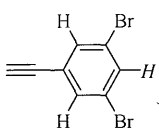
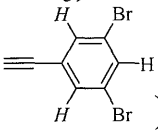


2-Methyl-3-butyn-2-ol (2.8 mL, 30 mmol) was added to 1,3,5-tribromobenzene (9.4 g, 30 mmol), bis(triphenylphosphine)palladium(II) chloride (0.14 g, 0.20 mmol), triphenylphosphine (0.21 g, 0.80 mmol) and copper(I) iodide (0.22 g, 1.2 mmol) in dry triethylamine (150 mL) under a nitrogen atmosphere. The solution was stirred for 16 h at 90°C to precipitate a white solid. The solid was filtered out, and the solvent of the filtrate was concentrated by evaporation. The crude product was purified by silica-gel column chromatography with ethyl acetate / hexane = 1 / 4 as an eluent to give **4**.  $R_f = 0.4$  (ethyl acetate / hexane = 1 / 4). Appearance: yellow solid.

Weight: 6.9 g.

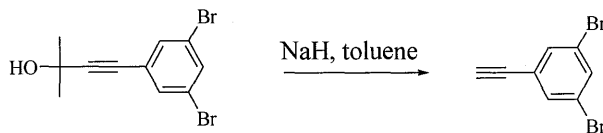


Yield: 76%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, δ): 7.60 (t, 1H, *J* = 1.5 Hz, , 7.49 (d, 2H, *J* = 1.5 Hz, , 2.10 (s, 1H, OH), 1.60 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>) ppm.  
<sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, δ): 133.12, 122.22, 95.15, 94.09, 81.22, 65.59, 31.37ppm.

IR (KBr; cm<sup>-1</sup>): 3484 (OH), 2988 (C-H), 2356 (C≡C).

#### 4.2.3.2 . 3,5-Dibromophenylacetylene (18).<sup>1</sup>



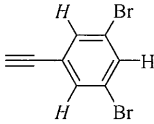
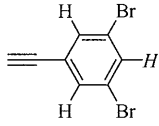
Sodium hydride (0.62 g, 14 mmol) was added to a toluene solution (70 mL) of **4** (4.4 g, 14 mmol). The mixture was heated to 90°C and stirred under nitrogen flow for 2 h. It was allowed to room temperature slowly. The reaction mixture was filtered. The solvent of the filtrate was concentrated by evaporation. 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 **18**.

*R*<sub>f</sub> = 0.5 (hexane).

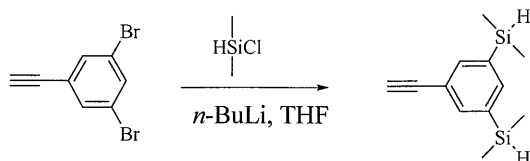
Appearance: white solid.

Weight: 3.0 g.

Yield: 82%.

<sup>1</sup>H NMR(CDCl<sub>3</sub>, TMS, δ): 7.58(t, 1H, *J* = 1.5 Hz, , 7.53(d, 2H, *J* = 1.5 Hz, , 3.11(s, 1H, HC≡C) ppm.  
 IR (KBr; cm<sup>-1</sup>): 3300(C-H), 2316 (C≡C).

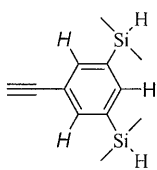
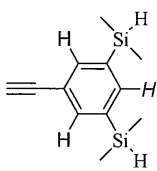
#### 4.2.3.3. Synthesis of 3,5-bis(dimethylsilyl)phenylacetylene(3)<sup>1</sup>.



A 200-mL round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen gas. 3,5-dibromophenylacetylene (8.0 g, 30.6 mmol) and dry THF (100 mL) were placed in the flask at -75 °C. At the same temperature, a hexane solution of *n*-butyllithium (56.4 mL, 1.63 M, 92.0 mmol) was added dropwise, and the reaction mixture was stirred for 4 h. A solution of dimethylchlorosilane (5.8 g, 61.3 mmol) in dry THF (30 mL) was added dropwise, and it was allowed to 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. The diethyl ether layer was washed with water, then dried over anhydrous sodium sulfate. Diethyl ether was concentrated by evaporation. The crude product was purified by flash column chromatography (Merck, silica-gel 60; eluent, hexane) to give the desired product **3**.  
 Appearance: colorless liquid.

Weight: 2.2 g.

Yield: 35%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, δ): 7.67 (s, 2H, , 7.50 (s, 1H, , 4.42 (heptet, 2H, SiH), 3.08 (s, 1H, C≡CH), 0.34 (d, 12H, Si(CH<sub>3</sub>)<sub>2</sub>).ppm

<sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, δ): 138.4, 132.9, 127.9, 121.6, 84.2, 77.6, -3.8 ppm.

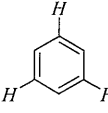
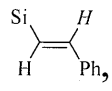
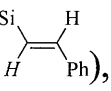
IR (KBr, cm<sup>-1</sup>): 3300, 2957, 2923, 2861, 2120, 1572, 1373, 1250, 1133, 880, 838, 763, 640.

#### 4.2.4.1 Polyaddition of **3** (Synthesis of hyperbranched macromonomer polyp(**3**))<sup>1</sup>

A typical polymerization procedure was as follows: To a solution of **3** (80 mg, 0.38 mmol) in dry toluene (2.5 mL) at 25 °C under nitrogen, a solution of RhCl(PPh<sub>3</sub>)<sub>3</sub> (1.2 mg, 1.3 μmol) and NaI (0.20 mg, 1.3 μmol) in dry toluene (1.0 mL) was added. The mixture was kept at 80 °C for 2 h to give a solution of polyp(**3**). The formed polymer was purified by precipitation of the toluene solution in a large amount of methanol and dried in vacuum to give polyp(**3**). *Mn* = 3.2×10<sup>3</sup> (Table 1, no. 7).

Appearance: white solid.

Yield: 83%.

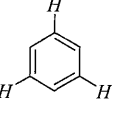

<sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, δ): 7.7-7.1 (m, 25H, ) 6.90, (d, 8H, *J* = 19.2, , 6.60, (d, 8H, *J* = 19.2, , 5.90 (d, 0.2H, *cis*-vinylene), 4.44(m, 13H, -SiH), 3.12(s, 1H, C≡CH), 0.6-0.1(m, 61H, -Si(CH<sub>3</sub>)<sub>2</sub>H). The other polymerizations were also conducted similarly.

#### 4.2.4.2 Addition polymerization of **3**(Synthesis of poly**a**(**3**))<sup>3</sup>

A typical polymerization procedure was as follows: To a solution of **3** (108 mg, 0.50 mmol) in dry toluene (2.5 mL) at 25 °C under nitrogen, a solution of [RhCl(nbd)]<sub>2</sub> / **PEA** (121 mg, 1.0 mol) in dry toluene (1.0 mL) was added. The mixture was kept at room for 12 h to give a solution of poly**a**(**3**). The formed polymer was purified by precipitation of the toluene solution in a large amount of methanol and dried in vacuum to give a poly**a**(**3**). *M<sub>n</sub>* = 1.1×10<sup>4</sup> (Table 1, no. 5).

Appearance: yellow solid.

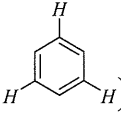



Yield: 74%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, δ): 7.4-6.8(m, , 5.8(s, 1H, , 4.22(m, 2H, -SiH), 0.13(s, 12H, -Si(CH<sub>3</sub>)<sub>2</sub>H). The other polymerizations were also conducted similarly.

**4.2.4.3. Synthesis of poly(hyperbranched acetylene-type macromonomers) by simultaneous addition polymerization and polyaddition. (Synthesis of poly**aps**(**3**))**

A typical polymerization procedure was as follows: To a solution of **3** (209 mg, 0.50 mmol) in dry toluene (2.5 mL) at 25 °C under nitrogen, a solution of [RhCl(nbd)]<sub>2</sub> / amine (**Ia**, **Ib**, **IIA**, **TEA**) (1.0 mol) in dry toluene (1.0 mL) was added. The mixture was kept at room temperature for 12 h to give a solution of poly $\alpha$ p(**3**). The formed polymer was purified by precipitation of the toluene solution in a large amount of methanol and dried in vacuum to give poly $\alpha$ p(**3**).  $M_n = 6 - 21 \times 10^3$  (Table 1, nos. 1-4). Appearance: yellow solid.

Yield: 29-87%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS,  $\delta$ ): 7.5-6.8 (m, , 6.90, (d, 8H,  $J = 19.2$ , , 6.60, (d, 8H,  $J = 19.2$ , , 5.8(s, 1H, , 4.22(m, 2H, -SiH), 0.13(s, 12H, -Si(CH<sub>3</sub>)<sub>2</sub>H). ppm.

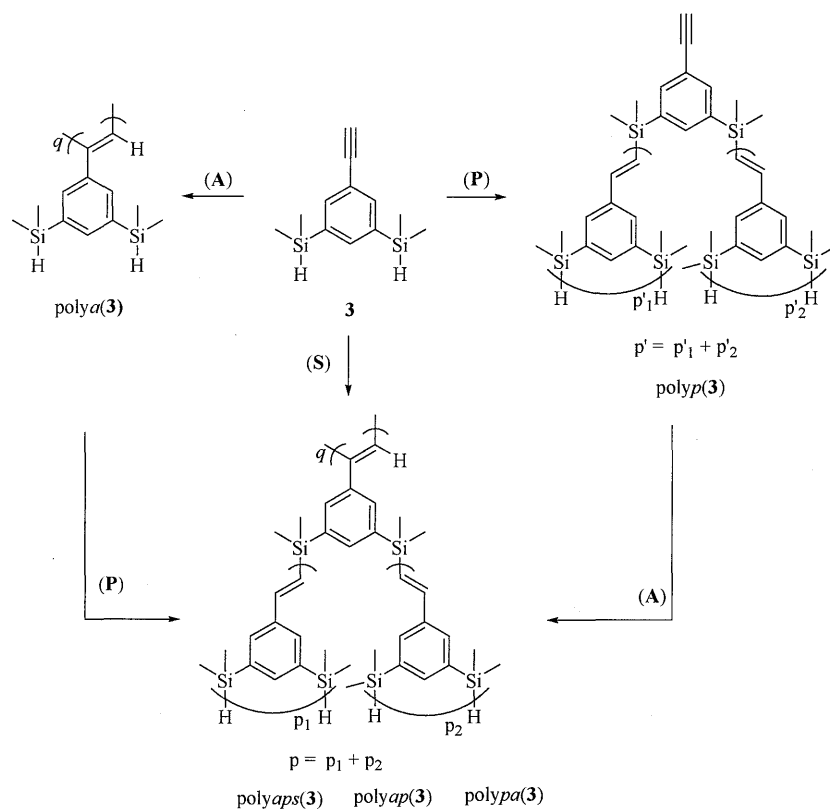
#### 4.2.4 Membrane preparation.

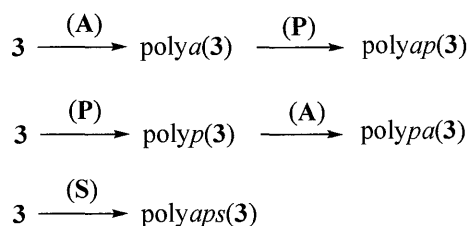
The blend membranes were fabricated by poly $\alpha$ p(**3**) (1, 5, 10, 15 mol%) with poly $\alpha$ (**5**). A 5wt%(w/v) solution of a polymer in chloroform or toluene as cast on a Teflon sheet, and the solvent was evaporated room temperature. The resulting of solid membrane was detached the sheet and dried in vacuo for 24 h. Thickness ( $L$ ) of the membranes was 76–105  $\mu\text{m}$ .

## 4.3 Results and discussion

### 4.3.1 Advantage of the one-pot simultaneous synthetic route to the new type of polyaps(3) and the comparison of the structures of the resulting polymers prepared by the other two-step methods

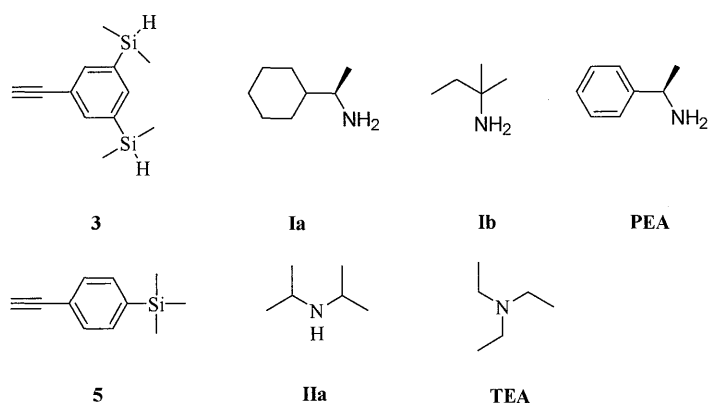
Main text paragraph to begin with, we report discovery of one-pot synthesis of a new type of polymer, poly(hyperbranched macromonomer) by the simultaneous polymerization of two different types of polymerizations, i.e., addition polymerization and polyaddition of one AB<sub>2</sub> monomer (**3** in Scheme 4-2) by using one catalyst .





**Scheme 4-2.** Polymerization of **3** by using (A): Addition polymerization by  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / phenylethylamine(PEA); (P): Polyaddition by  $\text{Rh}(\text{PPh}_3)_3$  / NaI; (S): Simultaneous polymerization by  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / amine (**Ia**, **Ib**, **IIa**, **TEA**)(see Chart S1.).

The monomer **3** having one terminal triple bond and two Si-H groups was synthesized (see Scheme4-1) and polymerized with  $\text{RhCl}(\text{PPh}_3)_3$  / NaI



**Chart 4-1.** Monomers and cocatalysts in this study.

or  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / various amines (see Chart 4-1) such as triethylamine (**TEA**), phenylethylamine (**PEA**), and so on. Table 4-1 shows the results of the polymerization of **3**. And according to the GPC and  $^1\text{H}$  NMR of the resulting polymers, respectively. Here we defined and calculated some

original values ( $p / q$ ,  $X(\%)$ ,  $G$ ,  $C(\%)$  and  $D(\%)$ ) in Table 4-1 to estimate the polymerizations and structures of the resulting polymers with  $^1\text{H}$  NMR

When  $\text{RhCl}(\text{PPh}_3)_3 / \text{NaI}$  was used as a catalyst, **3** was polymerized only by hydrosilation between the terminal triple bond and the two Si-H groups in polyaddition mode ((**P**) in Scheme 4-2) to yield a hyperbranched acetylene type macromonomer ( $\text{polyp}(\mathbf{3})$  in Scheme 4-2, no.8 in Table 4-1 ) because **3** is an  $\text{AB}_2$  type monomer. When at the terminal triple bonds in addition polymerization mode ((**A**) in Scheme 4-2) to yield  $\text{polya}(\mathbf{3})$  as shown in Scheme 4-2 (no.6 in Table 4-1). On the other hand, when  $[\text{Rh}(\text{nbd})\text{Cl}]_2 / \text{TEA}$ , 2-hydroxymethyl-2-aminoethanol(**Ia**), 2-ethyl-2-aminoethanol(**Ib**), or 1-cyclohexylethylamine(**IIA**) was used as a catalyst (For the structures, see Chart 4-1), **3** was polymerized simultaneously both in polyaddition mode and addition polymerization mode ( (**S**) in Scheme 4-2, no.6 in Table 4-1) to yield  $\text{polyaps}(\mathbf{3})$  as shown in Scheme 4-2 ( nos.1-4 in Table 4-1). The structure of  $\text{polyaps}(\mathbf{3})$ , that is, poly(hyperbranched acetylene-type macromonomer) was confirmed by GPC and  $^1\text{H}$  NMR as follows: As model polymers for  $^1\text{H}$  NMR assignments,  $\text{polya}(\mathbf{3})$  and  $\text{polyp}(\mathbf{3})$  were used. They showed clear difference on the peaks assigned to the methyl and hydrogen in the dimethylsilyl



**Table 4-1.** Polymerization of monomer (**3**)<sup>a</sup>

no.	catalyst <sup>b</sup>	yield <sup>c</sup> (%)	$M_n$ <sup>d</sup> ( $\times 10^4$ )	$M_w$ $/M_n$	$p/q$	X(%) <sup>f</sup>	G <sup>g</sup>	C <sup>h</sup>	D <sup>i</sup>	polymer <sup>b</sup>	membrane <sup>j</sup> appearance
1	[Rh(nbd)Cl] <sub>2</sub> / <b>Ia</b>	34	6.2	1.8	1.2	54	1.4	0.38	4.5	polyaps( <b>3</b> )	-
2	[Rh(nbd)Cl] <sub>2</sub> / <b>Ib</b>	35	16	2.7	1.3	57	1.7	0.39	4.8	polyaps( <b>3</b> )	+
3	[Rh(nbd)Cl] <sub>2</sub> / <b>IIa</b>	29	8.5	2.3	2.0	67	2.0	0.62	5.6	polyaps( <b>3</b> )	-
4	[Rh(nbd)Cl] <sub>2</sub> / <b>TEA</b>	87	21	4.5	2.2	69	2.1	0.52	6.5	polyaps( <b>3</b> )	+
5	RhCl(PPh <sub>3</sub> ) <sub>3</sub> / NaI	83	14	3.8	1.2	54	1.3	0.40	13	polyap( <b>3</b> )	+
6	[Rh(nbd)Cl] <sub>2</sub> / <b>PEA</b>	74	11	2.6	0.6	38	1.4	0.23	29	polya( <b>3</b> )	-
7 <sup>k</sup>	[Rh(nbd)Cl] <sub>2</sub> / <b>PEA</b>	92	9.0	3.4	13	93	3.7	0.65	7.6	polypa( <b>3</b> )	-
8 <sup>l</sup>	RhCl(PPh <sub>3</sub> ) <sub>3</sub> / NaI	83	3.2	1.5	13	93	3.7	1.00	2.0	polyp( <b>3</b> )	-

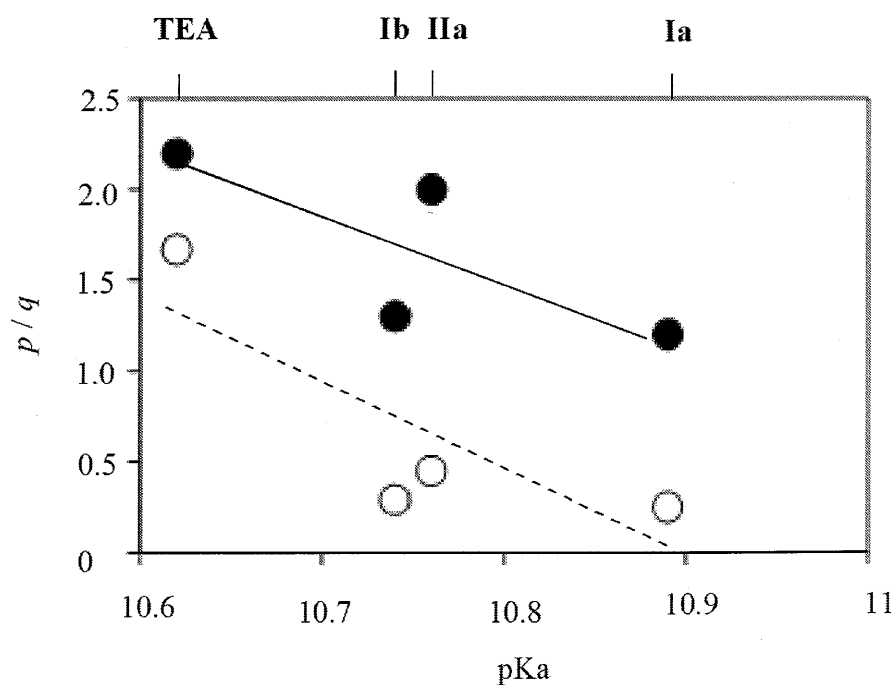
<sup>a</sup>Reactions were carried out at room temperature for 12 h in toluene. [Monomer] = 0.01 mol/L, [Monomer] / [Rh(nbd)Cl]<sub>2</sub> = 250; <sup>b</sup>For the codes, see Scheme 1 and Chart 1.; <sup>c</sup>Insoluble part in methanol; <sup>d</sup>Determined by GPC correlating polystyrene standard with THF eluent; <sup>e-i</sup>Determined by <sup>1</sup>H NMR. For the assignment for A<sub>H</sub>, T<sub>H</sub>, P<sub>H</sub>, Q<sub>H</sub>, B<sub>Me</sub>, P<sub>Me</sub>, Q<sub>Me</sub>, I<sub>Me</sub>, see Scheme S3. <sup>e</sup> $p/q = B_{Me} / \{6A_H(\text{or } 6T_H)\}$ ; <sup>f</sup> $X(\%) = p / (p + q) \times 100$ ; <sup>g</sup>G(Average generation) =  $\log\{(P_H + Q_H) / (A_H(\text{or } T_H))\} / \log 2$ ; <sup>h</sup>C =  $P_H / (P_H + Q_H)$ ; <sup>i</sup>D =  $I_{Me} / (P_{Me} + Q_{Me} + B_{Me} + I_{Me}) \times 100$ ; <sup>j</sup>Membrane forming ability: -, poor; +, brittle; ++, tough; <sup>k</sup>The poly(**a**) contained 5% of polyaps(**3**) judging from the peak at 4.40 ppm assigned to P<sub>H</sub>. For P<sub>H</sub> See Chart S2; <sup>l</sup>Polyp(**3**) (no. 7) was polymerized as a starting polymer with [Rh(nbd)Cl]<sub>2</sub> / **PEA**.

Main text paragraph groups. The NMR for poly $aps(3)$  had the both peaks assigned to poly $a(3)$  and poly $p(3)$ . Judging from the  $^1\text{H}$  NMR, it was confirmed that it contained both a polyacetylene main chain (the degree of the polymerization =  $q$  and  $q'$  in Scheme 4-2) and a hyperbranched chains (the degree of the polymerization =  $p$  or  $p'$  in Scheme 4-2). In addition, since the GPC curve was unimodal, it was thought to be poly(hyperbranched macromonomer), not a mixture of the two types of polymers, poly $a(3)$  and poly $p(3)$ .

In summary, synthesis of a complex polymer, poly(hyperbranched macromonomer) by one-pot simultaneous polymerization of the two different types of polymerizations, *i.e.*, addition polymerization and polyaddition of one new monomer(3) having one terminal triple bond and two Si-H groups has been achieved by using  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / various amines. To the best of our knowledge, the two findings, *i.e.*, synthesis of the new type of complex polymer, poly(hyperbranched macromonomer) and the simultaneous polymerization method of one monomer<sup>5</sup> by using one catalyst were the first examples.

#### **4.3.2 Control of the ratio of polyaddition and addition polymerization in the simultaneous polymerization of 3 by changing amine cocatalysts**

To check the advantage of the one-pot simultaneous synthetic route to the new type of polymer, poly(hyperbranched macromonomer), we tried to synthesize polymers having structures similar to polyaps(3) by two two-step procedures (See Scheme 4-1) yielding polyap(3) and polypa(3) having similar structure to polyaps(3). However the structures of the resulting polymers, polyap(3) obtained by polyaddition of polya(3) prepared by addition polymerization of 3, and polypa(3) obtained by addition polymerization of polyp(3) prepared by polyaddition of 3 were not complete compared with polyaps(3) by the one-pot simultaneous method.



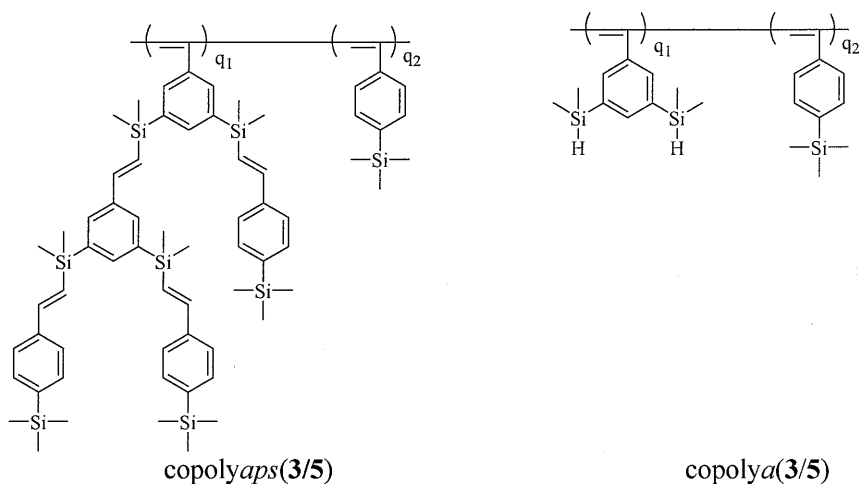
**Figure 4-1.** Relationship between  $p/q$  and  $pK_a$  (● : poly(3); ○: model reaction) (For TEA, Ib, IIa, Ia).

In conclusion, the simultaneous one-pot procedure we reported first here was found to be better one than the two two-stepwise methods. The poly(hyperbranched macromonomer)(poly $aps(3)$ ) having both large degree of the polymerization of the addition polymerization( $q$ ) and the high degree of the branches( $p$ ) was synthesized by the simultaneous one-pot procedure for the first time. The reason why the simultaneous polymerization gave the best structures having the best balance of  $p$  and  $q$  was explained.

The ratio of the two kinds of the polymerization *i.e.*, polyaddition and addition polymerization ( $= p / q$  or  $X(\%)$ ) in the simultaneous polymerization could be controlled by changing kinds of amines (Table 4-1, nos. 1- 4) having different substituents and pKa (Chart 4-1) used as a cocatalyst promoting addition polymerization. For example, when phenylethylamine(PEA) was used, only addition polymerization happened and almost no polyaddition occurred to give poly $a(3)$  ( no. 6 in Table 4-1). When triethylamine(TEA) was used, both addition polymerization and polyaddition occurred to give poly $aps(3)$  (no. 4 in Table 4-1). As shown in Table 1, nos.1-4, the ratios of the two degrees of the polymerizations were controlled by changing the cocatalyst. The values showing the ratio,  $p / q$ ,  $X(\%)$ ,  $G$  and  $C(\%)$  were changed largely. The amine having higher pKa tended to produce poly $aps(3)$  having a higher  $p / q$  value, *i.e.*, higher degree of branches.

### 4.3.3 Gas separation properties of membranes containing poly(3)

Since the new types of polymers synthesized for the first time in this study had a unique branched structure having a linear rigid backbone, they were expected to show good properties as a gas permselective membrane materials due to the diffusion selectivity similarly to the case of poly(dendron) like poly(**6**) we previously reported<sup>3</sup> with good self membrane forming abilities.



The results of measurements of gas permeabilities through the polymer membranes are shown in Figure 4-2 and 4-3 and Table 4-2. The membranes of the poly(hyperbranched macromonomer / *p*-trimethylsilylphenylacetylene(**5**)) (polyaps(**3/5**)) (nos.1-4 in Figure 4-2, 4-3) showed higher permselectivity than membranes of the corresponding polymer (polya(**3/5**)) (no. 4 in Figure 4-2) without any branches. The permeabilities of poly(hyperbranched macromonomer / *p*-trimethylsilylphenylacetylene(**5**)) (polyaps(**3/5**))(nos. 1 and 2 in Figure

4-2, 4-3) increased than membranes of the corresponding dendronized polymer having regular branches (poly(**6**))(no.3 in Figure 3).

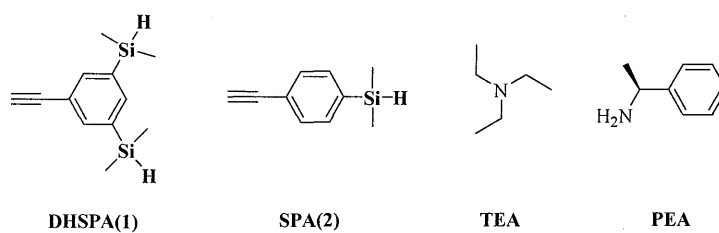


Chart 4-2

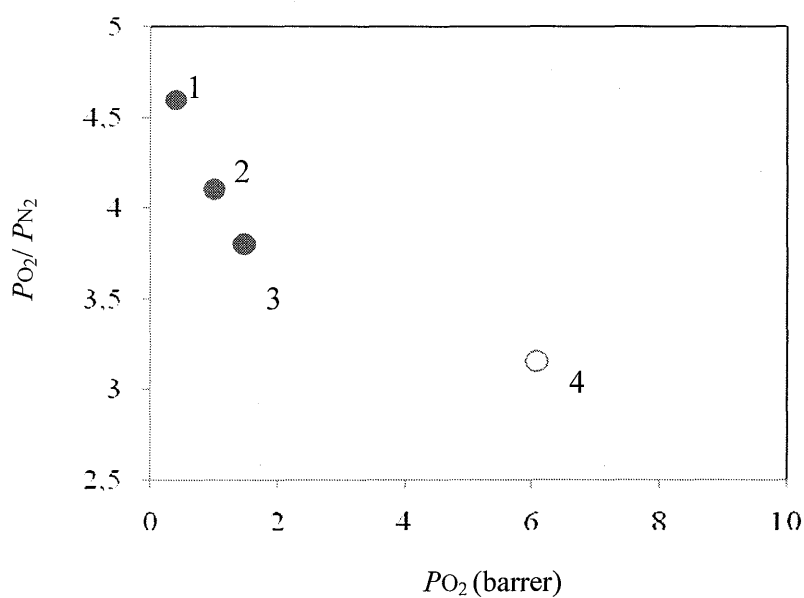


Figure 4-2. The relationship between permeability and permselectivity for  $O_2$  through the ●: copolyaps(3/5); ○: copolya(3/5). (Table 3-3, nos. 1-4)

Table 4-2. Simultaneous copolymerization of monomers **DHSPA(3)** with **SPA(5)**<sup>a</sup> and gas permeabilities of their membranes.

No.	Copolymer <sup>b</sup>	<b>5</b> unit <sup>c</sup> (mol%)	Yield (%)	$M_w$ <sup>d</sup> (x10 <sup>4</sup> )	$p/q$ <sup>e</sup>	$PO_2$ <sup>f</sup> (barrer)	$PCO_2$ <sup>f</sup> (barrer)	$PN_2$ <sup>f</sup> (barrer)	$PO_2$ <sup>f</sup> / $PN_2$	$PCO_2$ <sup>f</sup> / $PN_2$
1	copoly $aps(3/5)$	90	90	15	0.10	0.40	1.8	0.1	4.60	21.0
2	copoly $aps(3/5)$	94	88	18	0.060	0.36	1.8	0.1	4.10	20.8
3	copoly $aps(3/5)$	99	86	19	0.011	0.50	1.7	0.1	3.80	12.9
4 <sup>g</sup>	copoly $a(3/5)$	86	83	6.5	0	6.1	23	2.0	3.05	11.5

<sup>a</sup> At room temperature for 4 h in toluene. [monomer] = 0.2 mol/L, [monomer] / [ triethylamine (TEA)] / [Rh(nbd)Cl]<sub>2</sub> = 250 / 500 / 1; <sup>b</sup> For the codes, see Chart 1; <sup>c</sup> Composition determined by <sup>1</sup>H NMR; <sup>d</sup> Determined by GPC correlating polystyrene standard with THF eluent; <sup>e</sup> For  $p$  and  $q$  by <sup>1</sup>H NMR; <sup>f</sup> Barrer: In 10<sup>-10</sup> cm<sup>3</sup>(STP)cm·cm<sup>-2</sup>·s<sup>-1</sup>·cmHg<sup>-1</sup>; <sup>g</sup> At room temperature for 4 h in toluene. [monomer] = 0.2 mol/L, [monomer] / [ phenylethylamine (PEA)] / [Rh(nbd)Cl]<sub>2</sub> = 250 / 500 / 1.

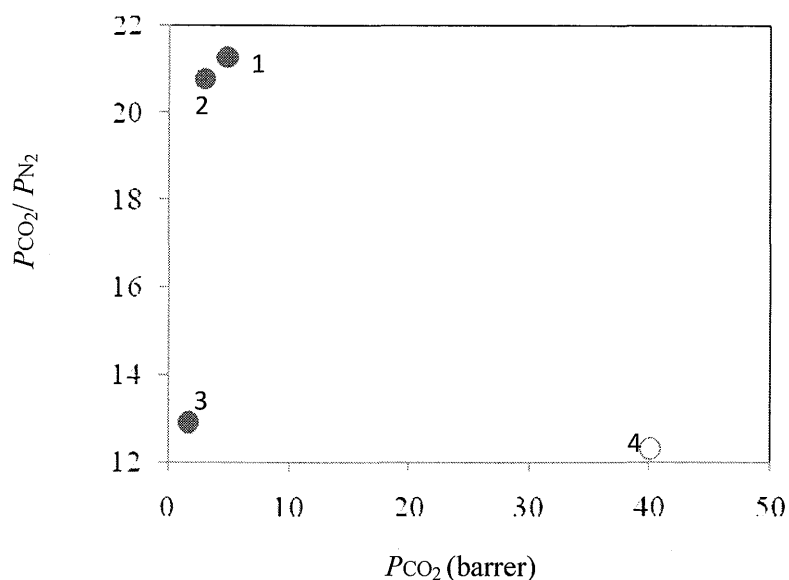


Figure 4-3. The relationship between permeability and permselectivity for  $CO_2$  through the  
 ●:copolyaps(3/5);○:copolya(3/5) (Table 3-3, Nos. 1-4)

In addition, blend membranes of polyp(3) with polya(5)(Figure 4-4., Table 4-3) showed very good performance. Therefore, the effectiveness of the hyperbranched structure on the permselectivities was proved.

Table 4-3. Gas permeabilities of membranes from blend polymers of polyp(3) with polya(5)<sup>a</sup>

No.	Polymers <sup>a</sup> (3 unit mol%)	$PO_2$ (barrer) <sup>b</sup> ( $\times 10^2$ )	$PN_2$ <sup>b</sup> (barrer)	$PO_2$ / $PN_2$
1	polyp(3) / polya(5)(15)	0.75	17	4.4
2	polyp(3) / polya(5)(10)	1.1	32	3.4
3	polyp(3) / polya(5)(5)	1.4	42	3.3
4	polyp(3) / polya(5)(1)	1.8	60	3.0
5	polya(5)(0)	1.7	63	2.7

<sup>a</sup>For the codes, see Scheme 1, and Chart 1. <sup>b</sup>In  $10^{-10} \text{cm}^3(\text{STP})\text{cm cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$ .



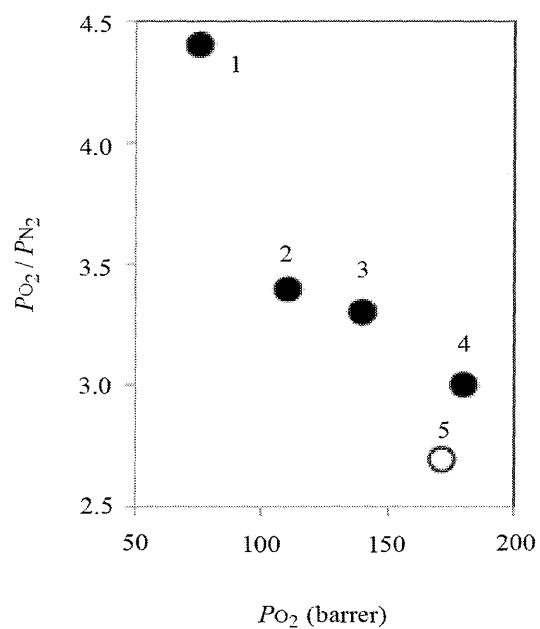


Figure 4-4. Plot of permselectivity to permeability for  $O_2$  through the polyp(3) / polya(5) (15, 10, 5, 1, 0 mol%) membranes (The numbers correspond to those in Table. 4-3).

#### 4.4 Conclusions

1. Poly $\alpha$ ps(**3**) which has good performance for gas separation membranes was synthesized very easily and regulatedly by the one-pot simultaneous polymerization method for the first time.
2. The control of the ratio of the two kinds of the polymerization, *i.e.*, polyaddition and addition polymerization ( $= p / q$  or  $X(\%)$ ) in the simultaneous polymerization by changing kinds of amines having different substituents and pKa.
3. Branched structures enhanced permselectivities in  $PO_2 / PN_2$  through poly $\alpha$ (**5**)-based blend membranes containing 1-15 mol% of polyp(**3**).

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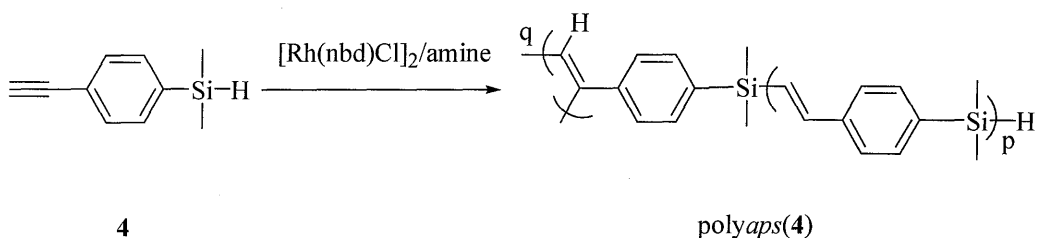
simultaneous chain- and step-growth radical polymerization.

*Macromolecules* **2011**, *44*, 2382–2386. (b) Mizutani, M.; Satoh, K.; Kamigaito, M. Metal-catalyzed simultaneous chain- and step-growth radical polymerization: Marriage of vinyl polymers and polyesters. *J. Am. Chem. Soc.* **2010**, *132*, 7498–7507.

**Chapter 5: One-pot synthesis polyaps(macromonomer) by simultaneous polymerization of two different modes of polymerizations *i.e.*, addition polymerization and polyaddition of *p*-dimethylsilylphenylacetylene(HSPA 4) by using one catalyst for gas permselective membranes**

## Abstract

Simultaneous polymerization of the two different types of polymerizations, *i.e.*, addition polymerization and polyaddition of one monomer(**4**) having one terminal triple bond and Si-H group has been achieved by using  $[\text{Rh}(\text{norbornadiene(=nbd))Cl}]_2$  / various amines. To our knowledge, this is the first example of such simultaneous polymerization of one monomer. In addition, the ratio of the two polymerizations could be controlled by changing amine cocatalyst. By this polymerization method, one-pot synthesis of poly(macromonomer) from **4** was realized. To the best of our knowledge, this is the first synthesis of such complex polymers. Membranes from the poly(macromonomer) had both the advantages



of poly(phenylacetylene)s and poly(dendron). Some of them showed the highest performance as oxygen or carbon dioxide permselective membranes among all the membranes reported. In summary, a new complex polymer, poly(macromonomer) showing good performance as gas separation membranes was synthesized very easily by the one-pot simultaneous polymerization method.



## 5.1 Introduction

Recently some kinds of new polymer molecules having unique structures have been reported. Among them highly branched polymers like dendrimers have received much attention because of their regular structures.<sup>1</sup> Dendrimers have highly regulated branched structures but generally they have two problems. One is synthesis of the polymers needs many steps and results in very low yields because they were prepared not by polymerization but by multi-step organic reactions. The other problem is their low ability for fabrication because of no entanglement.

To overcome the first problem, hyperbranched polymers have been reported.<sup>2</sup> They were prepared more easily by one polymerization of  $AB_2$  type monomers in higher yields. To solve the second problem, we reported a new type of branched polymers, that is, poly(dendron macromonomer)(for example, polymers of **6**) which was a highly branched polymer having a linear rigid backbone prepared by addition polymerization of the acetylene group in the macromonomer having regularly branched dendritic structure<sup>3</sup> In addition, the resulting polymer showed good performance of gas permselectivity due to their regulated branched structures. Gas permselective membranes are very important and valuable because the necessity to remove impurities or purify mixtures of gases whose molecular sizes are very similar is enhancing because solving

the recent environmental problems has been focused on.<sup>4</sup> In general, tradeoff relationship between permeability and permselectivity is usually observed. To overcome this, more control of chemical structures of the side groups in the polymer used for permselective membranes are needed.

Poly(dendron macromonomer) was a valuable polymer having regulated structures and better membrane forming ability than dendrimers. However it had still the two problems as described above. (1) Multi-step synthetic route (low yield) and (2) Low membrane forming ability.

In this study to overcome the two problems, we designed a new type of polymer, *i.e.*, poly(macromonomer). In addition, we propose its new synthetic method, *i.e.*, one-pot synthesis by simultaneous polymerization of two types of polymerization of one monomer. In other words, in this communication, we report a new complicated polymer and its very simple preparation method. The complex polymer could be synthesized by very easy one-pot procedure. In addition, we report significantly better performance of gas permselectivities of the resulting polymer membranes which are on the Robeson's upper boundary line.<sup>4d</sup>

## 5.2 Experimental part

### 5.2.1 Materials.

All the solvents used for synthesis and polymerizations of the monomers were distilled as usual. The polymerization initiator,  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  ( $\text{nbd} =$

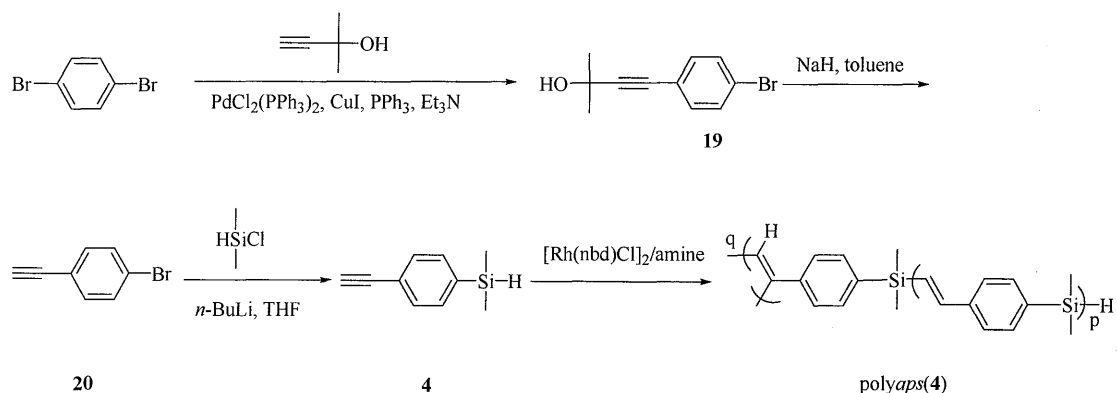
2,5-norbornadiene) and amines purchased from Aldrich Chemical were used as received. According to the literature procedures<sup>5</sup>, *p*-dimethylsilylphenylacetylene(**4**, in chart 1), was prepared.

### 5.2.2 Measurements.

<sup>1</sup>H NMR (400 MHz) spectra were recorded on a VARIAN-400 spectrometer. The average molecular weights (*M<sub>n</sub>* and *M<sub>w</sub>*) 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, carbon dioxide and nitrogen permeability coefficients (*P<sub>O<sub>2</sub></sub>*, *P<sub>CO<sub>2</sub></sub>*, and *P<sub>N<sub>2</sub></sub>* : cm<sup>3</sup>(STP)cm·cm<sup>-2</sup>·s<sup>-1</sup>·cmHg<sup>-1</sup>) and the oxygen separation factor (*P<sub>O<sub>2</sub></sub>* / *P<sub>N<sub>2</sub></sub>*, *P<sub>CO<sub>2</sub></sub>* / *P<sub>N<sub>2</sub></sub>*) were measured by a gas chromatographic method at 25 °C using YANACO GTR-10 according to Ref. [3]. The area of membrane was 1.77 cm<sup>2</sup>, and the initial feed gas pressure was 1 atm.

### 5.2.3 Synthetic procedures and characterization of monomer (**4**).

All the following reaction procedures were conducted under dry nitrogen.



## Scheme 5-1 Synthesis of the monomer(4)

### 5.2.3.1 4-Bromophenylacetylene (20).<sup>1</sup>

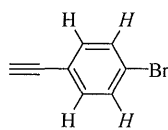
Sodium hydride (1.8 g, 41.5 mmol) was added to a toluene solution (100 mL) of **19** (8.0 g, 33 mmol). The mixture was heated to 90 °C and stirred under a nitrogen flow for 2 h. It was allowed to room temperature slowly. The reaction mixture was filtered. The solvent of the filtrate was concentrated 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 **20**.  $R_f = 0.4(\text{hexane})$ .

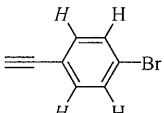
Appearance: white solid.

Weight: 3.0 g.

Yield: 89%.

$^1\text{H}$  NMR( $\text{CDCl}_3$ , TMS,  $\delta$ ): 7.58(d, 2H,  $J = 7.6$  Hz), 7.38(d,



2H, ,  $J = 7.6 \text{ Hz}$ ), 3.11(s, 1H,  $\text{HC}\equiv\text{C}$ ).ppm

IR (KBr;  $\text{cm}^{-1}$ ): 3300(C-H), 2316 ( $\text{C}\equiv\text{C}$ ).

**5.2.3.2 Synthesis of *p*-dimethylsilyl]phenylacetylene(4)<sup>5</sup>.** A 200-mL round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen gas. *p*-bromophenylacetylene (5.2 g, 28.7 mmol) and dry THF (100 mL) were placed in the flask at  $-75^\circ\text{C}$ . At the same temperature, a hexane solution of *n*-butyllithium (35.5 mL, 1.63 M, 57.5 mmol) was added dropwise, and the reaction mixture was stirred for 4 h. A solution of dimethylchlorosilane (2.8 g, 30.2 mmol) in dry THF (30 mL) was added dropwise, and it was allowed to 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 flash column chromatography (Merck, silica-gel 60; eluent, hexane) to give the desired product **4**.

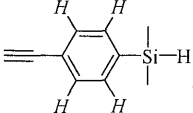
Appearance: colorless liquid

Weight: 2.2 g.

Yield: 35%

IR (KBr): 3300, 2957, 2923, 2861, 2120, 1572, 1373, 1250, 1133, 880,

838, 763, 640  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , TMS): 7.6 (s, 4H, ) 4.42 (heptet, 1H, SiH), 3.11 (s, 1H,  $\text{C}\equiv\text{CH}$ ), 0.34 (d, 6H,  $\text{Si}(\text{CH}_3)_2$ ).ppm

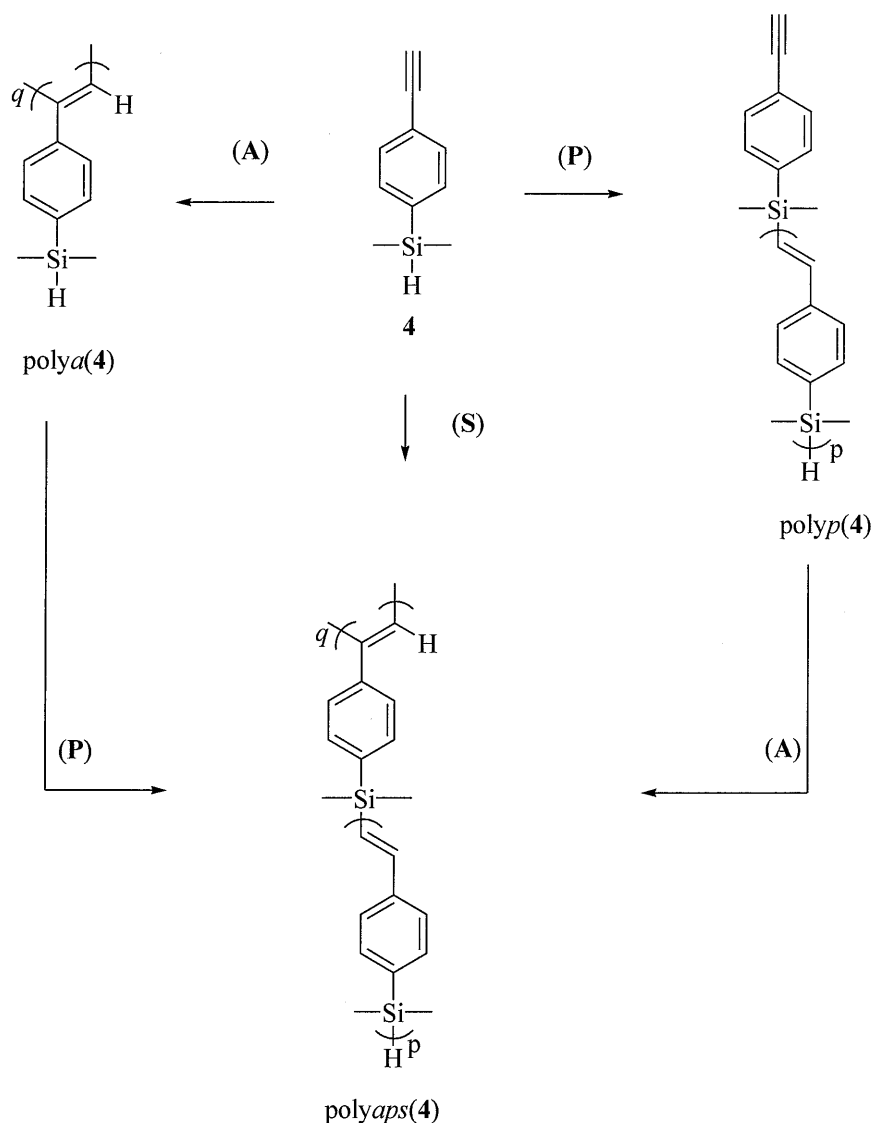
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , TMS): 138.4, 132.9, 127.9, 121.6, 84.2, 77.6, -3.8.  
ppm

### 5.2.3.3 Polymerization.

Simultaneous addition polymerization and polyaddition were carried out by catalyst of  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / amine. Polyaddition were carried out by  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  / NaI. Addition polymerization were carried out by  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / PEA.

## 5.3 Results and discussion

**5.3.1 Advantage of the one-pot simultaneous synthetic route to the new type of poly(4) and the comparison of the structures of the resulting polymers prepared by the other two-step methods**



Scheme 5-1. Polymerization of **4** by using (A):  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / **PEA** (P):  $\text{RhCl}(\text{PPh}_3)_3$  /  $\text{NaI}$  (S):  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / amine

The monomer **4** having one terminal triple bond and one Si-H group was synthesized<sup>1</sup> (see Scheme 5-1) and polymerized with  $\text{RhCl}(\text{PPh}_3)_3$  /  $\text{NaI}$  or  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / various amines (see Scheme 5-2, Chart 5-1) such as triethylamine (**TEA**), phenylethylamine (**PEA**), and so on. Table 5-1 shows the results of the polymerization of **4**. GPC and  $^1\text{H}$  NMR of the resulting polymers, such as  $M_n$ ,  $p / q$  were showed in Table 5-1 When  $\text{RhCl}(\text{PPh}_3)_3$  /  $\text{NaI}$  was used as a catalyst, **4** was polymerized only by

hydrosilation between the terminal triple bond and the two Si-H groups in polyaddition mode ((**P**) in Scheme 5-2) to yield an acetylene type macromonomer (polyp(**1**) in Scheme 5-2, no.8 in Table 5-1. because **4** is an AB type monomer. When at the terminal triple bonds in addition polymerization mode ( (**A**) in Scheme 5-2) to yield poly $\alpha$ (**4**) as shown in Scheme 5-2 ( no.6 in Table 5-1). On the other hand, when [Rh(nbd)Cl]<sub>2</sub> / TEA, 2-hydroxymethyl-2-aminoethanol(**Ia**), 2-ethyl-2-aminoethanol(**Ib**), or 1-cyclohexylethylamine(**Ic**) was used as a catalyst ( For the structures, see Chart 5-1), **4** was polymerized simultaneously both in polyaddition mode and addition polymerization mode ((**S**) in Scheme 5-2, no.6 in Table 5-1) to yield poly $\alpha$ ps(**4**) as shown in Scheme 5-2 ( nos.1-4 in Table 2-1).

### **5.3.2 Control of the ratio of polyaddition and addition polymerization in the simultaneous polymerization of **4** by changing amine cocatalysts**

The structure of poly $\alpha$ ps(**4**), that is, poly(macromonomer) was confirmed by GPC and <sup>1</sup>H NMR as follows: As model polymers for <sup>1</sup>H NMR assignments, poly $\alpha$ (**4**) and polyp(**4**) were used. They showed clear difference on the peaks assigned to the methyl and hydrogen in the dimethylsilyl groups. The <sup>1</sup>H NMR for poly $\alpha$ ps(**4**) had the both peaks assigned to poly $\alpha$ (**4**) and polyp(**4**). Judging from the <sup>1</sup>H NMR, it was confirmed that it contained both a polyacetylene main chain ( the degree



of the polymerization =  $q$  and  $q'$  in Scheme 2-1) and a chains(the degree of the polymerization =  $p$  or  $p'$  in Scheme 5-2).

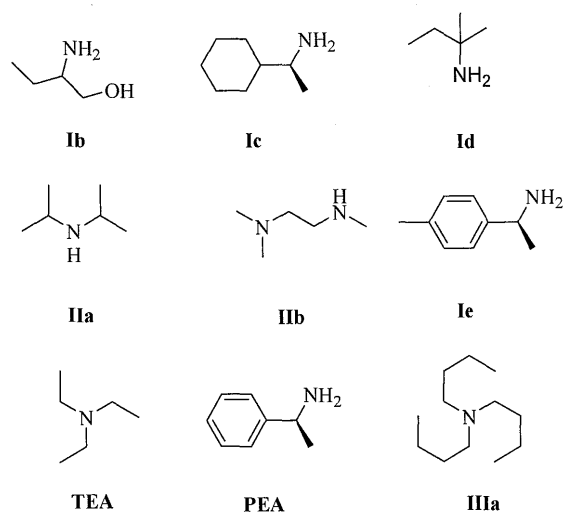


Chart 5-1. The structure of amines

Table 5-1. Polymerization of monomer (**4**)<sup>a</sup>

No.	Initiator <sup>a</sup>	Yield(%) <sup>b</sup>	$M_n^c$ ( $\times 10^3$ )	$p / q^d$	Polymer	Membrane <sup>e</sup> forming ability
1	[Rh(nbd)Cl] <sub>2</sub> / <b>Ib</b>	15	7.6	0.11	polyaps( <b>4</b> )	-
2	[Rh(nbd)Cl] <sub>2</sub> / <b>Ic</b>	45	16	0.33	polyaps( <b>4</b> )	+
3	[Rh(nbd)Cl] <sub>2</sub> / <b>Id</b>	67	11	0.25	polyaps( <b>4</b> )	-
4	[Rh(nbd)Cl] <sub>2</sub> / <b>Id</b>	25	15	0.29	polyaps( <b>4</b> )	-
5	[Rh(nbd)Cl] <sub>2</sub> / <b>IIa</b>	35	18	0.45	polyaps( <b>4</b> )	+
6	[Rh(nbd)Cl] <sub>2</sub> / <b>IIb</b>	25	9.0	0.51	polyaps( <b>4</b> )	-
7	[Rh(nbd)Cl] <sub>2</sub> / <b>IIIa</b>	32	8.5	1.10	polyaps( <b>4</b> )	-
8	[Rh(nbd)Cl] <sub>2</sub> / <b>TEA</b>	77	25	1.67	polyaps( <b>4</b> )	+
9	[Rh(nbd)Cl] <sub>2</sub> / <b>PEA</b> <sup>f</sup>	90	6.7	14	polypa( <b>4</b> )	+
10	RhCl(PPh <sub>3</sub> ) <sub>3</sub> /NaI	83	2.2	14	polyp( <b>4</b> )	-
11	RhCl(PPh <sub>3</sub> ) <sub>3</sub> /NaI <sup>g</sup>	70	115	0.2	polyap( <b>4</b> )	++
12	[Rh(nbd)Cl] <sub>2</sub> / <b>PEA</b>	84	96	0	polya( <b>4</b> )	++

<sup>a</sup> Reactions were carried out at room temperature for 12 h in toluene. [Monomer] = 0.01 mol/L, [Monomer] / [Rh(nbd)Cl]<sub>2</sub> = 250; <sup>b</sup> Insoluble part in methanol; <sup>c</sup> Determined by GPC correlating polystyrene standard with THF eluent; <sup>d</sup> Determined by <sup>1</sup>H NMR; <sup>e</sup> Membrane forming ability: -:poor, +: brittle, ++: tough; <sup>f</sup> Polyp(**4**) (no. 10) was polymerized as a starting polymer with [Rh(nbd)Cl]<sub>2</sub> / **PEA**; <sup>g</sup> Polya(**4**) (no. 12) and **4** were polymerized as a starting polymer with RhCl(PPh<sub>3</sub>)<sub>3</sub> / NaI.

### 5.3.3 Copolymerization and gas separation properties of membranes containing poly(4)

The homopolymerizations of **4** using  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / trimethylamine (TEA) or  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / phenylethylamine(PEA) catalytic system were carried out as shown in **Scheme 5-2**. The results are listed in **Table 5-2**

**Figure 5-1** shows the FT-IR and  $^1\text{H}$ -NMR spectra of poly $\alpha$ (**4**) prepared by a different catalytic system. From the  $^1\text{H}$ -NMR spectra of poly $\alpha$ (**4**) prepared by  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / PEA, we can observe the sharp single peak of the silane hydrogen and from the content of it we can infer that the polymerization carried out as addition polymerization to generate a linear polymer as shown in Scheme 5-1). The  $n$  value can be confirmed through the GPC result of the polymer.

While from the  $^1\text{H}$ -NMR spectra of poly(**4**) by  $[\text{Rh}(\text{nbd})\text{Cl}]_2$ /TEA, the peaks were very broad and complex, the decrease in the content of the silane hydrogen in polymerization indicates that the polymerization process not only on the main chain but also between the silane hydrogen and the triple bond which generate a branched polymer as shown in Scheme 5-2). The  $p$  and  $q$  value can be estimated by the GPC and NMR results.

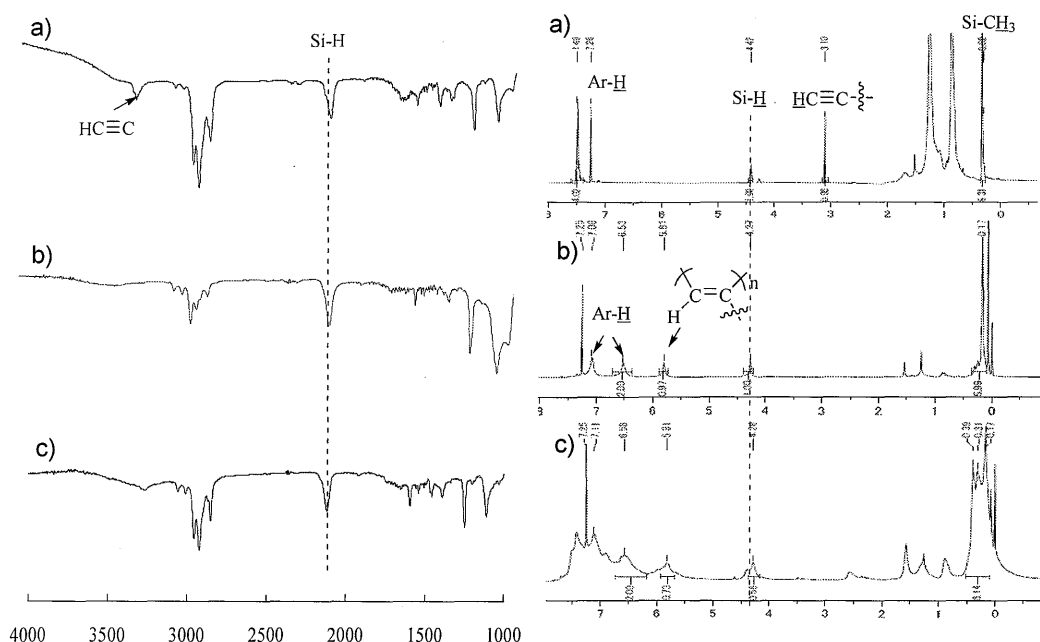


Fig. 1. IR and  $^1\text{H}$ -NMR spectra of **a)** HSPA monomer, **b)** poly(HSPA) prepared by  $[\text{Rh}(\text{nbd})\text{Cl}]_2/\text{PEA}$  system and **c)** poly(HSPA) prepared by  $[\text{Rh}(\text{nbd})\text{Cl}]_2/\text{TEA}$  system.

The copolymerization of **4** and **5** using  $[\text{Rh}(\text{nbd})\text{Cl}]_2/\text{PEA}$  catalytic system is shown in **Scheme 5-2** and the results are listed in **Table 5-2**. **Figure.5-2** shows the FT-IR and  $^1\text{H}$  NMR spectra of an copolymer, copoly(**4/5**):50 mol%).

With increasing the ratio of **4** monomer in feed, the absorption strength of silane hydrogen in IR spectra increased, at the same time the ratio of the **4** unit in the copolymer which were determined by the NMR spectra increased, which indicates that the **4/5** were copolymerized successfully, and then the content of the silane hydrogen in the  $^1\text{H}$ -NMR spectra of copoly(**4/5**) indicated that no polyaddition happened during this copolymerization.

**Table 5-2.** Copolymerization of **4** and **5** using PEA as a cocatalyst<sup>a)</sup>.

Run	<b>4</b> in feed (mol %)	Yield (%)	<b>4</b> unit in copolymer(mol% )	Mw <sup>b)</sup> ( $\times 10^4$ )	Mw/Mn <sup>b)</sup>	Cis % <sup>c)</sup>	Membrane forming ability <sup>d)</sup>	Color
1	100 (poly( <b>4</b> ))	84	100	8.9	2.5	100	--	yellow
2	80	85	76	3.6	1.8	70	-	yellow
3	50	91	48	9	2.6	100	+	yellow
4	25	90	24	16	3.0	99	+	yellow
5	20	92	19	16	2.8	99	++	yellow
6	10	91	10	29	2.7	97	++	yellow
7	0(poly( <b>4</b> ))	91	0	24	2.7	100	++	yellow

a) Polymerization at r.t. in toluene for 4 h. [M]=0.3M. Catalyst:[Rh(nbd)Cl]<sub>2</sub>, [M]/[Cat.] =150, [M]/[Cocat.]=0.5.

b) Determined by GPC correlationg polystyrene standard with CHCl<sub>3</sub> eluent.

c) From the <sup>1</sup>H-NMR spectra of the polymers.

d) ++ : tough; +: good; -- : very brittle.

The copolymerization of **4** and **5** using  $[\text{Rh}(\text{nbd})\text{Cl}]_2/\text{PEA}$  catalytic system is shown in **Scheme 5-2** and the results are listed in **Table 5-2**. **Figure. 5-2** shows the FT-IR and  $^1\text{H}$ -NMR spectra of an copolymer, copoly(**4/5**): 50 mol%).

With increasing the ratio of **4** monomer in feed, the absorption strength of silane hydrogen in IR spectra increased, at the same time the ratio of the **4** unit in the copolymer which were determined by the NMR spectra increased, which indicates that the **4/5** were copolymerized successfully, and then the content of the silane hydrogen in the  $^1\text{H}$ -NMR spectra of copolya(**4/5**) indicated that no polyaddition happened during this copolymerization.

Gas permeation through copolya(**4/5**) membranes. Oxygen permeation of copolya(**4/5**) membranes prepared by  $[\text{Rh}(\text{nbd})\text{Cl}]_2 / \text{PEA}$  catalytic system.

Results of the oxygen permeation through copolya(**4/5**) membranes are shown in **Table 5-3**. **Fig. 5-3** shows the relationship between the permeability and permselectivity of the membranes. With increasing the **4** unit in the copolymer, the permselectivity of the polymeric membranes increased while the permeability decreased.

**Table 5-3** .Oxygen permeation of copolya(4/5) membranes prepared using PEA as cocatalyst<sup>a)</sup>

No.	4 unit in copolymer (mol %) <sup>b)</sup>	$P_{O_2}$ , (barrer) <sup>c)</sup>	$P_{O_2}/P_{N_2}$	Density (g/cm <sup>3</sup> )
1	50	76	4.03	0.871
2	24	107	3.35	0.852
3	19	122	3.13	0.835
4	10	160	3.06	0.826
5	0 (poly(5))	171	2.71	0.810

a) The membranes of polymer were fabricated using solvent-casting method from  $CHCl_3$  solution .

b) From  $^1H$ -NMR spectra.

c) In  $10^{-10} \text{cm}^3(\text{STP})\text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$ .

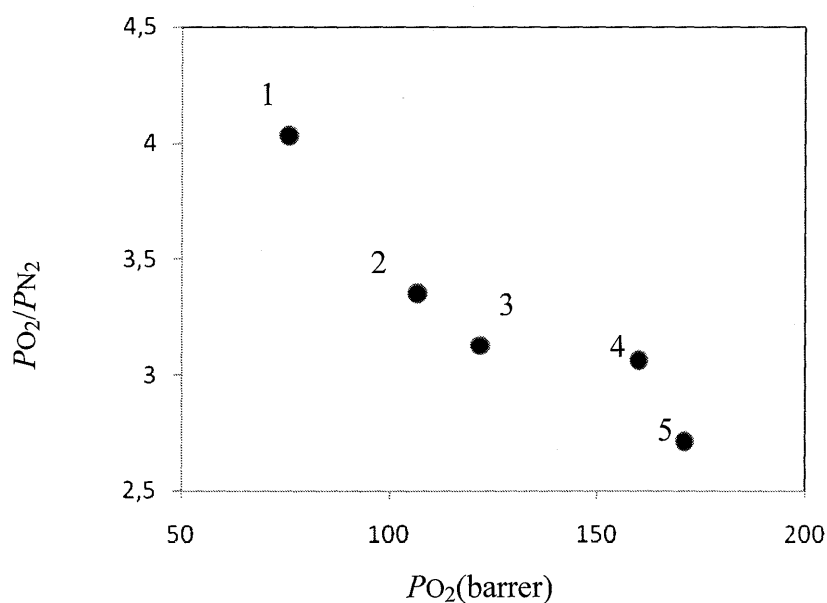


Figure 5-3. Relationship between the permeability and permselectivity of  $O_2$  through the membranes.( The numbers in the figure correspond to those in Table 5-3.)

Judging from the density, this increase in permselectivity and decrease in permeability of the copolya(4/5) membranes was owing to

the dimethylsilyl group in poly(**4**) smaller than the trimethylsilyl group in poly(**5**) which makes the membrane of the copolymer more compact than that of poly(**5**).

**Table 5-4.** Carbon dioxide permeation of copoly (**4/5**) membranes prepared using PEA as cocatalyst<sup>a)</sup>.

No.	HSPA unit in copolymer (mol %) <sup>b)</sup>	$P_{CO_2}$ , barrer <sup>c)</sup>	$P_{CO_2}/P_{N_2}$	Density (g/cm <sup>3</sup> )
1	50	554	16.1	0.871
2	19	1180	12.3	0.835
3	10	1380	13.2	0.826
4	0(poly( <b>5</b> ))	1640	11.1	0.810

a) The membranes of polymer was fabricated using solvent-casting method from CHCl<sub>3</sub> solution. b) From <sup>1</sup>H-NMR spectra.

c) In 10<sup>-10</sup>cm<sup>3</sup>(STP)cm·cm<sup>-2</sup>·s<sup>-1</sup>·cmHg<sup>-1</sup>.

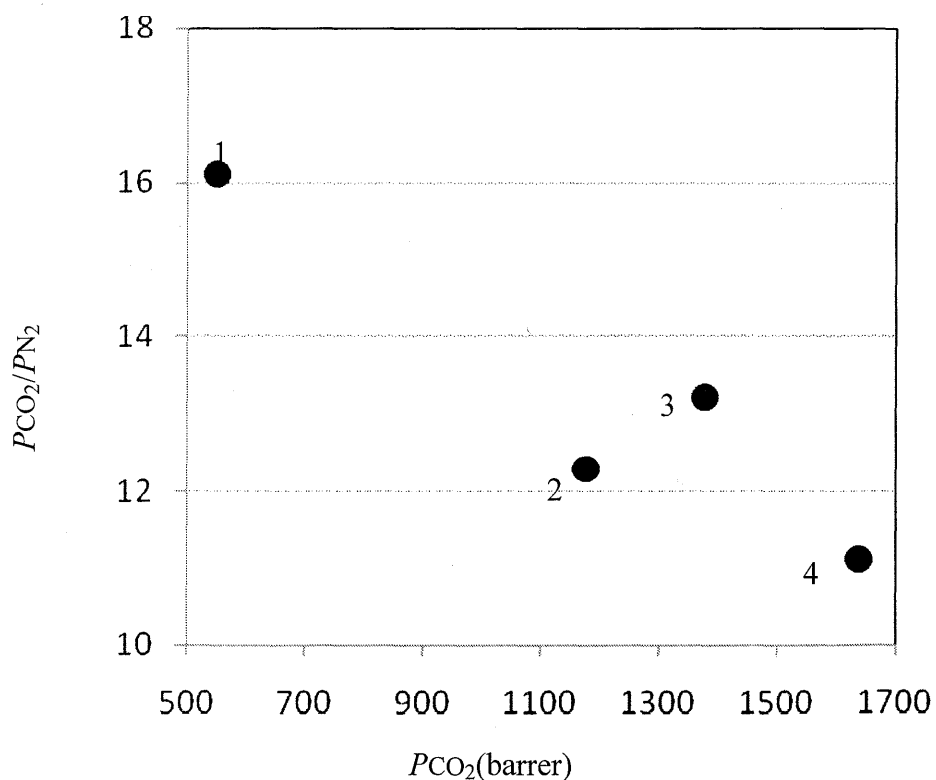


Figure 5-4. Relationship between the permeability and permselectivity of CO<sub>2</sub> through the membranes.( The numbers in the figure correspond to



those in Table 5-4.)

Results of the CO<sub>2</sub> permeation through the poly(4) and copoly(4/5) membranes are shown in Table 5-4. Fig. 5-4 shows the relationship between the permeability and permselectivity of the membranes to CO<sub>2</sub>, similar to the oxygen permeation, with the increasing of the 4 unit in copolymer, the permselectivity of the polymeric membranes increased while the permeability decreased. This result also was caused by the smaller dimethylsilyl groups in poly(4) made a smaller spaces in the membrane compared with poly(5).

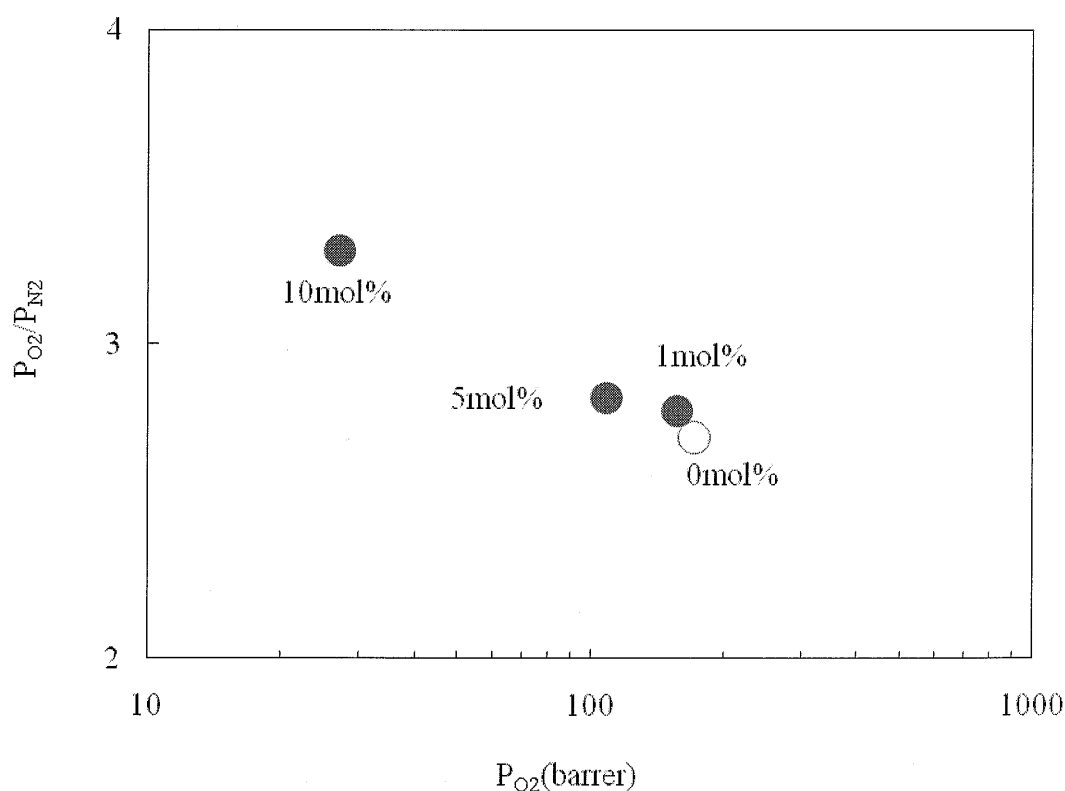


Figure 5-5. The relationship between permeability and permselectivity for O<sub>2</sub> through the poly(*p*(4) (10, 5, 1, 0 mol%)/poly(*a*(5)) membranes.

The blend membranes of poly(*p*(4) with poly(*a*(5) (Figure 5-5) showed good permselectivities.

## 5.4 Conclusions

1. A new complex polymer, polyaps(4) which has good performance for gas separation membranes was synthesized for the first time.
2. The complex and valuable polymer could be synthesized very easily and regulatedly by the one-pot simultaneous polymerization method we developed in this study.
3. The ratio of the two kinds of the polymerization, *i.e.*, polyaddition and addition polymerization ( $= p / q$ ) in the simultaneous polymerization could be controlled by changing kinds of amines
4. Branched structures enhanced permselectivities in  $P_{O_2} / P_{N_2}$  through poly $\alpha$ (5)-based blend membranes containing 1, 5, and 10 mol% of polyp(4)

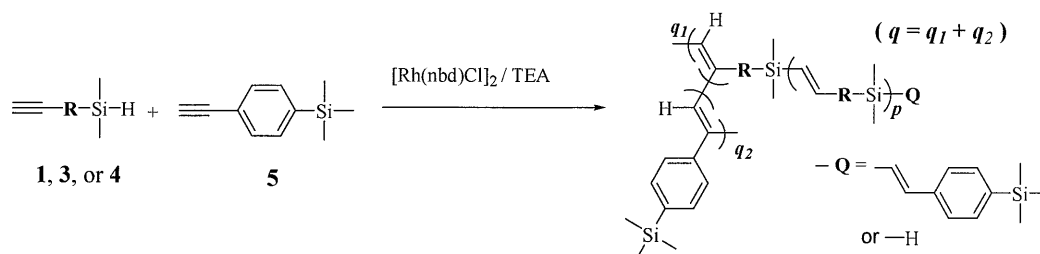
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**Chapter 6: Enhanced gas permselectivity of copoly(hyperbranched  
macromonomer) synthesized by one-pot simultaneous  
copolymerization of dimethylsilyl-containing phenylacetylenes**

## Abstract

Copoly(hyperbranched macromonomer)s, *i.e.*, polyphenylacetylenes having many branches were synthesized by one-pot simultaneous



**Scheme** One-pot synthesis of copoly(*aps*(hyperbranched macromonomer / **5**))s by simultaneous copolymerization of monomers **1**, **3**, or **4** with **5**. TEA = triethylamine.

copolymerization of two kinds of dimethylsilylphenylacetylenes. Membranes from the copoly(hyperbranched macromonomer)s having several kinds of branches showed higher permselectivities for oxygen and carbon dioxide over nitrogen than those of the corresponding copoly(hyperbranched macromonomer)s without any branches. In particular, the copoly(hyperbranched macromonomer)s having long and rigid branches had the both the advantages of polyphenylacetylenes and poly(dendron)s. In summary, copoly(hyperbranched macromonomer)s showing good performance as gas separation membranes were synthesized very easily by the one-pot simultaneous polymerization method. To our knowledge, this is the first synthesis of such complex copolymers showing good performance as gas separation membranes.

## 6.1 Introduction

Gas permselective membranes are very important and valuable because necessity to remove impurities or purify mixtures of gases whose molecular sizes are very similar is enhancing because solving the recent environmental problems has been focused on.<sup>1</sup> In general, trade off relationship between permeability and permselectivity is usually observed. To overcome this, more control of chemical structures of the side groups in the polymer used for permselective membranes are needed.

Highly branched polymers like dendrimers have received much attention because of their possibility to application of permselective membranes.<sup>2</sup> However, dendrimers as membrane materials generally have two problems. One is synthesis of the polymers needs many steps and results in very low yields because they were prepared not by polymerization but by multi-step organic reactions. The other problem is their low ability for fabrication because of no entanglement of the polymer chains.

To overcome the first problem, hyperbranched polymers have been reported.<sup>3</sup> They were prepared more easily by one polymerization of AB<sub>2</sub> type monomers in higher yields. To solve the second problem, we reported a new type of branched homopolymers, that is, homopoly(dendron macromonomer)(for example, a homopolymer of **6** in

In our previous study to overcome the two problems, we designed a new type of homopolymer, *i.e.*, homopoly(hyperbranched

macromonomer) of monomer **1** (Chart 6-1).<sup>5</sup> In addition, we proposed its new synthetic method, *i.e.*, one-pot synthesis by simultaneous polymerization of two types of polymerization of one monomer. In other words, we reported a new complicated polymer and its very simple preparation method.

## 6.2 Experimental part

### 6.2.1 Materials.

All the solvents used for synthesis and polymerizations of the monomers were distilled as usual. The polymerization initiator,  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  (nbd = 2,5-norbornadiene) and amines purchased from Aldrich Chemical were used as received.

### 6.2.2 Measurements.

$^1\text{H}$  NMR (400 MHz) spectra were recorded on a VARIAN-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). The infrared spectra were recorded on FT/IR-4200 (JASCO). Oxygen and nitrogen and carbon dioxide/nitrogen permeability coefficients ( $P_{\text{O}_2}$ ,  $P_{\text{CO}_2}$  and  $P_{\text{N}_2}$  :  $\text{cm}^3(\text{STP})\text{cm}\cdot\text{cm}^{-2}\text{s}^{-1}\text{cmHg}^{-1}$ ) 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°C using YANACO GTR-10 according to Ref. [3e]. The area of membrane is 1.77 cm<sup>2</sup>, and the initial feed gas pressure 1 atm.

### 6.2.3 Synthesis of copoly(1/5), copoly(3/5), copoly(4/5)

#### 6.2.3.1 Simultaneous addition polymerization and polyaddition of **1** and **5** (Synthesis of copoly(1/5))<sup>3</sup>

A typical polymerization procedure was as follows: To a solution of **1** and **5** (198 mg, 1.0 mmol) and TEA (202 mg, 2.0 mol) in dry toluene (5.0 mL) at 25 °C under nitrogen, a solution of [RhCl(nbd)]<sub>2</sub> in dry toluene (2.0 mL) was added. The mixture was kept at room for 4 h to give a solution of copoly(1/5). 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 copoly(1/5) (Scheme1) (Chart S1).  $M_n = 16\text{-}19 \times 10^4$  (Table 1, nos. 1-3). The other polymerizations were also conducted similarly.

Yield: 86-95%.

#### 6.2.3.2 Addition polymerization of **1** and **5** (Synthesis of copoly(1/5))

To a solution of **1** and **5** (198 mg, 1.0 mmol) in dry toluene (5.0 mL) at 25 °C under nitrogen, a solution of [RhCl(nbd)]<sub>2</sub>/PEA (242 mg, 2.0 mol) in dry toluene (2.0 mL) was added. The mixture was kept at room for 4h to give a solution of copoly(1/5). 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 copoly(**1/5**) Yield: 92%.  $M_n = 12 \times 10^4$  (Table 1, no. 4)

#### **6.2.3.3. Simutaneous addition polymerization and polyaddition of 3 and 5 (Synthesis of copoly(**3/5**))<sup>3</sup> (Scheme2)**

A typical polymerization procedure was as follows: To a solution of **3** and **5**(178 mg, 1.0 mmol) and TEA(202 mg, 2.0 mol) in dry toluene (5.0 mL) at 25 °C under nitrogen, a solution of  $[\text{RhCl}(\text{nbd})]_2$  in dry toluene (2.0 mL) was added. The mixture was kept at room for 4 h to give a solution of copoly(**3/5**). 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 copoly(**3/5**) (Chart S2). Yield: 86-90%.  $M_n = 15\text{-}19 \times 10^4$  (Table 1, nos. 5-7). The other polymerizations were also conducted similarly.

#### **6.2.3.4 Addition polymerization of 3 and 5(Synthesis of copoly(**3/5**))**

To a solution of **1** and **5**(178 mg, 1. 0 mmol) in dry toluene (5.0 mL) at 25 °C under nitrogen, a solution of  $[\text{RhCl}(\text{nbd})]_2$  / **PEA** (242 mg, 2.0 mol) in dry toluene (2.0 mL) was added. The mixture was kept at room for 4h to give a solution of copoly(**3/5**).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 copoly(**3/5**) Yield: 83%.  $M_n = 6.5 \times 10^4$  (Table 1, no.8)

#### **6.2.3.5 Simutaneous addition polymerization and polyaddition of 3**

### **and 5(Synthesis of copoly(4/5))<sup>3</sup> (Scheme 3)**

A typical polymerization procedure was as follows: To a solution of **4** and **5**(172 mg, 1.0 mmol) and TEA(202 mg, 2.0 mol) in dry toluene (5.0 mL) at 25 °C under nitrogen, a solution of [RhCl(nbd)]<sub>2</sub> in dry toluene (2.0 mL) was added. The mixture was kept at room for 4 h to give a solution of copoly(**4/5**). 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 copoly(**4/5**) (Chart 6-3). Yield: 76-86%.  $M_n = 3.2-8.7 \times 10^4$  (Table 1, nos. 9-11). The other polymerizations were also conducted similarly.

#### **6.2.3.6 Addition polymerization of 4 and 5.(Synthesis of copoly(4/5))**

To a solution of **4** and **5**(172 mg, 1. 0 mmol) in dry toluene (5.0 mL) at 25 °C under nitrogen, a solution of [RhCl(nbd)]<sub>2</sub>/**PEA** (242 mg, 2.0 mol) in dry toluene (2.0 mL) was added. The mixture was kept at room for 4h to give a solution of copoly(**4/5**).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 copoly(**4/5**) Yield: 91%.  $M_n = 2.9 \times 10^4$  (Table 1, no. 12)

### **6.3 Results and discussion**

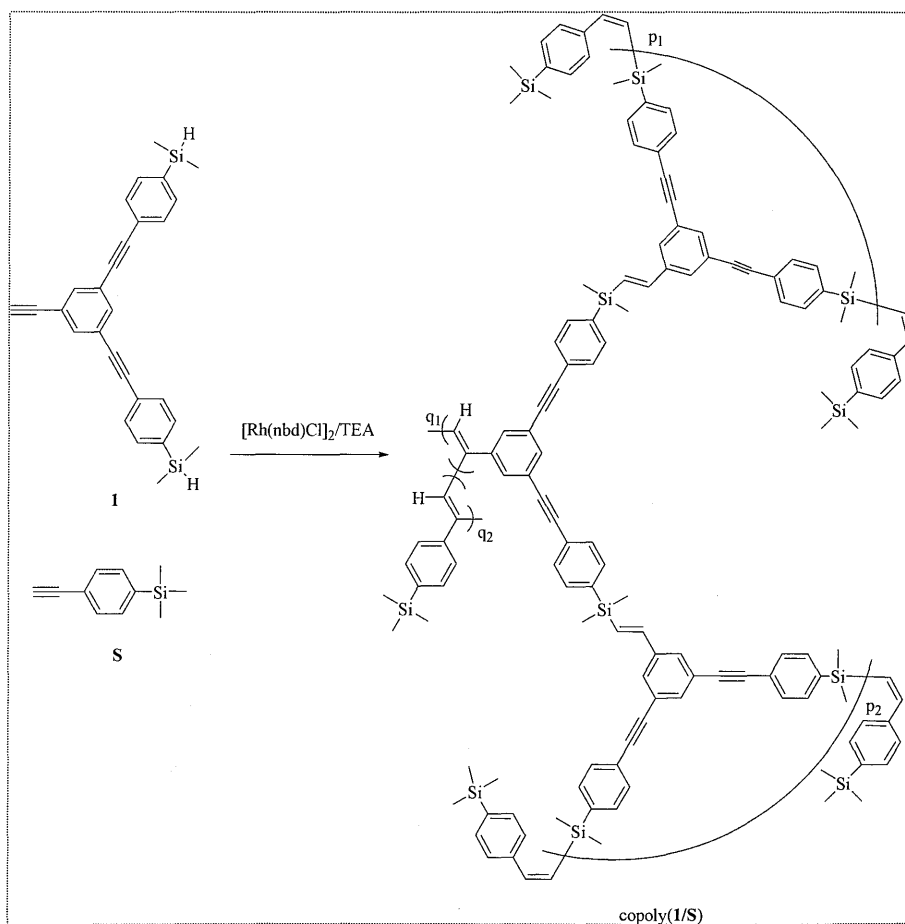
Definition of some values estimating the structure of copoly(**1/5**), copoly(**2/5**, and copoly(**3/5**). The values(  $p/q$  and **D**(%) ) shown in Table 1 were defined as follows:  $p/q$  : the ratio of the degree of polyaddition to

the degree of addition polymerization, **D**(%): the ratio of the methyl signals of dimethylsiloxanyl groups produced.

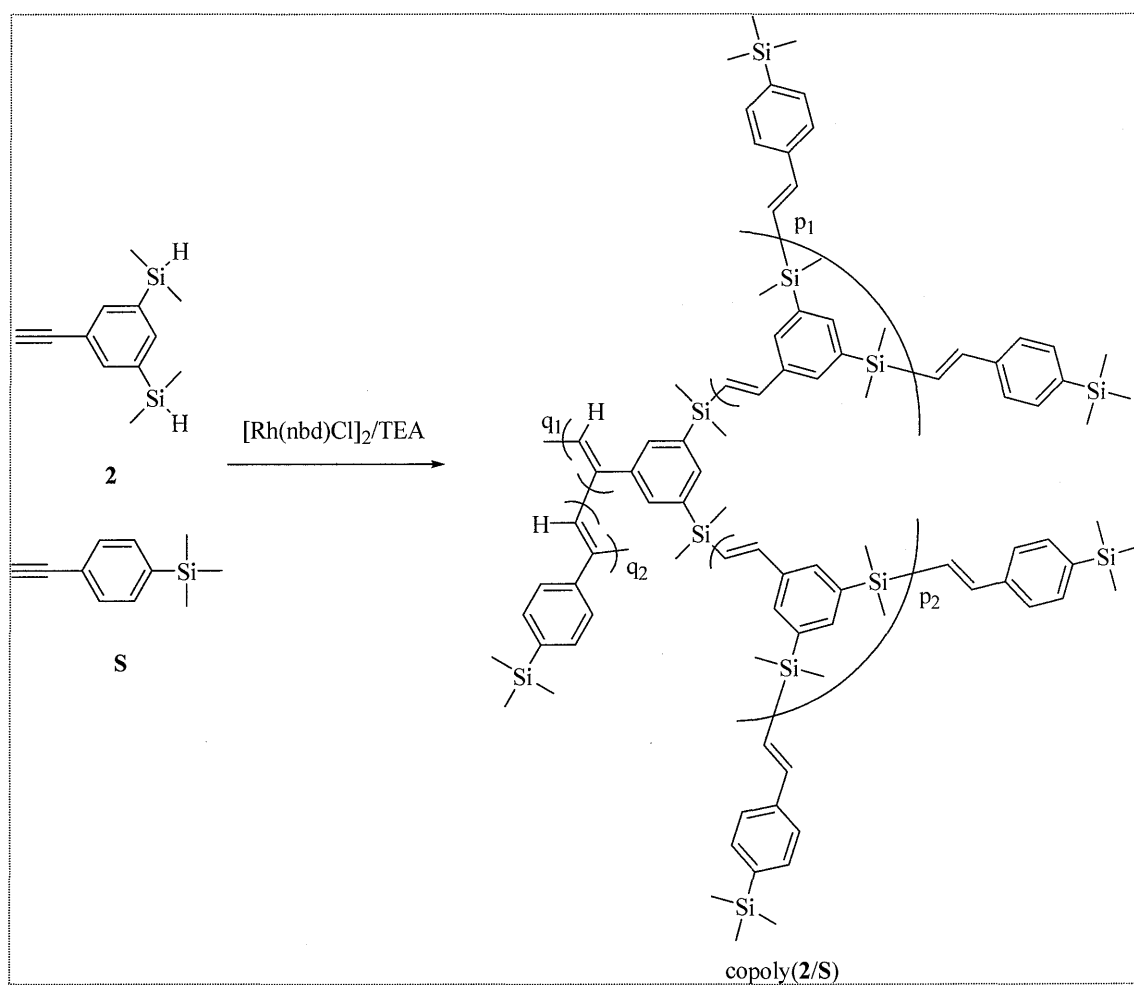
$$p/q = B_{-C=CH} / A_H; \quad (1)$$

$$D = I_{Me} / (P_{Me} + Q_{Me} + B_{Me} + I_{Me}) \times 100; \quad (2)$$

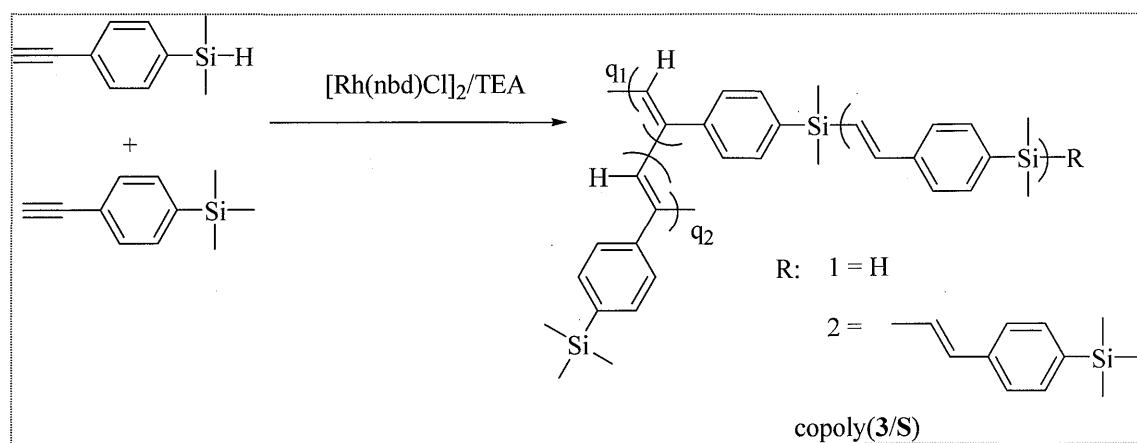
Simultaneous addition copolymerizations and polyadditions of **1**<sup>5</sup>, **3**<sup>3d</sup>, and **4**<sup>3c</sup> with **5** (Schemes 6-1, 6-2, 6-3) were carried out by a catalyst system  $[Rh(nbd)Cl]_2$ /triethylamine(TEA). Addition polymerizations without polyadditions were carried out by  $[Rh(nbd)Cl]_2$ /phenylethylamine(PEA). For the results and the condition, see Table 6-1.



**Scheme 6-1**



**Scheme 6-2**

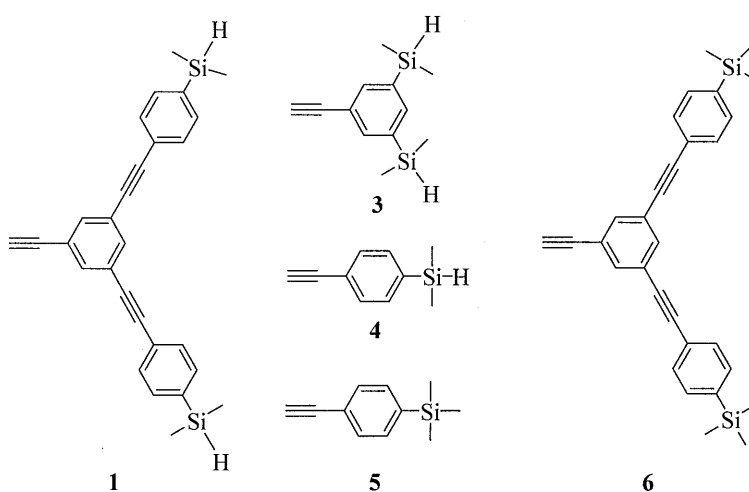


**Scheme 6-3**

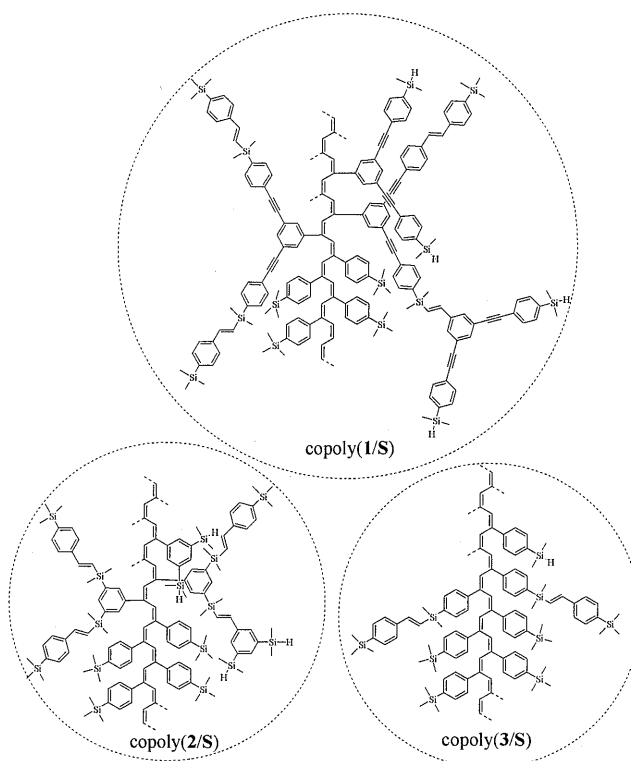
### 6.3.1 Simultaneous addition polymerization and polyaddition of 1, 3 or 4 with 5(Synthesis of copoly(1/5, copoly(3/5), copoly(4/5)))<sup>3</sup>

In this paper, we report synthesis of a new copoly(hyperbranched macromonomer / comonomer(**5**)) by simultaneous copolymerization of monomer **1**, **3**, **4** with **5** (Chart 6-1)

**Chart 6-1**



**Chart 6-2**





No.	Code <sup>b</sup>	<b>5</b> unit <sup>c</sup> (mol%)	Yield (%)	$M_w$ <sup>d</sup> ( $\times 10^4$ )	$p / q$ <sup>e</sup>	D <sup>f</sup>	$P_{O_2}$ <sup>g</sup> (barrer)	$P_{CO_2}$ <sup>g</sup> (barrer)	$P_{N_2}$ <sup>g</sup> (barrer)	$P_{O_2}$ <sup>g</sup> / $P_{N_2}$	$P_{CO_2}$ <sup>g</sup> / $P_{N_2}$
1	copoly( <b>1/5</b> )	88	95	18	0.13	0.003	184	1055	54	3.40	19.5
2	copoly( <b>1/5</b> )	94	93	16	0.063		181	987	55	3.30	18.0
3	copoly( <b>1/5</b> )	99	86	19	0.012		176	950	59	3.00	16.2
4 <sup>h</sup>	copoly( <b>1/5</b> )	87	92	12	0		172	930	60	2.85	15.5
5	copoly( <b>3/5</b> )	90	90	15	0.10	0.001	0.40	1.8	0.1	4.60	21.0
6	copoly( <b>3/5</b> )	94	88	18	0.060		0.36	1.8	0.1	4.10	20.8
7	copoly( <b>3/5</b> )	99	86	19	0.011		0.50	1.7	0.1	3.80	12.9
8 <sup>h</sup>	copoly( <b>3/5</b> )	86	83	6.5	0		6.1	23	2	3.05	11.5
9	copoly( <b>4/5</b> )	89	76	3.2	0.11	0	113	450	30	3.76	15.0
10	copoly( <b>4/5</b> )	95	85	6.5	0.050		122	542	37	3.30	14.8
11	copoly( <b>4/5</b> )	99	86	8.7	0.010		131	624	42	3.10	14.7
12 <sup>h</sup>	copoly( <b>4/5</b> )	84	91	2.9	0		160	686	52	3.06	13.2
13	poly( <b>5</b> ) <sup>i</sup>	100	94	21	0		171	895	63	2.71	12.1
14	poly( <b>6</b> ) <sup>j</sup>	0	83	250	0		70	370	20	3.50	18.5

<sup>a</sup> At room temperature for 4 h in toluene. [monomer] = 0.2 mol/L, [monomer]/[triethylamine (TEA)]/[Rh(nbd)Cl]<sub>2</sub> = 250 / 500 / 1; <sup>b</sup> For the codes, see Chart 1; <sup>c</sup> Composition determined by <sup>1</sup>H NMR; <sup>d</sup> Determined by GPC correlating polystyrene standard with THF eluent; <sup>e</sup> For  $p$  and  $q$ , see Scheme 1; <sup>e,f</sup> For the calculation, see Figure S1 and Chart S1.; <sup>g</sup> Barrer: In  $10^{-10} \text{ cm}^3(\text{STP})\text{cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ ; <sup>h</sup> At room temperature for 4 h in toluene. [monomer] = 0.2 mol/L, [monomer]/[phenylethylamine (PEA)]/[Rh(nbd)Cl]<sub>2</sub> = 250 / 500 / 1; <sup>i</sup> *ref.* 4a); <sup>j</sup> *ref.* 6).



synthesized in high yields (nos.1-3, 5-7, and 9-11). As a reference, copoly(1/5), copoly(3/5), and copoly(4/5) having  $p = 0$ , *i.e.*, copolymers prepared only by addition polymerization were synthesized by using  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  / phenylethylamine(PEA). (nos. 4, 8, and 12). The structures of copoly(hyperbranched macromonomer) were confirmed by NMR and GPC. In addition, as comparison, poly(*p*-trimethylsilylphenylacetylene)(poly(5)) having no branches and poly(first-generation dendron macromonomer) (poly(6)) having regular branches were also synthesized (nos. 13 and 14). All the copolymers had self-membrane forming ability and therefore their membranes were fabricated by solvent cast method of their toluene solution. Their gas permeabilities were measured by gas chromatographic method.

### **6.3.2 Copolymerization and gas separation properties of membranes containing poly(4)**

Table 6-1 and Figure 6-1 show gas permeabilities through the copolymers. All the copolymers having both sequences synthesized by addition polymerization and polyaddition (nos.1-3, 5-7, and 9-11) had higher permselectivities than the corresponding polymers( $p = 0$ ) having only a sequence synthesized by addition polymerization (nos.4, 8, and 12, respectively). It shows the good effect of the branches produced by polyaddition on the permselectivities. Permselectivities of  $P_{\text{CO}_2} / P_{\text{N}_2}$

through copoly(1/5) and copoly(3/5) were higher than those of copoly(3/5). It also supported the good effect of the branches.

When we compared copoly(hyperbranched macromonomer/5)s partly containing more than second-generation branches with poly(dendron macromonomer)(poly(6)) having only first-generation branches, some of the copoly(hyperbranched macromonomer/5) showed higher permselectivities. For example,  $PO_2 / PN_2$  values of poly(3/5)[ $p / q = 0.10$ ] (no.5), and poly(4/5)[ $p / q = 0.11$ ] (no.9) were higher than that of poly(6) (no.14). In particular, poly(1/5)[ $p / q = 0.13$ ] (no.1) showed not only higher  $PCO_2 / PN_2$  but also higher  $PCO_2$  than poly(6) (no.14) and poly(1/5)[ $p / q = p = 0$ ] (no.4). This copolymer showed the best performance in this study. The enhancement of  $PCO_2 / PN_2$  by introducing the higher- generation branches may be caused by enhancing diffusion selectivities. The reason of the simultaneous enhancement of  $PCO_2$  is not clear at present but it may be caused by enhancing solubility selectivities by the introduction of silane(Si-H). It was supported by a fact that all the other copolymers in this study showed higher permselectivities compared with poly(5) having no Si-H (no.13) as shown in Figure 6-1, 6-2, 6-5, 6-6. 6-7(A) and (B). In addition, small amount of SiH groups were converted to SiOH(the contents, D values were calculated (Table 6-1)) in the air judging from NMR. The Si-H(Si-OH) was also effective for enhancing  $PCO_2$  in addition to the branches.

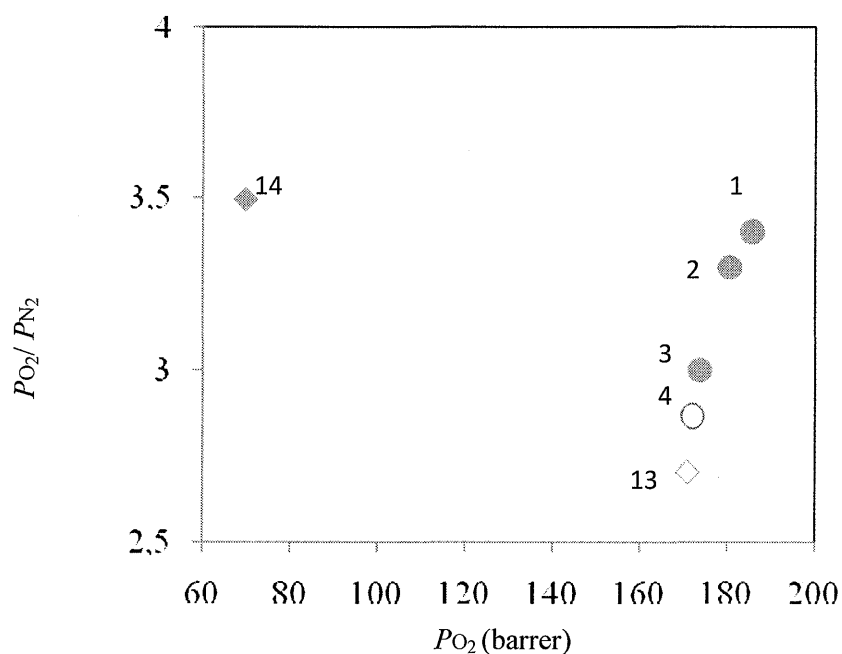


Figure 6-1. The relationship between permeability and permselectivity for  $O_2$  through the •:copolyaps(1/5);○:copolya(1/5) (The numbers in the figure correspond to those in Table 6-1)

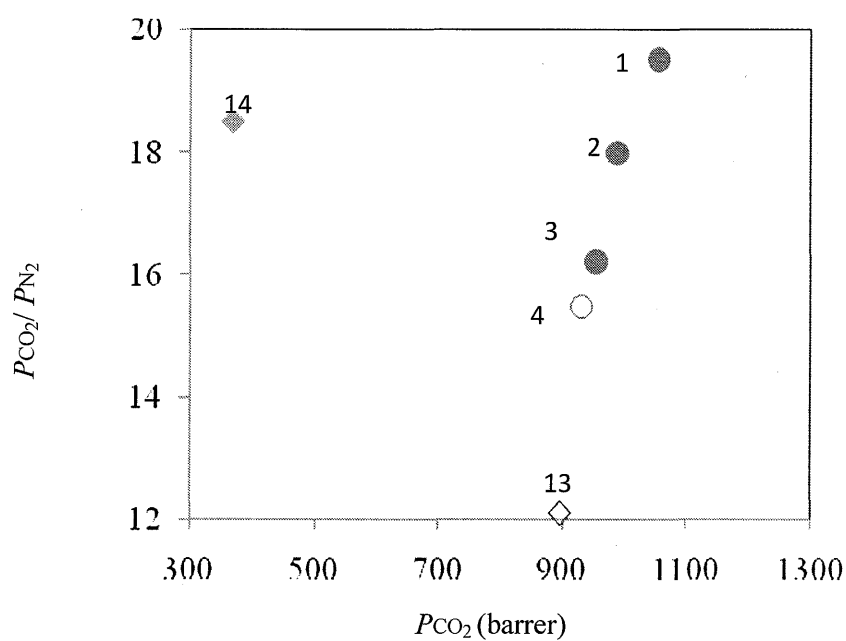


Figure 6-2. The relationship between permeability and permselectivity for  $CO_2$  through the •:copolyaps(1/5);○:copolya(1/5) (The numbers in the figure correspond to those in Table 6-1)

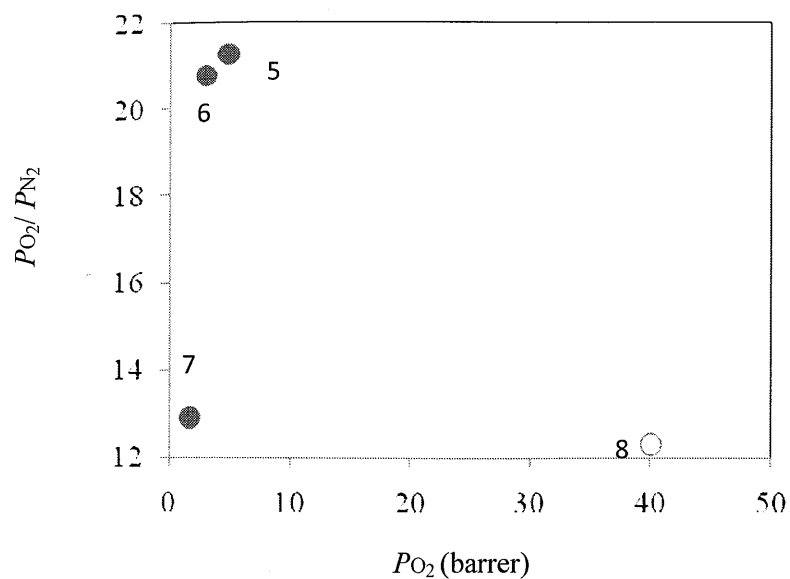


Figure 6-3. The relationship between permeability and permselectivity for  $O_2$  through the  $\bullet$ :copolyaps(3/5);  $\circ$ : copolya(3/5) (The numbers in the figure correspond to those in Table 6-1)

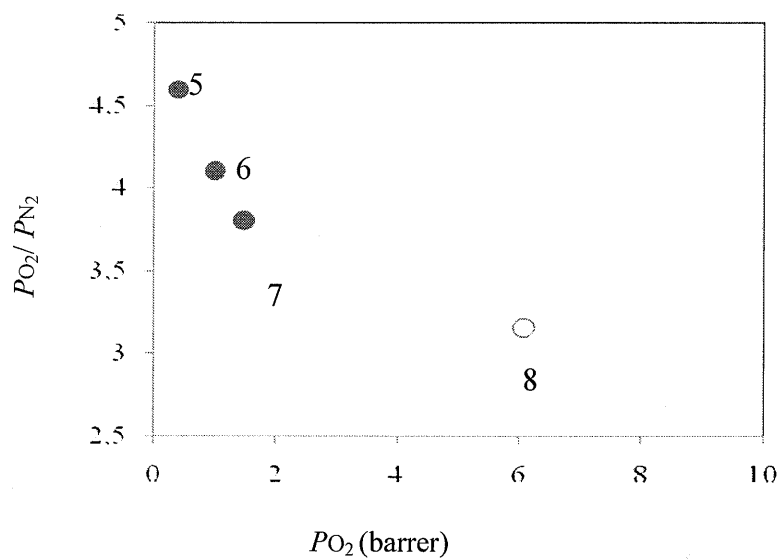


Figure 6-4. The relationship between permeability and permselectivity for  $O_2$  through the  $\bullet$ :copolyaps(3/5);  $\circ$ : copolya(3/5). (The numbers in the figure correspond to those in Table 6-1)

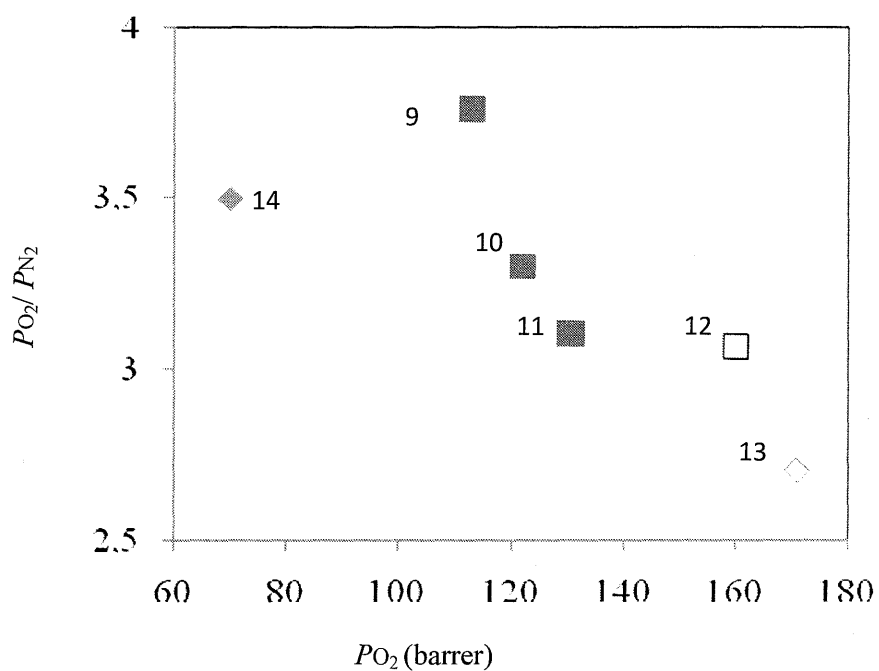


Figure 6-5. The relationship between permeability and permselectivity for  $O_2$  through the  $\bullet$ :copolyaps(4/5);  $\circ$ :copolya(4/5). (The numbers in the figure correspond to those in Table 6-1)

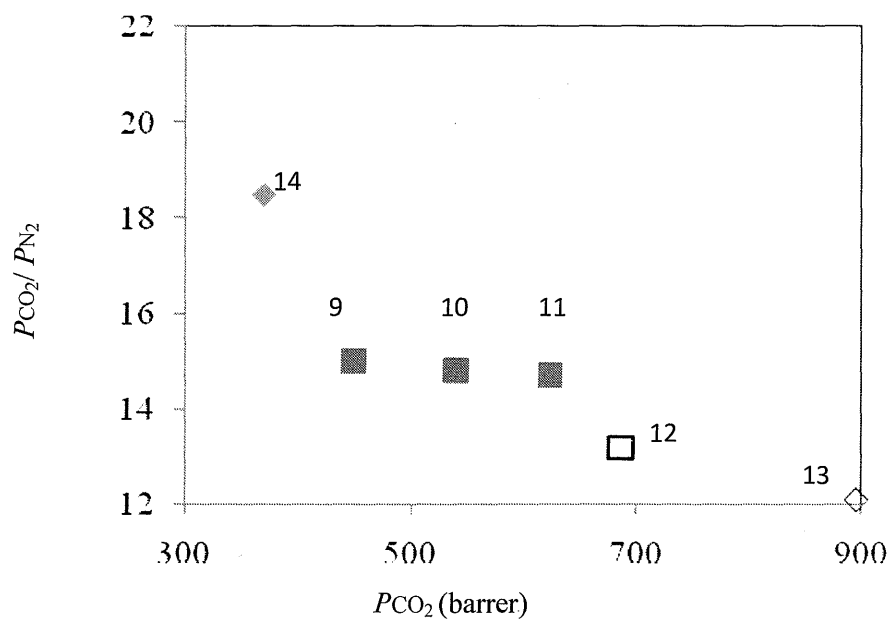
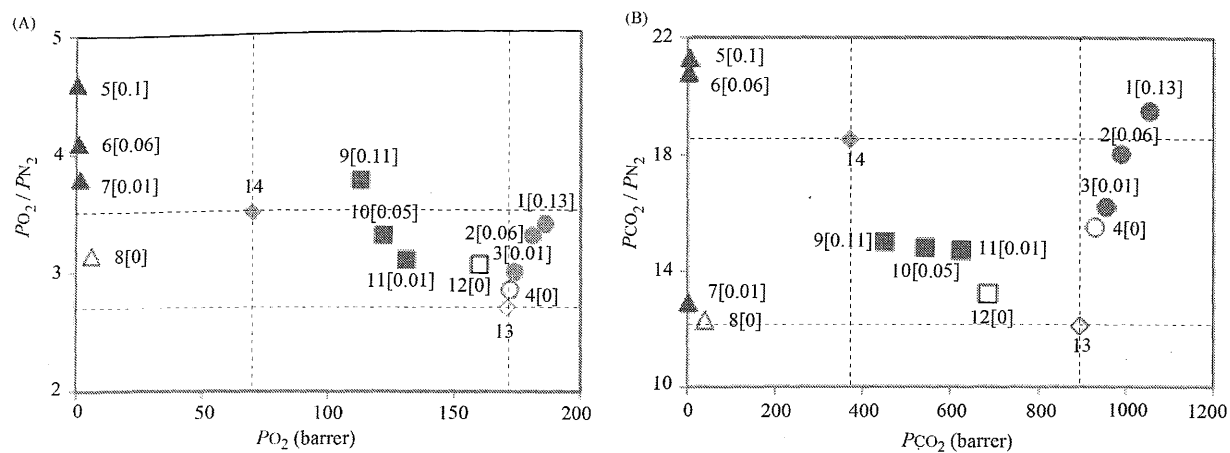


Figure 6-6. The relationship between permeability and permselectivity for  $O_2$  through the  $\bullet$ :copolyaps(4/5);  $\circ$ :copolya(4/5). (The numbers in the figure correspond to those in Table 6-1)



**Figure 6-7.** Plots of permselectivity versus permeability of (A):  $O_2$ , and (B)  $CO_2$  through the  $\bullet$ ,  $\circ$ : copoly(1/5);  $\blacktriangle$ ,  $\triangle$ : copoly(3/5);  $\blacksquare$ ,  $\square$ : copoly(4/5) membranes. The numbers in the figure correspond to those in Table 6-1. The values in the brackets are  $p/q$ .

## 6.4 Conclusions

In conclusion, new good complex copolymers as gas separation membrane materials, copoly(hyperbranched macromonomer) were synthesized for the first time very easily by the one-pot simultaneous polymerization method we developed before. It was found that introduction of the branched structures enhanced their permselectivities in  $P_{O_2} / P_{N_2}$  and  $P_{CO_2} / P_{N_2}$ . In addition, Si-H(Si-OH) was also effective for enhancing  $P_{CO_2}$ .

## References and Notes

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## Chapter 7: Conclusions

1. A series of new complex polymers, poly $aps$ (hyperbranched macromonomer)s which have good performance for gas separation membranes were synthesized for the first time.
2. The complex and valuable polymers could be synthesized very easily and regulatedly by the one-pot simultaneous polymerization method we developed in this study. The ratio of the two kinds of the polymerization *i.e.*, polyaddition and addition polymerization ( $= p / q$ ) could be controlled by changing kinds of amines
3. Oxygen permselectivities through copoly $aps$ (**1/5**) membranes were improved with increase in the contents of **1** unit.
4. Oxygen permselectivities through a homopolymer membrane of poly $aps$ (**1**) by direct preparation during polymerization showed very good performance. The permselectivities were close and almost on the upper boundary line reported by Robeson.
5. Oxygen permselectivities through poly $a$ (**5**)-based blend membranes containing 10-12.5 mol% of poly $p$ (**1**) were close the upper boundary line reported by Robeson.

6. New good complex copolymers as gas separation membrane materials, copolyaps(hyperbranched macromonomer) were synthesized for the first time very easily by the one-pot simultaneous polymerization method.

7. Branched structures enhanced copolyaps(1/5), copolyaps(3/5), and copolyaps(4/5) permselectivities in  $P_{O_2} / P_{N_2}$  and  $P_{CO_2} / P_{N_2}$ .

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