Synthesis and Direct Observation of Molecules of 2D Polymers: With High Molecular Weights, Large Areas, Small Micropores, Solubility, Membrane Forming Ability, and High Oxygen Permselectivity

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If ideal 2D polymer (2DP) macromolecules with small pores that are similar in size to gas molecules, large areas, small thickness, and excellent membrane-forming ability are synthesized, ultimate gas separation membranes would be obtained. However, as far it is known, such ideal well-characterized 2DP macromolecules are not isolated. In this study, an ideal 2DP macromolecule is synthesized by using the successive three reactions (Glaser coupling, SCAT reaction, and the introduction of octyl groups), in which the conjugated framework structure is maintained, from a fully conjugated 1D polymer. Because this exfoliated 2DP is *soluble*, the macromolecular structure can be fully characterized by ^{1}H-NMR, GPC, SEM, AFM, and its dense membrane with no defects can be fabricated by the solvent cast method. This *soluble* 2DP macromolecule has very small micropores (6.0 Å) inside the macromolecule, a large area (30 × 68 nm by SEM and AFM), high molecular weight ($Mn = 2.80 \times 10^5$ by GPC), and a small thickness (4.4 Å by AFM). This membrane shows the highest oxygen permselectivity exceeding Robeson's upper line because of the high molecular sieving effect of the controlled small micropores.

1. Introduction

In the case of membranes from 1D polymers (1DPs), their pores are formed between macromolecules. Therefore, the pores are relatively large, dynamic, and unstable. Since 3D polymers (3DPs) having network structures are insoluble, it is difficult to prepare tough thin membranes. On the other hand, in the case of membranes from 2D polymers (2DPs) having network

structures, the pores can be created inside macromolecules and therefore static and stable. In addition, the molecular shape of 2DP itself is one of the thinnest membranes. Therefore, if a membrane consisting of a monolayer of 2DP macromolecules is realized, it will be the best permselective membrane having the highest permeability and the perfect selectivity.

The ideal molecular structures and properties of 2DPs as gas permselective membranes are as follows.[1–7]

1) The pore sizes are similar to the sizes of gas molecules to be separated, that is, less than about 6 Å. 2) The thicknesses are the thinnest, about one atom depth (about 5 Å). 3) The areas with no defects are wider at least around 20 nm (the pore size of usual porous support membranes). 4) The ability to form dense bulk membranes with no defects from the pure polymer.

To realize the above requirements 1) to 3), 2DPs whose structures as organic macromolecules should be well-characterized in the solution state by ^{1}H-NMR, GPC, and so on. In other words, the macromolecules should be *soluble*. Requirement 4) can be also achieved by the *soluble* nature.

Although some 2DPs[1–7] were reported, most of them (e.g., covalent organic frameworks (COFs)[8–12]) had the following problems. (Although graphene and COFs were reported as 2DPs, graphene has no pores, and COFs' pores are more than 1 nm. In addition, both are strong stacked structures and insoluble. Therefore, some complex and sophisticated techniques were needed to use them as permeation membranes. As a result, it was difficult to discuss the effect of the molecular structures on their permselectivity.)

1) Their pore sizes were much larger than the sizes of gas molecules such as 3.46 Å (oxygen) and 3.64 Å (nitrogen). 2) Their thicknesses were high because they did not consist of a single layer of the molecule. 3) The areas without defects at the molecular level were unknown because they were not well-characterized because of their insolubility and crystallinity. 4) They had no membrane-forming ability by themselves because they were insoluble and crystalline due to their strong stacked structures.

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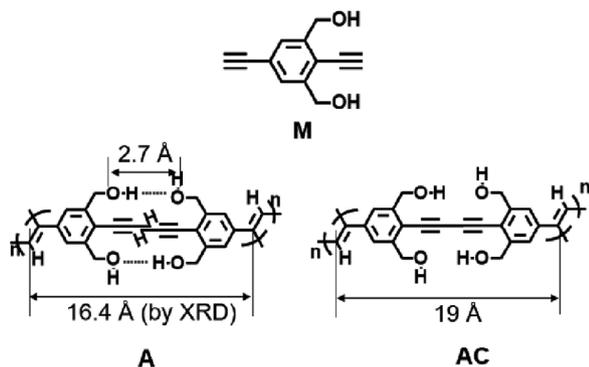1-1 Asahi-dai, Nomi 923–1292, Japan
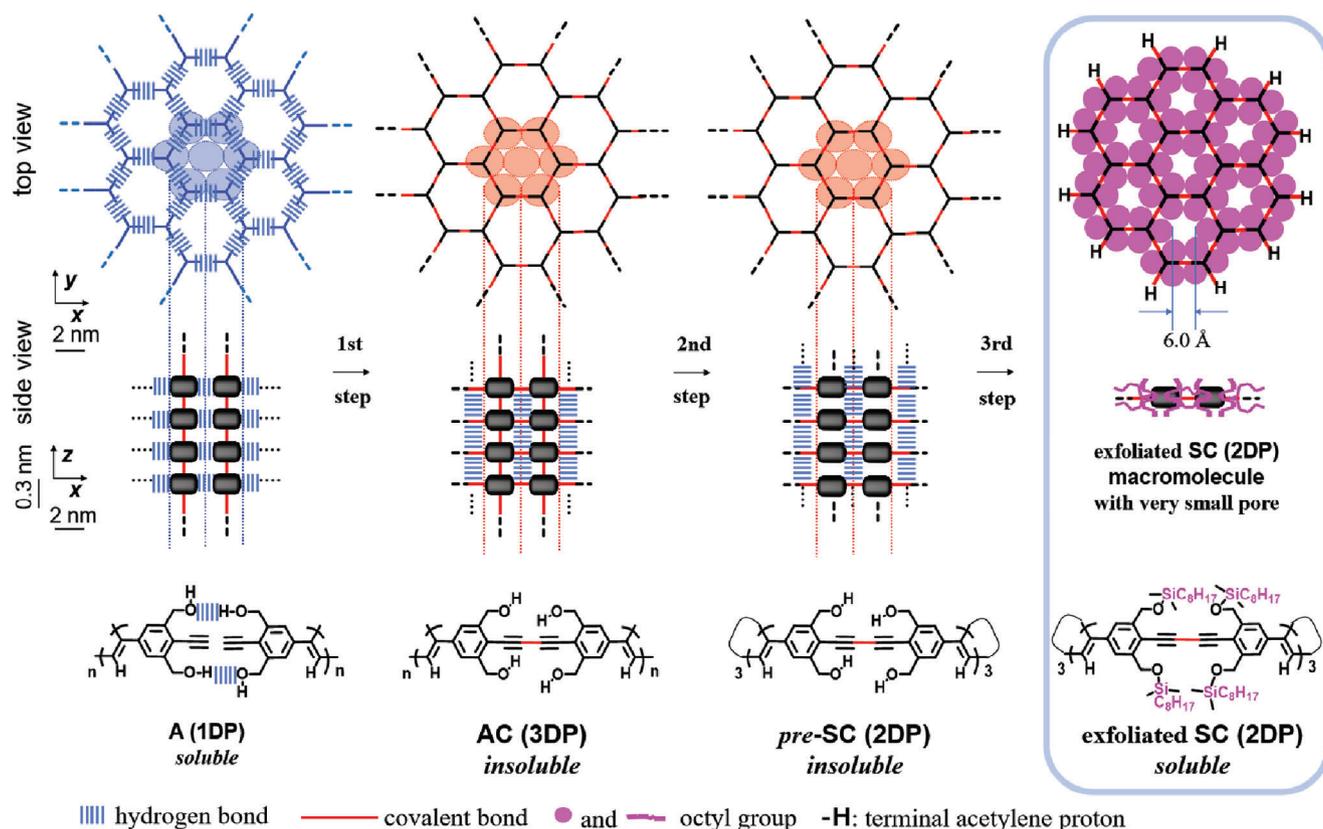
Scheme 1. Schematic drawing of the three-step synthesis to 2D polymer (2DP) in the membrane state. A (addition polymer): *soluble* 1D polymer (1DP) with a hexagonal columnar structure, AC (addition and condensation polymer): *insoluble* 3D polymer (3DP) with a network structure. *pre*-SC: *insoluble* high molecular weight stacked 2DP with small micropores inside the macromolecule, SC(condensation polymer after SCAT): *soluble* high molecular weight exfoliated (isolated) 2DP with very small micropores inside the macromolecule. 1st step: Glaser coupling, 2nd step: SCAT reaction, 3rd step: substitution of hydroxyl groups with octylsilyl groups.

To solve these above problems, we developed a new synthetic procedure for 2DP(SC) including three steps from the starting 1D polymer (A, 1DP) via 3D polymer (AC, 3DP) as shown in **Scheme 1** (see Schemes S1-1-3, Supporting information). The advantages of this multi-step reaction method from 1DP to 2DP via 3DP were as follows: 1) thin membranes can be easily prepared from 1DP as a starting membrane and 2) the thin membranes of the resulting network polymers (2DP) can be directly synthesized in the membrane state. Because preparing thin membranes from highly networked polymers is usually difficult due to their low solubility, this method is useful. Since the starting 1DP had an ordered hexagonal columnar structure in the membrane state (Figure S1, Supporting Information), the x-y plane works as a template for the honeycomb types of 2DP (Scheme 1 left; Scheme S1-1, Supporting Information). To remove the original polymer main chain from the template 1DP in the z-direction in the network 3DP, the highly selective photocyclic aromatization (SCAT reaction, Scheme S2, Supporting Information),[13–17] which we developed before, was used (Scheme 1 middle; Scheme S1-2, Supporting Information). (The SCAT (highly selective photo cyclic aromatization) reaction is a quantitative reaction from cis-cis poly(substituted acetylene)s to the corresponding cyclic trimer, which is, 1,3,5-trisubstituted benzene derivatives only by visible-light irradiation on the start-

ing polymer membranes without any solvents and catalysts the authors developed.[17] The reaction can be easily traced by ^{1}H-NMR and GPC. In ^{1}H-NMR,[14] the original peak assigned for the main chain proton completely disappears and instead, a new benzene nucleus peak appears. In GPC,[15] the original high MW broad peak completely disappears and a low MW sharp peak appears. When this reaction is applied to some derivatives of cis-cis poly(substituted acetylene)s, GPC and ^{1}H-NMR are always effective tools to confirm the reaction progress if the product is soluble.) At the final step, one layer of the 2DP macromolecule (SC) was exfoliated by the substitution of the hydroxyl groups with long alkyl groups (Scheme 1 right; Scheme S1-3, Supporting Information). In addition, the alkyl groups reduced the pore sizes.

Because the starting polymer (1DP) in this study is a fully-conjugated structure and all three reactions maintained them, the resulting 2DP has a fully-conjugated framework. In addition, since the pendant groups in the starting polymer (1DP) of monomer M (**Figure 1**) have no flexible spacers, the resulting 2DP can form controlled rigid small pores inside the macromolecules. Furthermore, since the pendant groups in A (1DP) have two hydroxyl groups and can interact with each other by hydrogen bonds as shown in Figure 1, the 2D formation reaction by Glaser coupling[18,19] (Scheme 1, 1st step, and Scheme S1-1, Supporting Information) can be promoted.

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Figure 1. Monomer M and hydrogen bonds in polymers A (1DP) and AC (3DP).

In this paper, we report the synthesis and direct observation of the macromolecule of *soluble* high molecular weight well-defined fully-conjugated 2DP s with very small micropores inside the

macromolecule and the good oxygen permselectivity of its pure dense membrane exceeding the Robeson upper boundary line.

2. Results and Discussion

By the first-step reaction from A (1DP) to AC (3DP) (Figure 1) by Glaser coupling[18,19] in the membrane state, the original supramolecular 2D x–y plane was transformed to the covalent 2D x–y plane. (Scheme 1) (The hydrogen bonds must be also changed from the x-y direction to the z-direction after the reaction from A to AC as shown in Scheme 1 and Scheme S1-1 (Supporting Information). This was supported by the XRD results (Figure S1, Supporting Information). The tight helical cis-cisoidal structure of the backbone of poly(substituted acetylene)(A) was supported by the SCAT activity according to our previous result.[14]) Since the original A was *soluble* but the resulting AC was completely *insoluble*, the progress of the network formation reaction was confirmed. By the SCAT reaction (Scheme S2, Supporting Information)[13] from AC to *pre*-SC (stacked 2DP) in the membrane state at the second step, the backbone derived
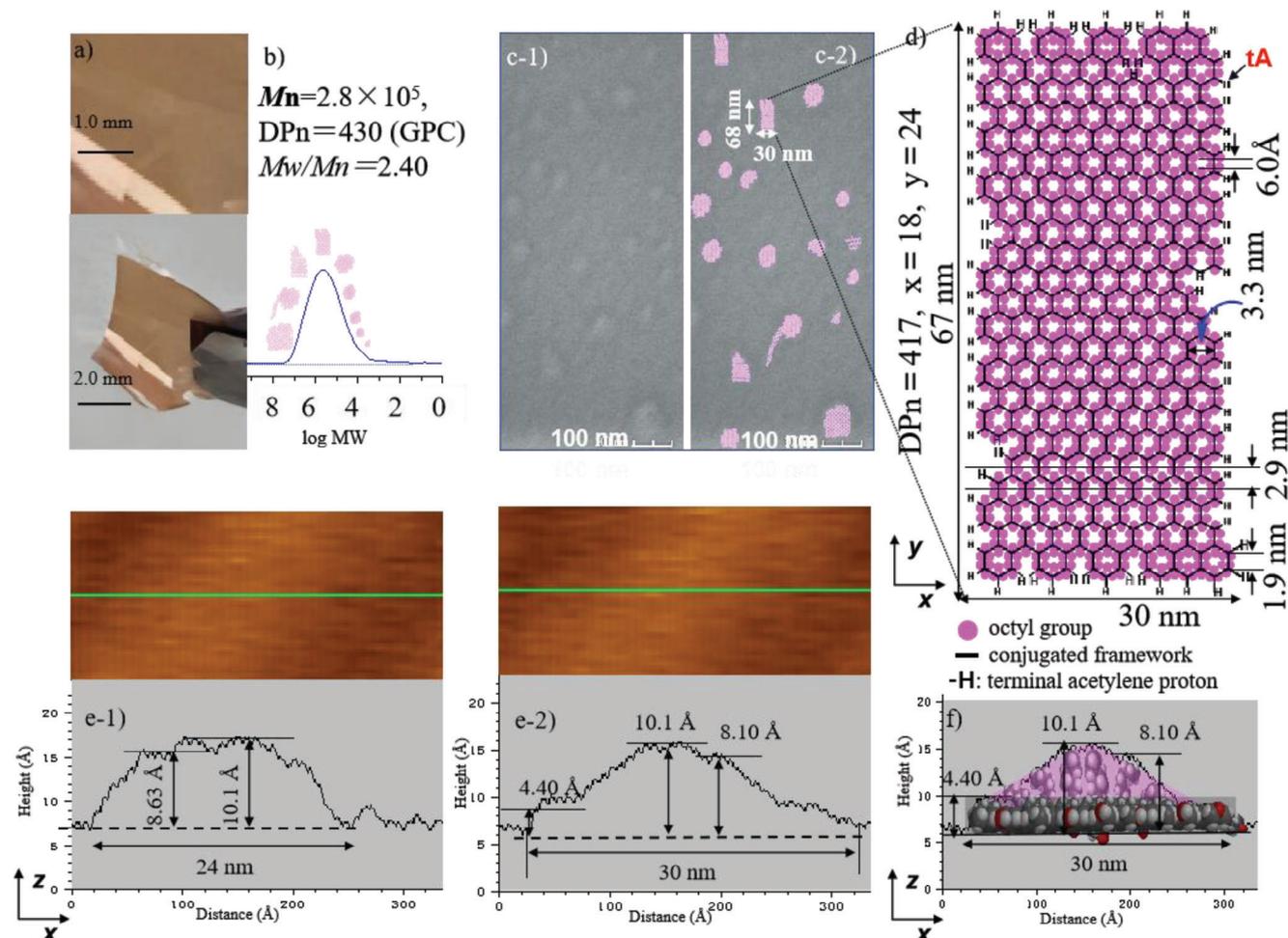
Figure 2. Characterization of *soluble* high molecular-weight well-defined 2DP (SC-OcSi) with very small micropores inside the macromolecule. a) photograph of the self-standing membrane from the THF solution, b) GPC(THF) trace, c-1) SEM, c-2) SEM overlapped with frameworks of the possible 2DP molecules (x-y plane), d) enlarged frameworks of the most plausible 2DP molecule determined by GPC, SEM, and ¹H-NMR (see Figure 3), e-1) and e-2) AFM for the membrane surface, and f) AFM (e-2) overlapped with the possible shape of the 2DP molecule (x–z cross-section).
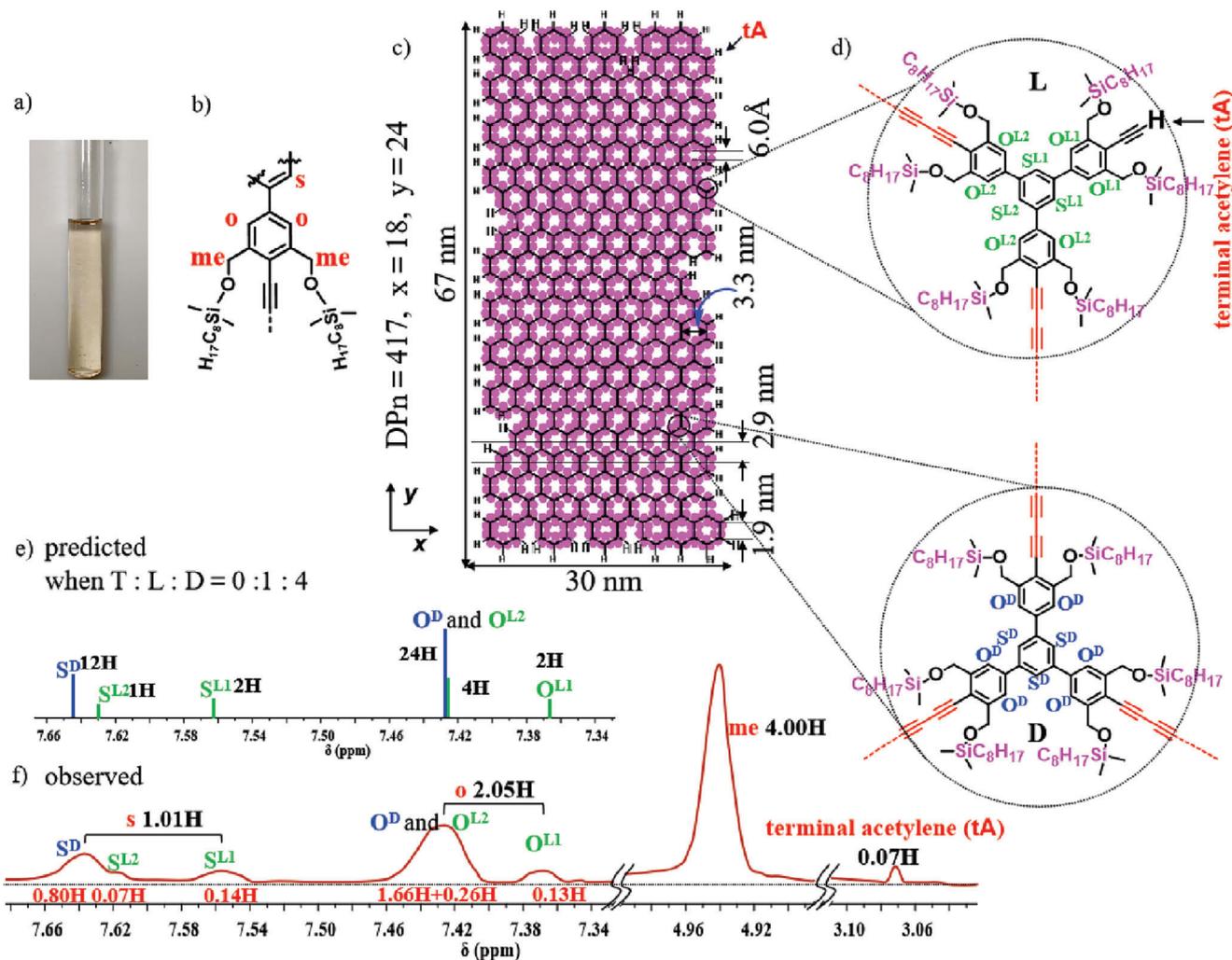
Figure 3. Chemical structure of *soluble* high molecular-weight well-defined 2DP (SC-OcSi) with very small micropores inside the macromolecule determined by ^{1}H-NMR(CDCl$_3$). a) Photograph of the THF solution, b) the repeating unit, c) the total chemical framework determined by GPC (Figure 2b), SEM (Figure 2c), and ^{1}H-NMR(Figure 3e,f), d) chemical formulas for L (linear) and D (dendritic) units, e) predicted ^{1}H-NMR when T: L: D = 0 : 1 : 4 (for the detail, see Figure S2-1-3 and Table S1, Supporting Information), and f) observed ^{1}H-NMR(CDCl$_3$), T: L: D = 0: 1: 4.1.

from A was completely decomposed to form the corresponding cyclic trimers.

(Although the conversion of the SCAT reaction of AC was 100% which was determined by 1H-NMR of SC-OcSi, the resulting SCAT product (pre-SC) was almost(92%) insoluble. It was thought that the molecular size, which is, the molecular weight of pre-SC was high and the macromolecules had strong stacking by the z-direction hydrogen bonds (Scheme 1). In fact, since the resulting compound (SC-OcSi) became soluble after the final reaction where the hydroxyl groups disappeared (Scheme S1-3, Supporting Information), the stacked structure formation by the z-direction hydrogen bonds was supported in pre-SC.) By the substitution of the hydroxyl groups with octylsilyl groups in the membrane state at the final step, the hydrogen bonds by hydroxyl groups between 2DP macromolecular layers in *pre*-SC were broken and the stacked layers were exfoliated to yield isolated SC-OcSi (exfoliated 2DP). In addition, this introduction of octylsilyl groups made the pore size inside the macromolecule smaller.

The conversion and crude yield of the first step were 79% and 100%, respectively. The conversion was 100% for the second step. The SCAT product (s) of unreacted A (8%) at the first step reaction was removed by washing the crude *pre*-SC with methanol. The yield at the final step was 55% and the degree of substitution of SC-OcSi was 100%. Therefore, the total yield from A to isolated SC-OcSi was 51%.

Since the final product (SC-OcSi) was *soluble*, it could be fabricated to a dense membrane (**Figure 2**a) and its GPC measurement was possible. One high molecular weight peak ($Mn = 2.80 \times 10^5$) with a symmetrical monomodal shape appeared with no low molecular-weight impurities in the GPC trace (Figure 2b). Therefore the product was a *soluble* macromolecule with high purity. When the cyclic trimer of M (= the SCAT product (s) of A) minus three protons is taken as the repeating unit of the 2DP, the number average degree of polymerization (DPn) was 430. The possible total framework of this macromolecule is shown in Figure 2d, if the 2DP macromolecule (SC-OcSi) has no

Table 1. Molecular model (Figure 3c) of the 2DP macromolecule (SC-OcSi) created by direct observation.

| code[a]	observed[b]	model formula[b]
DPn	430 (GPC)	417
L : D	1 : 4.1 (NMR)	1 : 4.5 (=76 : 341)
x	30 nm (SEM ,AFM)	30 nm (=3.3 nm × 9)
y	68 nm (SEM)	67 nm (=2.9 nm × 23)

[a] See Figures 2 and 3, Figure S2 and S3 (Supporting Information); [b] see Figures 2 and 3, one plausible model molecular structure of the macromolecule satisfying all the observation data.

defect. The molecular size of the SC-OcSi is estimated as 30 × 67 (x × y) nm from this chemical formula. Since the size of this framework is consistent with that (30 × 68) observed by SEM as shown in Figure 2c, the framework (Figure 2d) is reasonable. In other words, one macromolecule of the 2DP was directly observed by this SEM. The reliability of this framework structure will be fully discussed below by using ^{1}H-NMR assignments. (**Figure 3**)

The thicknesses of this 2DP macromolecule were estimated by AFM of the membrane surface (Figure 2e). These AFMs show that the cross-sections of the macromolecule have 4.4 to 10.1 Å thicknesses (z) and 30 nm width (x). The thickness is reasonable for the chemical structure (Figure 2f) and the value for the width (30 nm) agrees with that observed by SEM (Figure 2c). In addition, the size satisfies the molecular model estimated by ^{1}H-NMR (Figure 2d).

The molecular structure including the total size and pore size of the product as shown in Figure 2d and Figure 3c was reasonably determined by ^{1}H-NMR (Figure 3f and Figures S2–S5, Supporting Information) and GPC(Figure 2b) for the solution samples and also the total size was supported by SEM (Figure 2c) and AFM (Figure 2e) for the solid samples. For example, the width of 30 nm of the macromolecule having the chemical structure (Figure 2d) determined by GPC and ^{1}H-NMR agreed that determined by the direct observation using SEM and AFM as shown in Figure 2. In other words, the molecular structure (Figure 2d and Figure 3c) was determined by the four pieces of evidence, ^{1}H-NMR, GPC, SEM, and AFM. Therefore, this final polymer was chemically almost pure. The detailed assignment of ^{1}H-NMR for this 2DP macromolecule will be discussed later (Figure 3).

The procedure of determination of the chemical structure (Figure 3c,d) of one molecule in the 2DPs is summarized as follows. 1) The probable framework of the repeating unit of the molecule was determined from the absence of T peaks and the integral value ratio (L/D) by the ^{1}H-NMR (Figure 3f). Since the determined structure of the molecule includes ring (= pore) structures in the conjugated rigid framework, the pore size was determined similarly to the case of COFs[8–12] reported. 2) By adding the DPn information obtained by GPC (Figure 2b), the total framework of this molecule (Figure 3c) was determined. (Since no TOF-MS peak was observed, we used this GPC data although the DPn value was a relative one. Since most COFs[8–12] were insoluble and no information on their DPn's was reported, this information was valuable.) The molecular structure satisfies the ^{1}H-NMR results including the integral value ratio (L/D) and the peak ratio of the terminal acetylenes. 3) The size of the
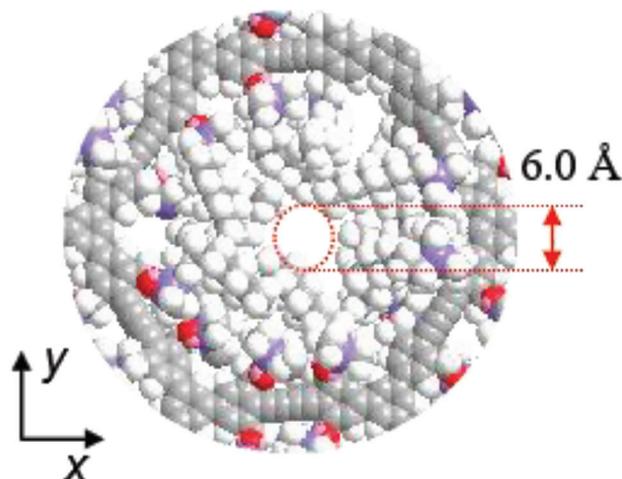
Figure 4. The structure of the very small pore in well-defined 2DP (SC-OcSi).

molecule (Figure 3c) determined in (2) is consistent with that of SEM and AFM. Therefore, the chemical structure of the molecule (Figure 3c) was supported by ^{1}H-NMR, GPC, SEM, and AFM (**Table 1**).

The precise molecular structure of 2DP macromolecule SC-OcSi, whose molecular size was estimated as DPn = 430 and 30 × 68 nm by GPC and SEM (Figure 2), respectively, was determined by ^{1}H-NMR (Figure 3). Figure 3a shows the solution sample for the ^{1}H-NMR measurement. Figures 3b–d show the total chemical structure of this *isolated* 2DP macromolecule (SC-OcSi) reasonably determined by ^{1}H-NMR (Figures 3e,f; Figure S3 (Supporting information), For the detailed procedure of the assignment, see Section S6, and Figure S2-1-3, Supporting information). Figure 3c (= Figure 2d) shows a plausible molecular model of this 2DP supported by all the observed data, that is, GPC, SEM, AFM, and ^{1}H-NMR. Table 1 summarizes this procedure for the determination of the model chemical structure of the 2DP macromolecule. Judging from this macromolecular chemical structure, the minimum pore size inside the macromolecules is estimated as 6.0 Å by this chemical formula calculated using Spartan (**Figure 4**). This pore size is much smaller than that in most COF compounds (usually > 10 Å).[8–12] This small pore size is expected to be effective for highly selective gas permeation. The detail is discussed below.

Table 2 summarizes the molecular structure of the 2DP macromolecules determined by GPC, SEM, ^{1}H-NMR, and AFM described above. It lists the data for SC-OcSi together with those for the related SCs having the same repeating unit and different pore sizes.

Figure 5 shows the plot of the oxygen separation factor ($\alpha = PO_2/PN_2$) versus oxygen permeability coefficient (PO_2: barrier) for the SC-OcSi membrane together with those for the related SC membranes having larger pore sizes than the SC-OcSi membrane. Because the properties of oxygen and nitrogen have only a small difference, the reported separation factors for oxygen and nitrogen were very low. In addition, since the difference between oxygen and nitrogen in their molecular size is very small, they are good probes to discuss the size of these small pores. To obtain high permselectivity for oxygen and nitrogen, controlled

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Table 2. Determination of the molecular structure of some 2DP macromolecules by GPC, SEM, ^{1}H-NMR, and AFM.

no.	SC [2DP]	$Mn^{a)}$ [×10^3]	$DPn^{a,b)}$	DB$^{c)}$ [%]	DR$^{d)}$ [%]	pore diameter$^{e)}$ [Å]		area $^{f)}$ [nm^2]	thickness$^{e)}$ [Å]	
						max.	min.		max.	min.
1	SC-OcSi (this study)	280	430	80	100$^{g)}$	15.0	6.0	2040$^{h)}$	10.1$^{i)}$	4.4$^{i)}$
2	SC-tBuSi (this study)	250	362	84	100$^{g)}$	17.0	15.0	1690	6.3	4.4
3	SC$^{j)}$	6.70	12.0	50	98	21.0	21.0	65	3.0	3.0
4	SCB$^{j, k)}$	20.4	12.4	95	45	32.0	32.0	117	3.0	3.0

$^{a)}$ By GPC; $^{b)}$ the degree of polymerization based on the cyclic trimer (**s**, Figure S2-1 Supporting Information); $^{c)}$ the degree of branching, DB = (D + T)/(T + L + D) × 100 by ^{1}H-NMR (Figure S2-2, Supporting Information); $^{d)}$ n^R: the number of the ring structure in the SC, n^R = (D–T) / 2 + 1 by ^{1}H-NMR, DR: the degree of the ring, DR = 6n^R / (T + L + D) × 100 by ^{1}H-NMR; $^{e)}$ from chemical formula created using Chem3D *ver18*; $^{f)}$ by GPC and ^{1}H-NMR; $^{g)}$ no T peaks were observed for the SC in ^{1}H-NMR; $^{h)}$ by SEM, and GPC, AFM; $^{i)}$ by AFM; $^{j)}$ the detail data will be reported in a separate paper; $^{k)}$ for the starting monomer, see Chart S1 (Supporting Information).
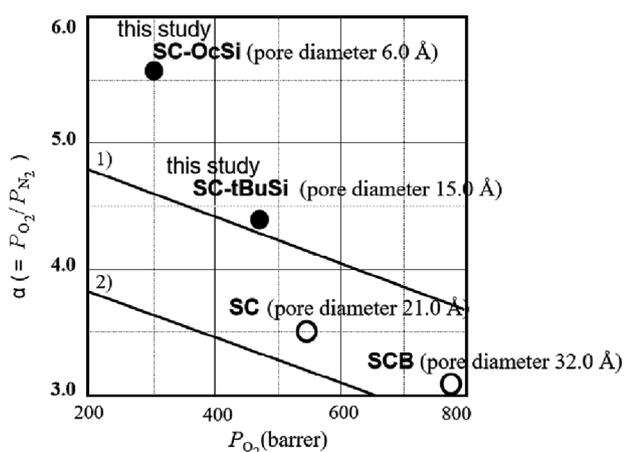
Figure 5. High oxygen permselectivity of 2DP (SC-OcSi) membrane with very small micropores inside the macromolecule and the related SCs with larger micropores.

and stable pores are suitable like this study. Therefore, we selected the gas pair in this study. The performance of the SC-OcSi membrane was the best and exceeded Robeson's upper bound line. The highest α was thought to be caused by the very small pores (6.0 Å). The pore size is still larger than the sizes of oxygen and nitrogen. However, since this membrane was actually composed of many layers of the 2DP macromolecules which can stack in a staggered manner, the pore size can be smaller than that of a single layer of the 2DP macromolecule. In fact, the high α was based on the high DO_2/DN_2 and this ratio was the highest among them as shown in **Table 3**. With decreasing the pore size

in the SC membranes, α and DO_2/DN_2 increased. This shows the effect of the micropores inside these 2DP membranes on the separation based on the molecular sieving mechanism.

3. Conclusion

The hexagonal columnar A(1DP) membrane of monomer M having two hydroxyl groups gave *pre*-SC (stacked 2DP) and the macromolecule of 2DP (SC-OcSi) was isolated by introducing octylsilyl groups to the hydroxyl groups of *pre*-SC. Since this macromolecule was *soluble*, the size and precise chemical framework were fully characterized by GPC (SEM and AFM) and ^{1}H-NMR, respectively. It contained only D and L units (D: L = 1: 4.1) determined by ^{1}H-NMR. The DPn was about 430 and the size in the x–y plane was 30 × 68 nm which were determined by GPC and SEM, respectively. The distance x was also confirmed by AFM and the thickness in the z-direction was 4.40 Å determined by AFM which was reasonably explained by the molecular model. The 2DP (SC-OcSi) had very small pores (Figure 4) inside the macromolecule. This 2DP macromolecule was so highly *soluble* that the self-standing membrane from the *pure* polymer was obtained by the solvent cast method. (The successive three reactions in this study used almost no organic reagents, that is, only Cu for the Glaser coupling, no reagents (just light irradiation) for the SCAT reaction, and only a chlorosilane for silylation of the hydroxyl groups, and only small molecules, that is, H2, nothing, and HCL were eliminated, respectively during the three reactions. They could be removed easily. Therefore, the product had almost no impurities.) The resulting membrane showed excellent oxygen permselectivity exceeding Robeson's upper line due to the very small pores of 6.0 Å. To the best of our knowledge, this

Table 3. Oxygen permselectivity of 2DP (SC-OcSi) membrane together with the related SC membranes.

no.	2DP	pore diameter$^{a)}$ (Å)	density$^{b)}$ (g cm^{-3})	$PO_2^{c)}$ (barrer)	$PO_2/PN_2^{c)}$	$DO_2/DN_2^{d)}$
1	SC-OcSi	6.0	0.835	300	5.6	4.9
2	SC-tBuSi	15.0	–	457	4.3	2.7
3	SC$^{a)}$	21.0	0.872	528	3.5	2.5
4	SCB$^{a)}$	32.0	–	797	3.1	2.2

$^{a)}$ See Table 2; $^{b)}$ by the floating method; $^{c)}$ PO_2 and PN_2: oxygen and nitrogen permeability coefficient; $^{d)}$ DO_2 and DN_2: oxygen and nitrogen diffusion coefficient.

is the first example of a fully characterized 2DP macromolecule with a large area, very small pores, and good membrane-forming ability leading to excellent oxygen permselectivity.

Although the product had a high molecular weight, surprisingly it was soluble. Therefore, the detailed molecular structure was determined by ^{1}H-NMR and GPC. In addition, the molecular size was supported by the direct observation by SEM and AFM. Since the polymer was synthesized by condensation polymerization, it had normal molecular distribution as shown in the GPC and SEM. To the best of our knowledge, this is the first example of a soluble high molecular weight 2DP macromolecule.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords

2D polymers, high molecular weights, high oxygen permselectivity, large area, small micropores, solubility, synthesis

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