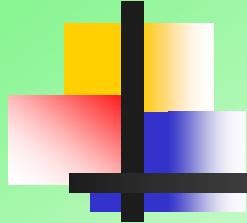


ケイ素系有機・無機ハイブリッド 材料とその新しい設計戦略

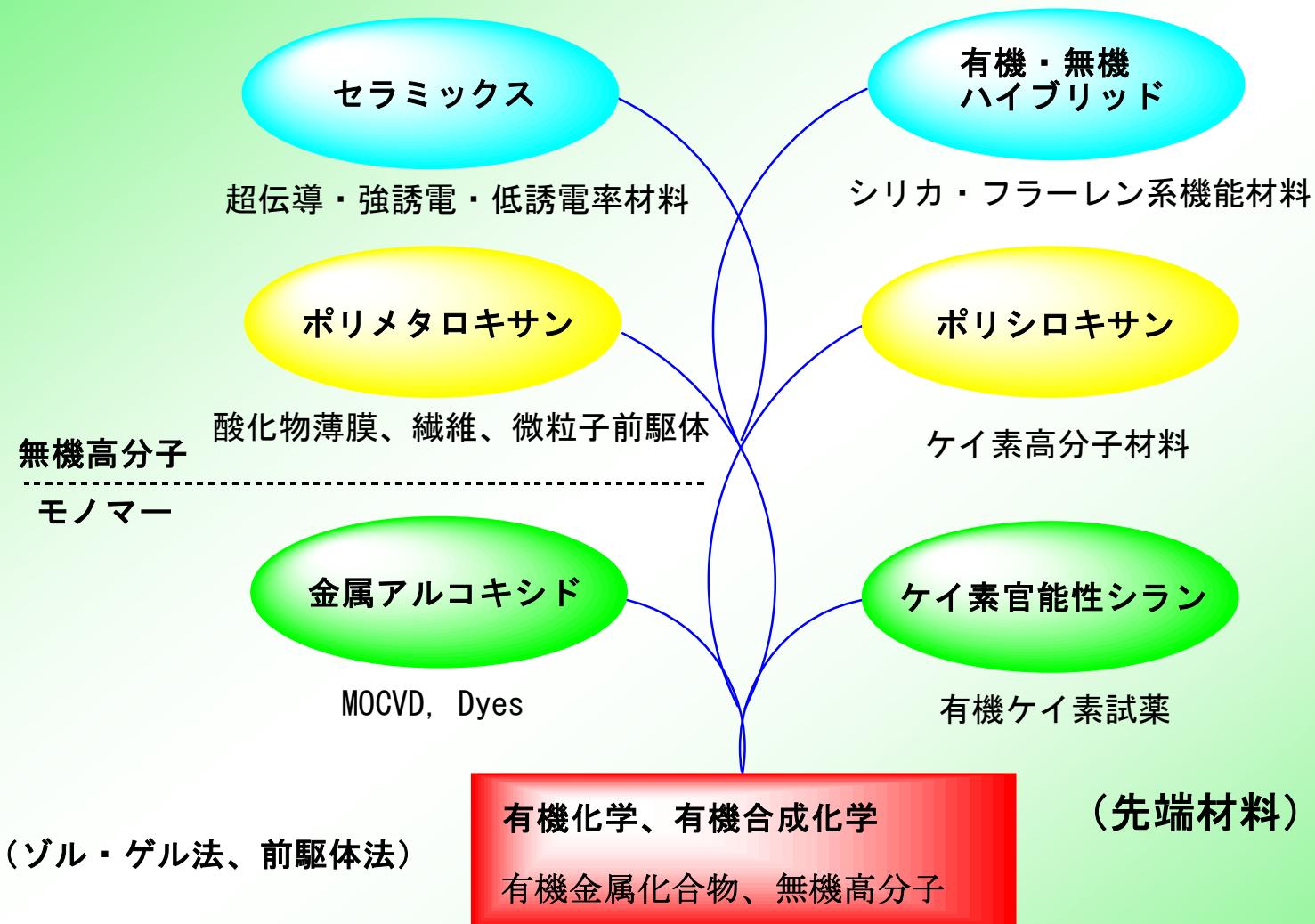


郡司 天博¹⁾、阿部 芳首²⁾

- 1) 東京理科大学 理工学部 准教授
- 2) 東京聖栄大学 健康栄養学部 教授
(東京理科大学 名誉教授)



マツモトファインケミカル技術講演会、2/22、2011



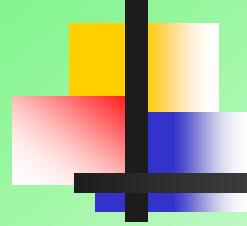
Scheme 1 研究の背景

講演内容

(ケイ素系有機・無機ハイブリッド材料とその設計戦略)

1. はじめに
2. 新しいケイ素系無機前駆体
3. ハイブリッドの新しい設計法
4. 新材料開発の現状
5. ハイブリッドに関する我々の研究
6. おわりに

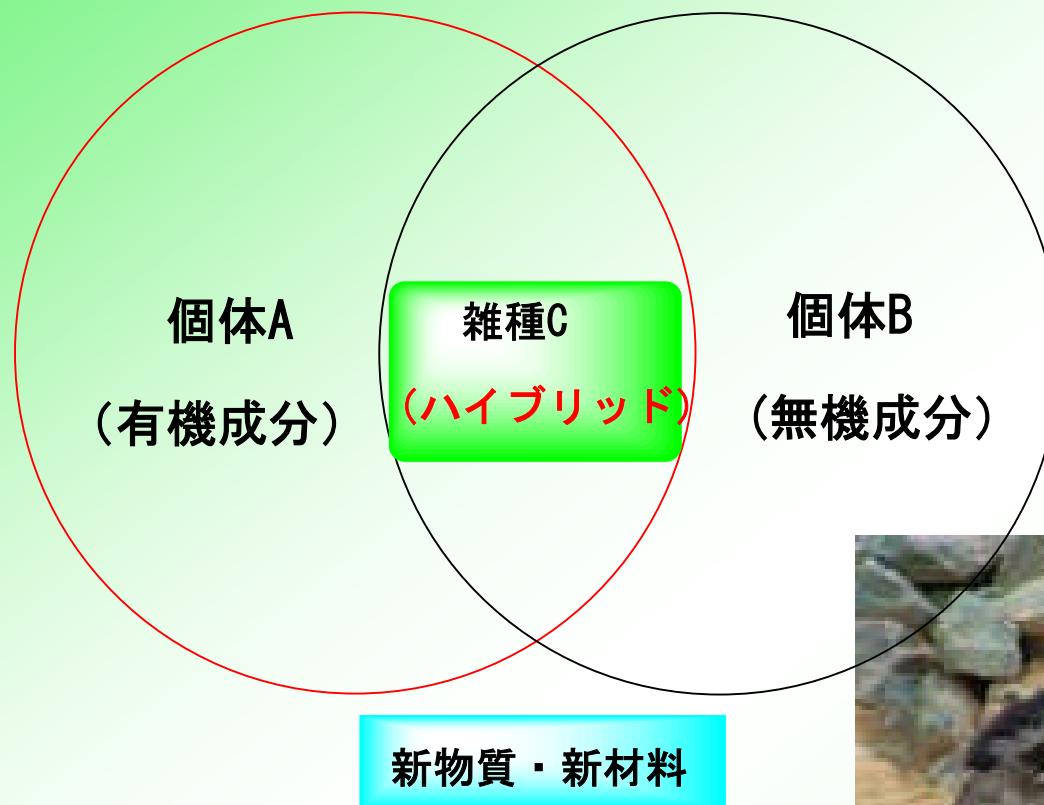
(以上の項目についてご紹介いたしますが、ページ数の関係で講演のPP
から一部削除して要旨を作成しておりますので、ご了承お願いいたします。)



1. はじめに

- 有機・無機ハイブリッドとは
- これは有機それとも無機？
- なぜハイブリッドか

有機・無機ハイブリッドとは



・学術論文 約200件(2004年)

・特許 約400件(2004年)

ハイブリッド

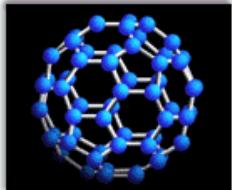
- ・遺伝学用語
 - ・レオポン(交配)
 - ・混成軌道
 - ・ハイブリッドカー
 - ・集積回路
 - ・計算機
- 我国では
(1960～1970)
頃から用いられる



ゾンキーと呼ばれるロバとシマウマ(縞馬)の種間雑種

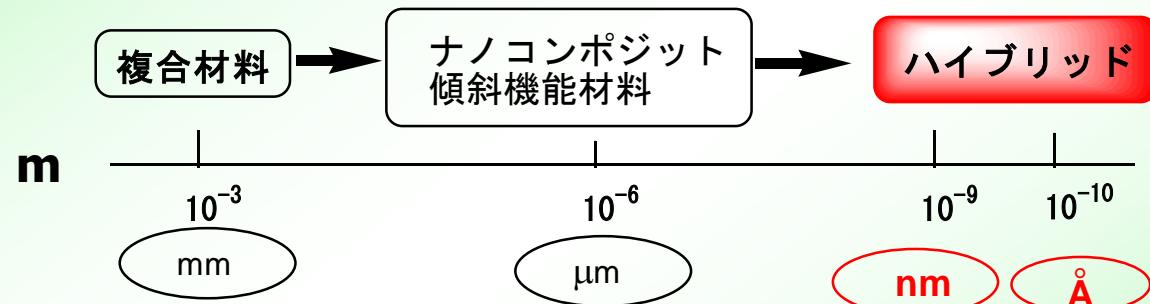
これは有機それとも無機材料？(元素組成からみて)

Are these recognized as hybrids ?

Compound	Content of the element(%) except for H & C
Furrerene 	0 (100) C_{60}
Polyacetylene $(-CH=CH-)_n$	0 (100)
T_8^H $(HSiO_{3/2})_n$ 	98
Polysilazane $(-H_2Si-NH-)_n$	93
Polyphosphazene $(-Cl_2P=N-)_n$	100

なぜ有機・無機ハイブリッドか？

1. 新物質・新材料



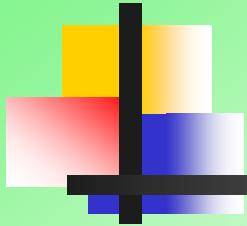
2. 高性能・高機能

物性

化学（耐熱、耐候、耐薬品、耐酸化）
光学（屈折、透過、吸収）
電気（導電、絶縁、誘電）
機械（弾性、硬度、膨張、収縮）

3. 構造設計

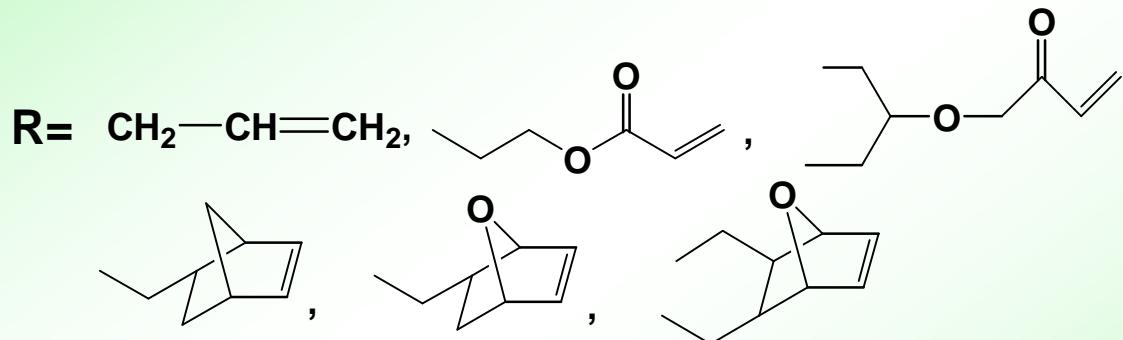




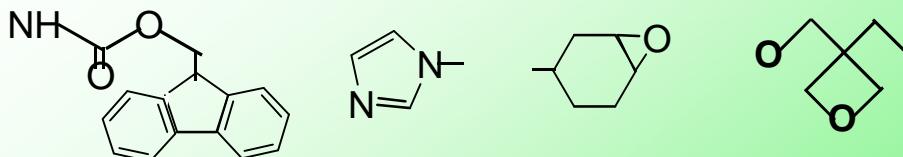
2. 新しいケイ素系無機前駆体

- 2. 1 Carbo- & sila-functional silanes
- 2. 2 Silanes for self-assembly
- 2. 3 Cubes and analogous
- 2. 4 Sila-functional cyclosiloxanes

2. 1 Carbo- and sila-functional silanes



$\text{X} = \text{Cl}, \text{OH}, \text{NH}_2, \text{NCO}, \text{SH}, \text{CN}, \text{NH(CH}_2)_3\text{NH}_2,$
epoxy, OCH_2 -epoxy, $\text{OCO(CH}_3)=\text{CH}_2,$
 $\text{O(CH}_2)_2\text{OCH=CH}_2,$
 $\text{NHCO(CH}_2)_2\text{CON[(CH}_2)_{15}\text{CH}_3]_2,$
 $\text{Br}^- \text{N(Me)}_2(\text{CH}_2)_5\text{CONHCH}_2\text{CON[(CH}_2)_{15}\text{CH}_3]_2,$
+

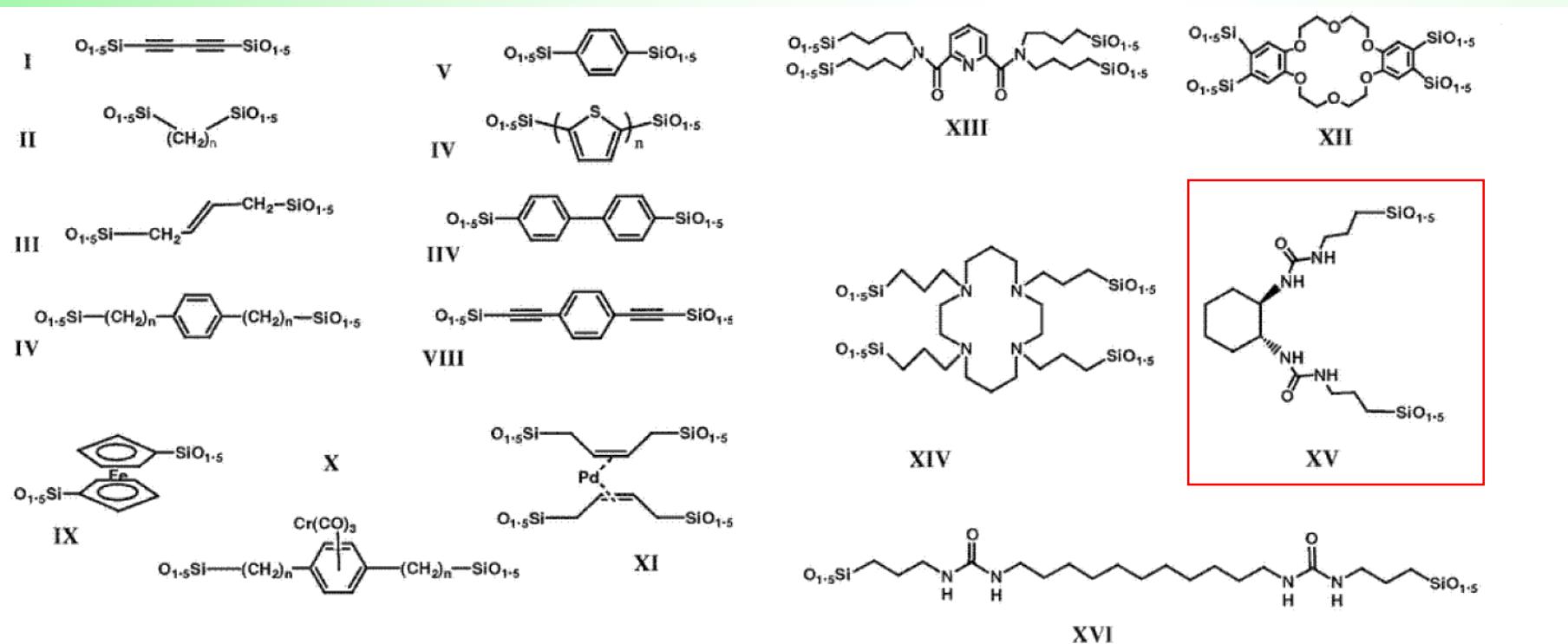


$\text{X} = \text{CH}_3, \text{CH=CH}_2, \text{CH=CH(CH}_2)_2\text{CH=CH}_2$

$\text{Y} = \text{Cl}, \text{OEt}, \text{OSi(OMe)}_3$

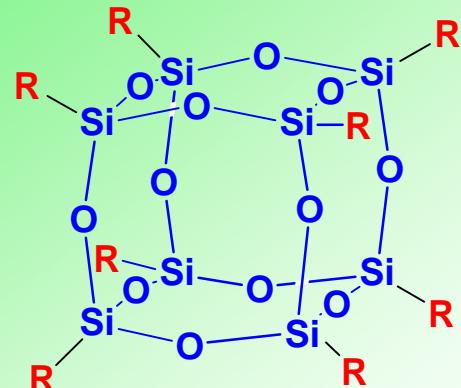
$n = 4 \sim 18$

2. 2 Silanes for self-assembly

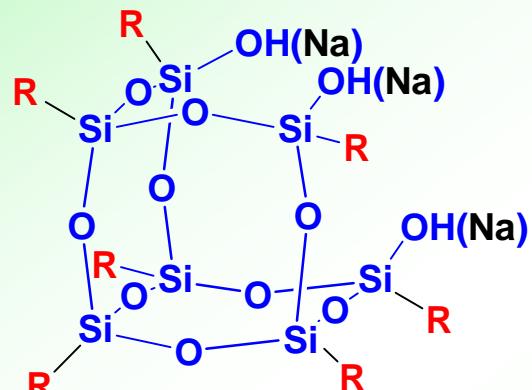


R-(OSiX₂)_nO-R ?
(X=OR', R')

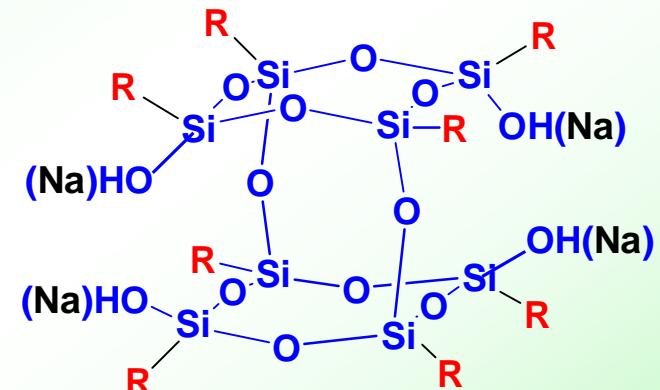
2. 3 Cubes and analogues as a potential precursor



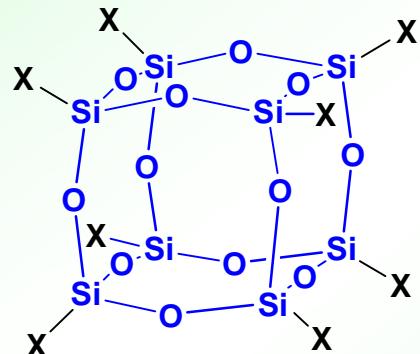
Cubes with various R groups



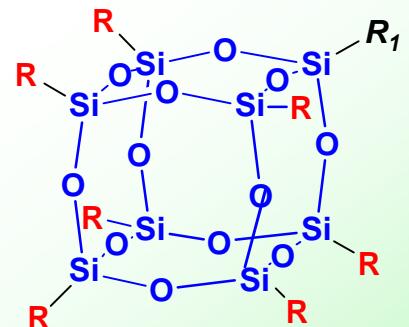
Open cage



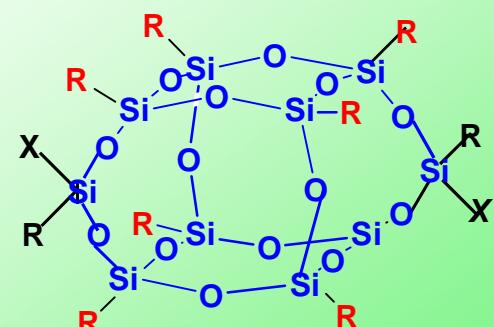
Double-decker



Sila-functional cubes

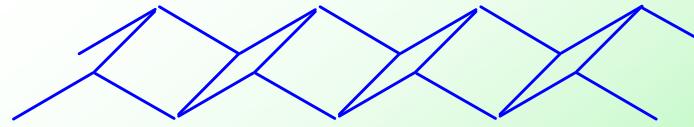
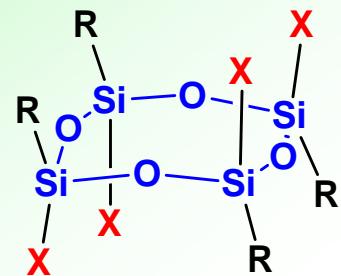
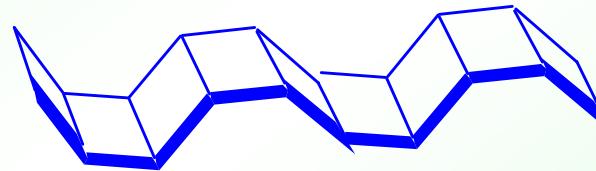
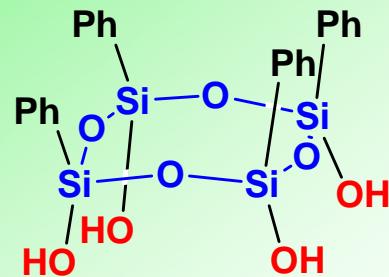


Cubes with one R_f groups

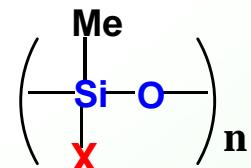


Cages from double decker

2. 4 Sila-functional cyclosiloxanes as a precursor for ladder silsesquioxanes

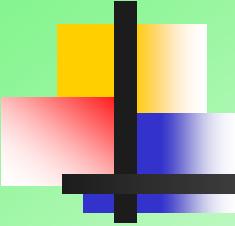


X = NCO(R=Me), Br(R=i-Pr)



Cyclosiloxanes

X = H(n=3~5), NCO(3~6)



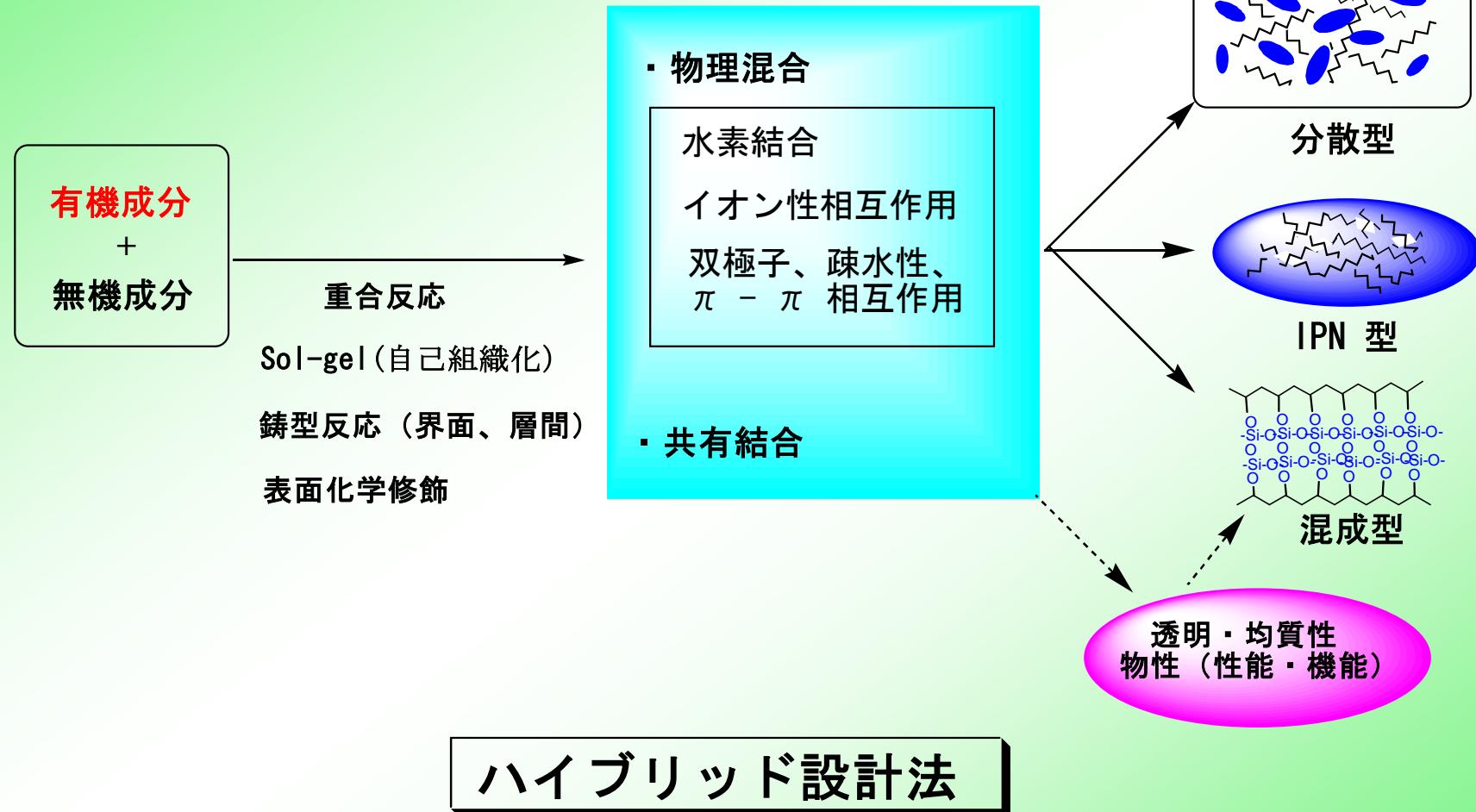
3. 有機・無機ハイブリッドの新しい設計法

3. 1 設計指針－1～5

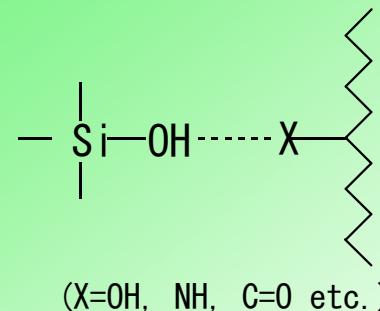
3. 2 合成例 1～7)(同時重合、共重合、混合)

3. 3 合成例(自己組織化)－1～10

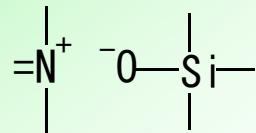
3. 1 設計指針－1



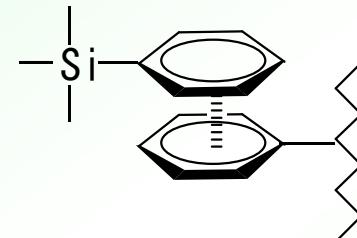
3. 1 設計指針－2



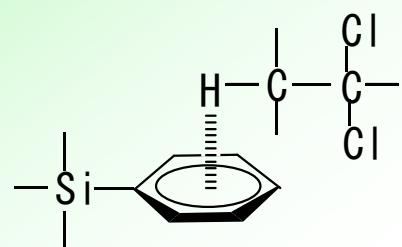
a) Hydrogen bond



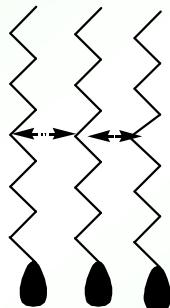
b) Ionic bond



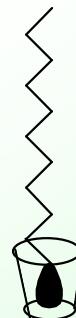
c) $\pi-\pi$ bonding



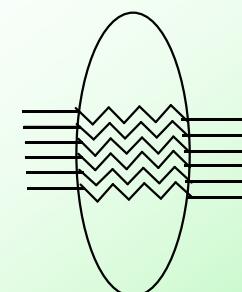
d) $\sigma-\pi$ bonding



e) Hydrophobic



f) Host-guest



g) Stereo-complexing

Schematic representation of various interactions

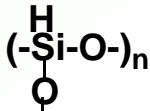
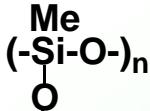
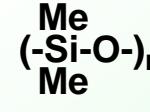
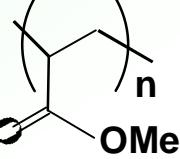
3. 1 設計指針－3

Preparation of organic-inorganic silica hybrids

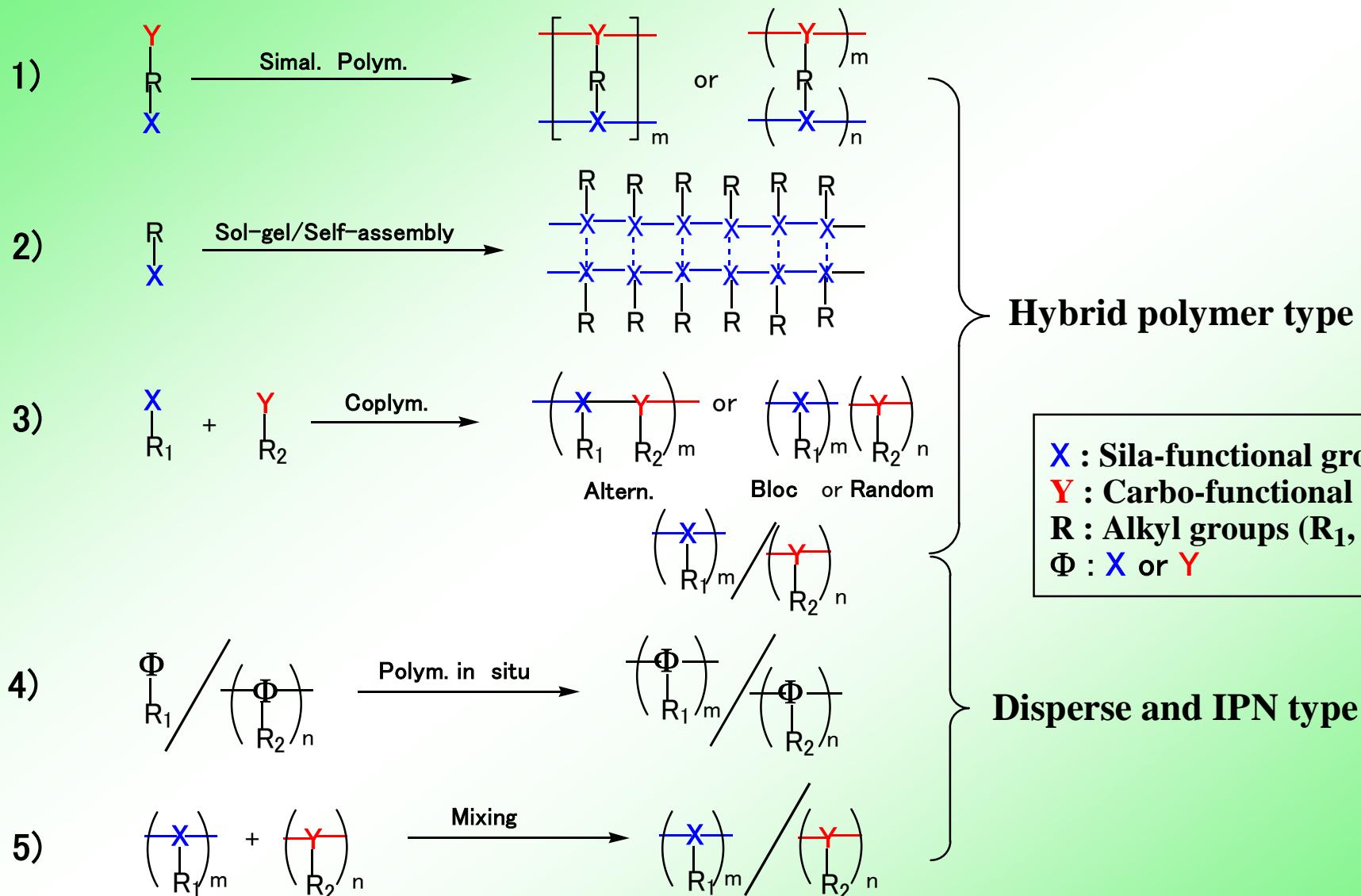
Organic polymer	Silica
R $(-CH_2-CH_2-)_n$ (modified or copolymerized)	Cray
$(-CH_2-CH(OH)-)_n$	SiO_2 (powder, sol, silicic acid)
	$(-Si(XO^-)_n)_n$ ($X=O^-, OH, OR$)
$(-COHN-RNH-COO-R' -O-)_n$	$\begin{matrix} R \\ \\ [-Si(O^-) \\ \\ -Si(O^-)]_n \\ \\ R \end{matrix}$
$[-(CH_2)_5-NHCO-]_n$	
$\text{Cyclopropyl-CH}_2-(O-R-O-R')-\text{CH}_2-$	$RSi(OMe)_3$ ($R = -(CH_2)_n-X$) $\left(X=\begin{cases} NH_2 \\ NCO \\ OCOCRCH=CH_2 \\ \text{Cyclopropyl} \end{cases} \right)$
$(-OH-CH_2-)_n$	Si(OEt)₄ (TEOS)
$(-OCO-R-COOR' -O-)_?$	

3. 1 設計指針—4

有機及び無機成分の溶解パラメータ δ (MJ/ m³) ^{1/2}

有機成分の構造	δ	無機成分の構造	δ
(-CH ₂ -CH ₂ -) _n	16.1	SiO ₂	24.8
(-CH ₂ -CH ₂ -O-) _n	17.8	(-Si-O-) _n 	23.2
(-CH-CH ₂ -) _n 	18.7	(-Si-O-) _n 	16.6
(-CH-CH ₂ -) _n OAc	19.2	(-Si-O-) _n 	14.6
	19.4	C ₆₀	85.4
PC	21.0		
PET	23.4		
6-Nylone	24.0-25.0		
Epoxy resins	23.6-24.7		

3. 1 設計指針－5



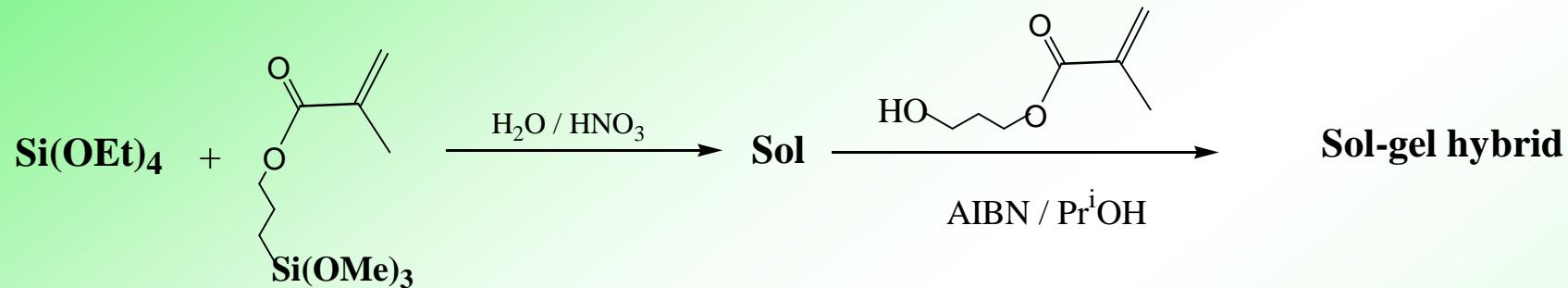
Molecular Design of Organic-Inorganic Hybrids

3. 2 合成例

混成型

2) Silica microgel hybrid as precursors of sol-gel coatings

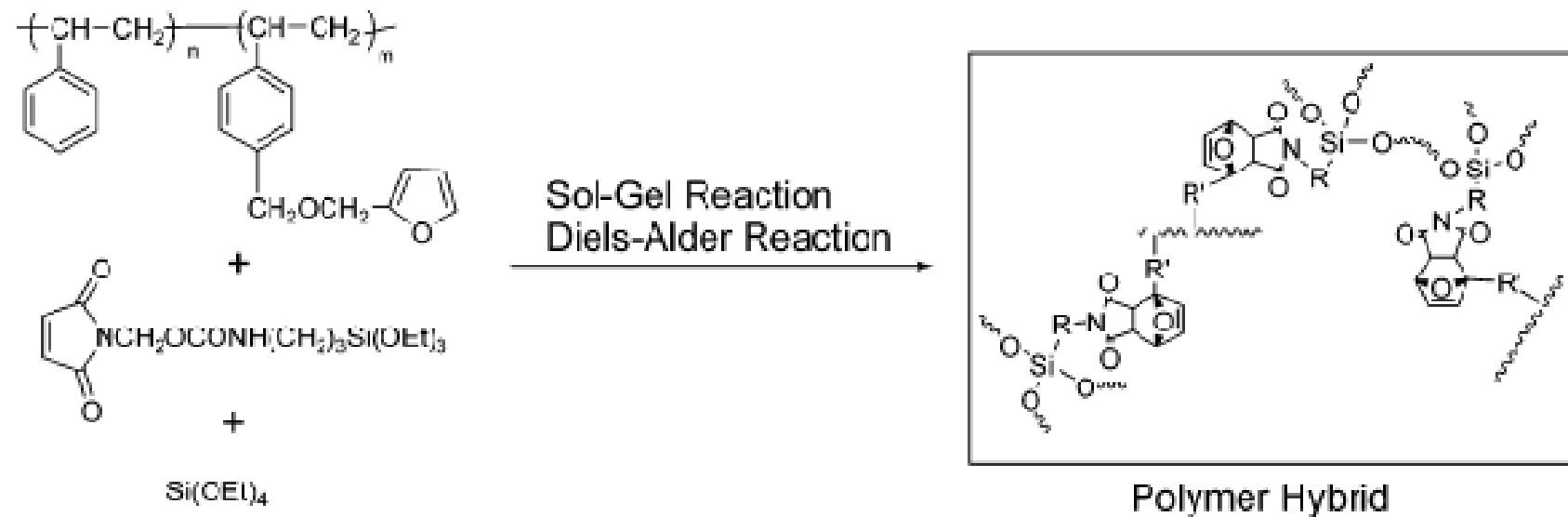
S. A. Pellice, et al, *J. Mater. Chem.*, 2006, 16, 3318–3325



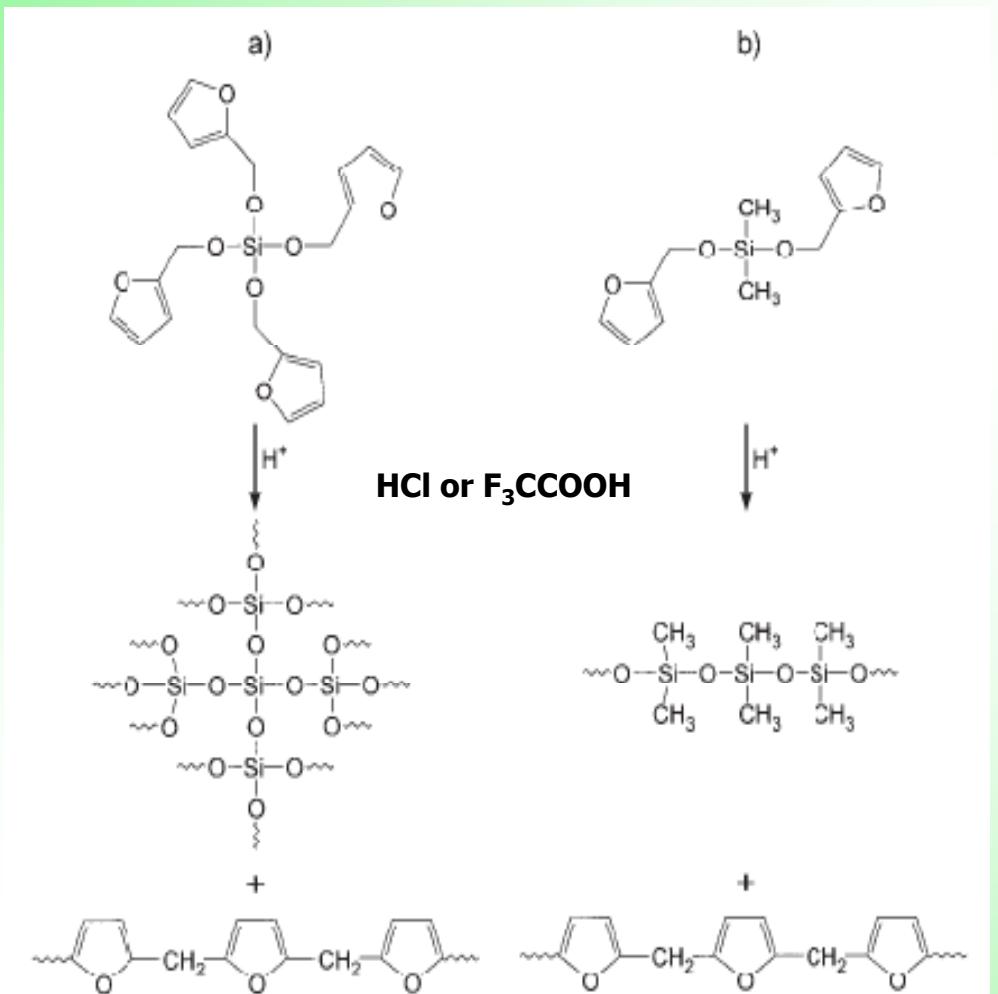
4) Organic-Inorganic Polymer Hybrids by Diels-Alder Reaction

Kaoru Adachi, Yoshiki Chujo et al, *Macromolecules* 2004, 37, 9793-9797

Scheme 3. Synthesis of Polymer Hybrids Utilizing DA Reaction



3) Twin Polymerization of the Single Monomers a) or b)

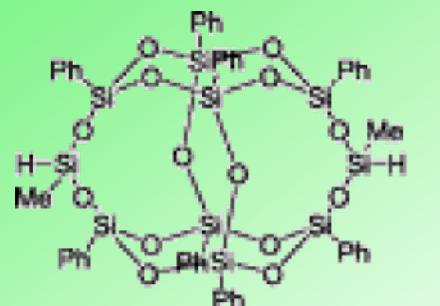


IPN型

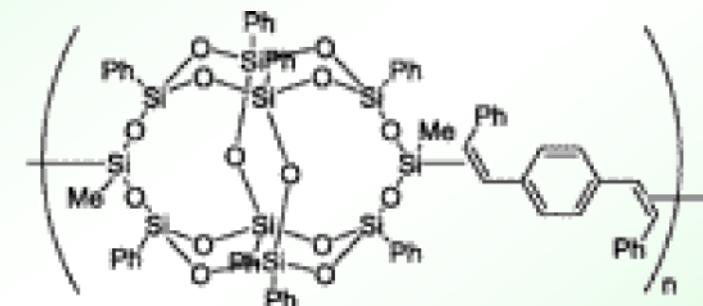
Scheme 1. Cationic polymerization of a) TFOS with formation of a SiO₂ network and PFA and b) DFOS with formation of poly(dimethylsilane) and PFA.

5) Hybrid by Polymerization of Double-decker-type Silsesquioxane with Diynes

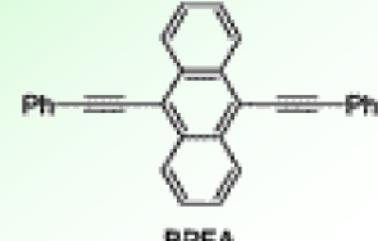
M. Seino, et al., Macromolecules, 2006; 39(10); 3473-3475.



Pt(dv)
toluene



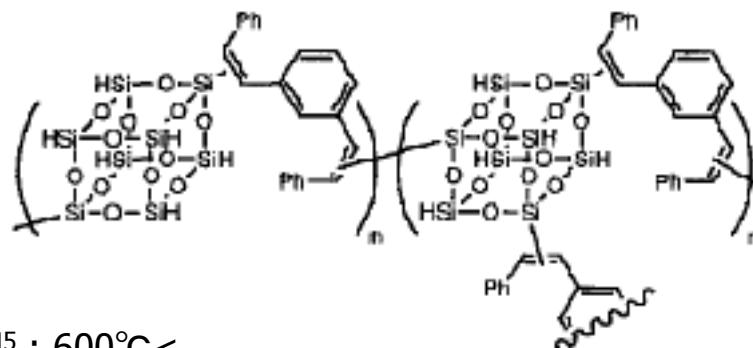
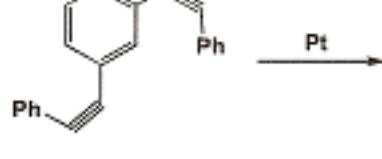
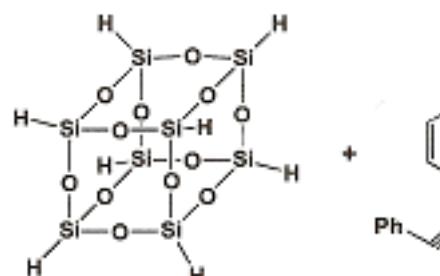
混成型



diyne	Yield(%),	Mn	Mw/Mn	Td
BPEB	97	29,100	4.1	518
BPEA	90	11,900	4.9	301
DEB	in soluble			

6) Highly Heat-Resistant Soluble Polymers by Polymerization of T_8^H and Diynes

T. Kobayashi, T. Hayashi and M. Tanaka, Chem. Letts , 1998 Vol. 27 No. 8 763-764

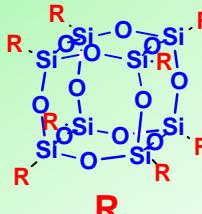


Td⁵ : 600°C<

Dyne/T₈^H = 1.23
Mw : 21,000
Td⁵ : 1,000 °C<
Residue : 95%

7) Hybrids from T_8^R and Org. polymer

分散型

Author	Year	Polymer	Properties
Lichtenhan 1996		 $\text{C}_8\text{H}_{16}\text{O}_4\text{Si}_8^{\text{R}}$ 3~6wt%	$\left(\text{CH}_2 - \overset{\text{Me}}{\underset{\text{COOMe}}{\text{C}}} \right)_n$ Transparent films but no improvement of thermal properties
Schwab 2000		$\text{CH}_2\text{CH}_2\text{Ph}$	$\left(\text{CH}_2 - \overset{\text{H}}{\underset{\text{C}_6\text{H}_5}{\text{C}}} \right)_n$ Homogeneous material even in 50% but no improvement of properties
Blansky 2001		Me 10 wt%	isotactic $\left(\text{CH}_2 - \overset{\text{Me}}{\underset{\text{H}}{\text{C}}} \right)_n$ Heterogeneous but improvement of mechanical and thermal properties
Blansky 2001		$\text{CH}_2\text{CH}_2\text{SiMe}_2\text{-Oct.}$	HDPE $\left(\text{CH}_2 - \text{CH}_2 \right)_n$ No improvement of inflammability

3. 3 合成例(自己組織化:Self-assembly; 1~10)

- ・特徴

- 三次元精密構造制御

- Without surfactants as a template

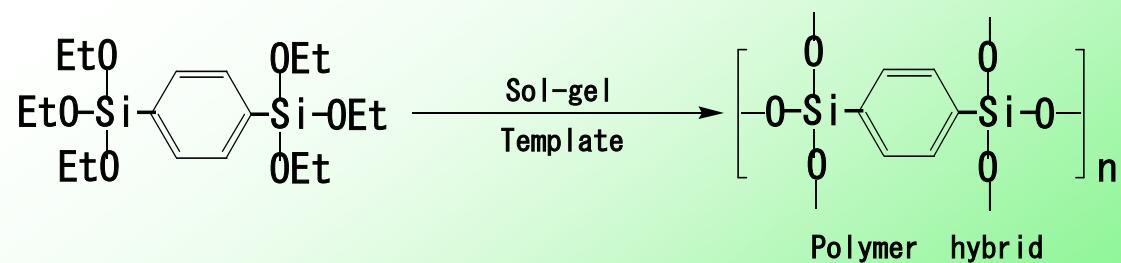
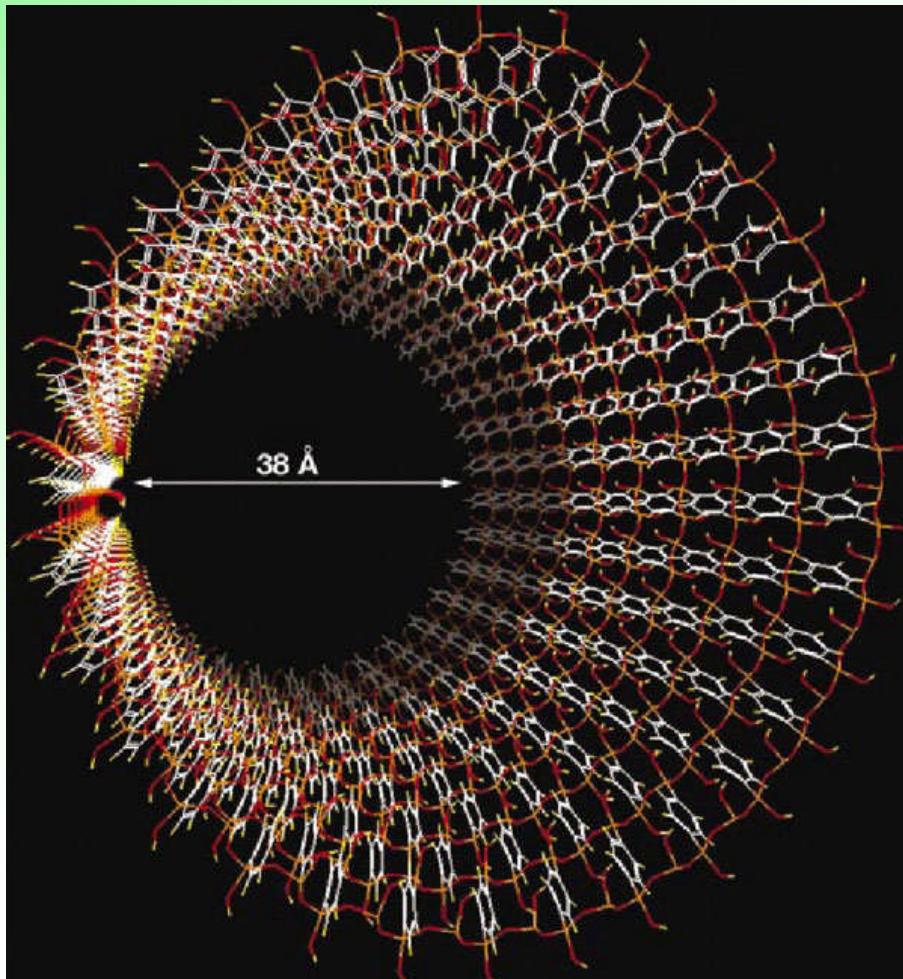
- Formation of capsules with silica outer shell

- 形状安定(分裂、融合を起こさない)

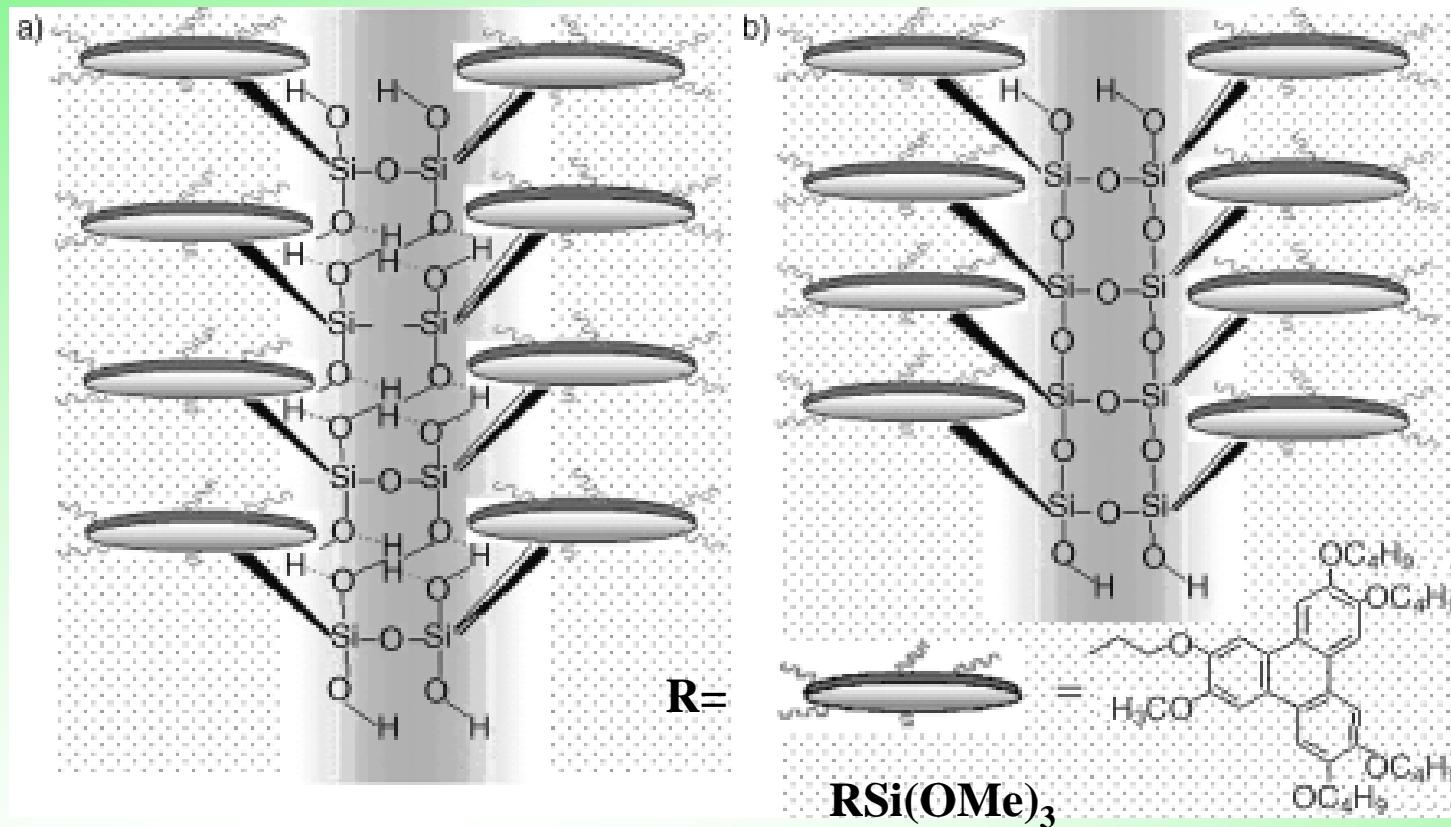
構造制御因子

- 1) Si-OHの水素結合による超分子形成
- 2) 有機基の構造と疎水基間相互作用
- 3) イオン間相互作用

1) 混成型ハイブリッド(ポリマーハイブリッド: 豊田中研 稲垣)



2) **cis**-Isotactic Ladder Polysilsesquioxane by Stacking and H-Bonding Superstructure, Xiaojing Zhang, Ping Xie, Prof. Et al , Angew. Chem. Inter. Ed. Vol. 45, 19, 3112-3116 (2007)



側鎖 π - π 相互作用, シラノール基の水素結合によりsupramolecular channelを形成

Brown solid, highly soluble in *n*-hexane, toluene, THF, $M_w=8.2 \times 10^5$, $[\eta]=2.25 \times 10^6 \text{ M}^{1.24}$,
 $T_g = 255.9 \text{ }^\circ\text{C}$, ^{29}Si NMR signal : Half-peak width $\Delta_{1/2} < 0.3 \text{ ppm}$

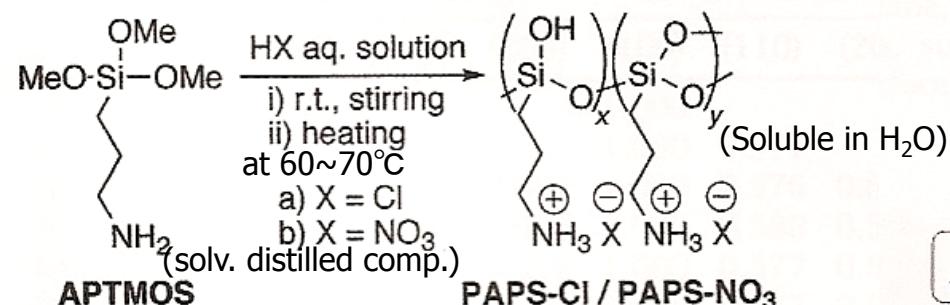
Figure 1. Schematic representation for the confined polycondensation of the monomer in ladder structure (a) to form the covalent ladder polymer (b).

4) Hexagonal-Structured Polysiloxane Material Prepared by Sol-Gel Reaction of Aminoalkyltrialkoxysilane without Using Surfactants (or long chain alkyl groups)

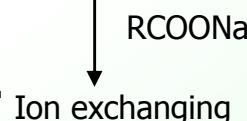
Y. Kaneko et al, Chem. Mater. 2004, 16, 3417-3423

界面活性剤や長鎖アルキル基モノマーを用いずにオーダーメードシロキサンを合成する始めての例

Scheme 1. Synthesis of Nanostructured Poly(3-aminopropyl)siloxane Complex Salts

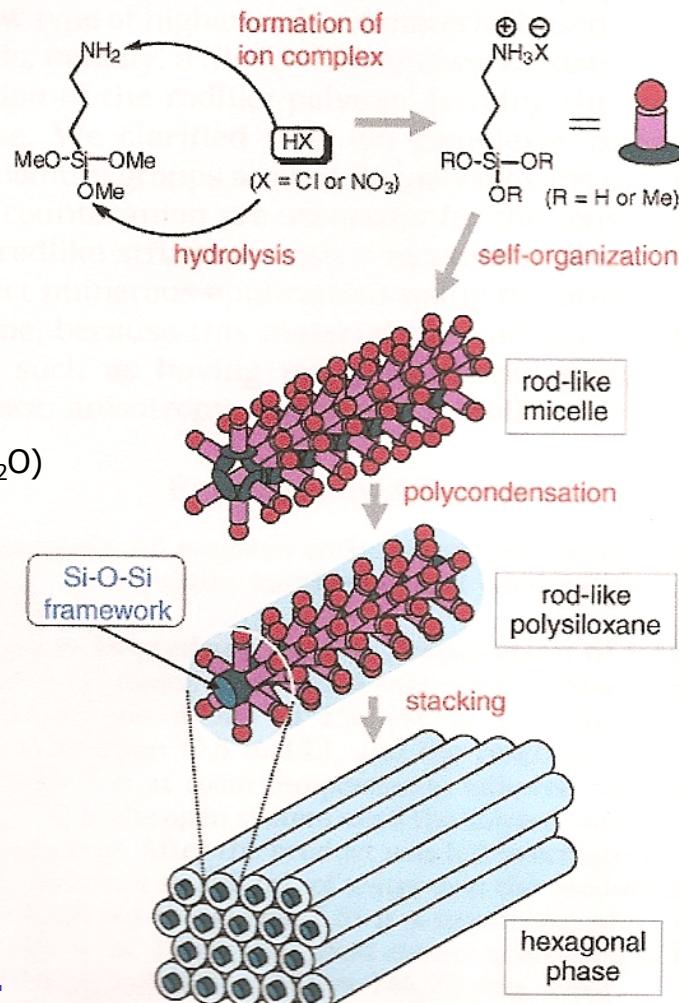


The method can also be used to
 $(\text{MeO})_3\text{Si}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$
Polymer 46(2005), 1828-1833

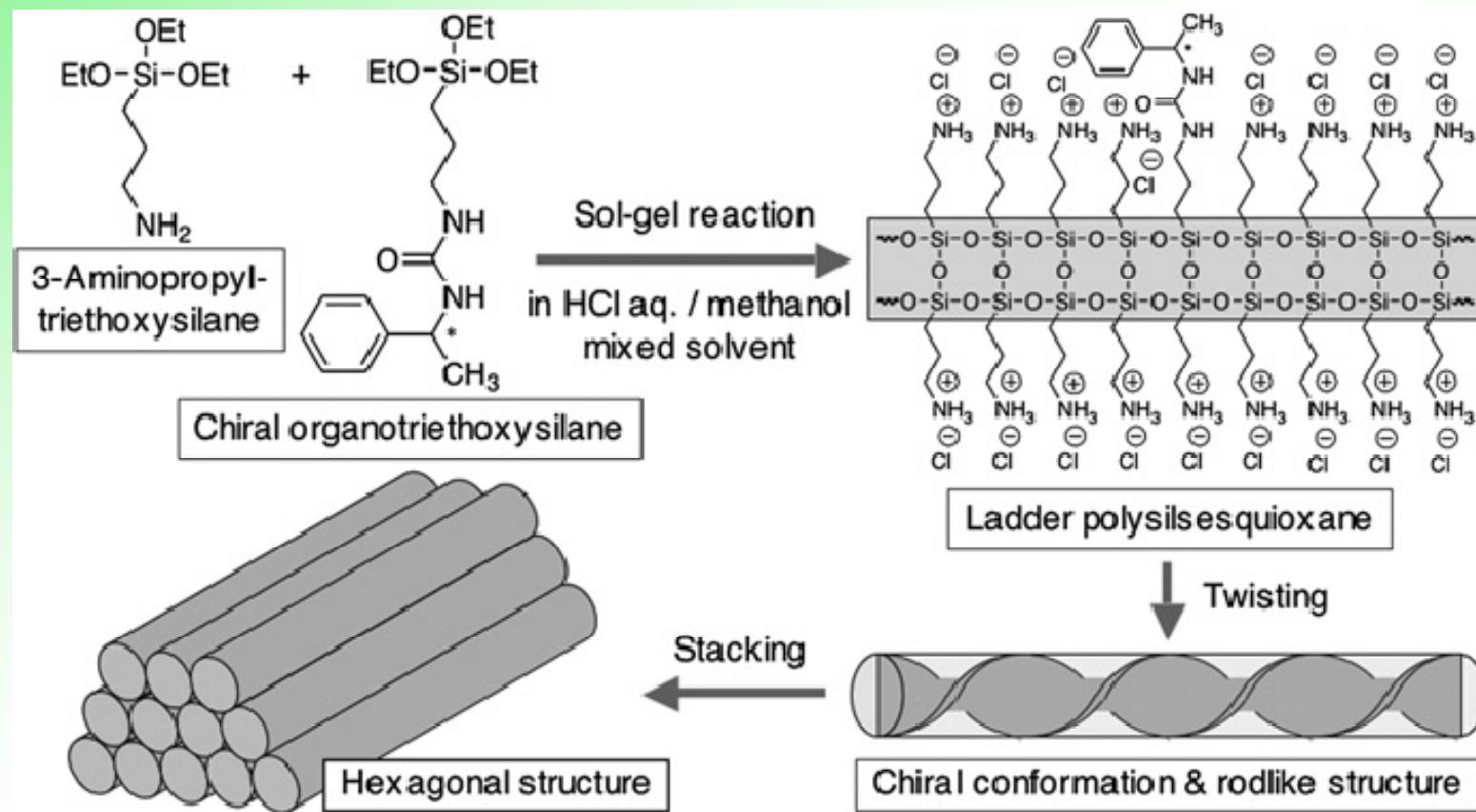


PAPS- HSO_4^- membranes as an anhydrous proton conduction PEFC at temps. higher than 100°C (cf Nafion). They are stable up to 300°C and show conductivity of 2×10^{-3} S cm $^{-1}$ at 200°C.
T. Tezuka, et al., JACS, 2006, 128, 1647

Scheme 3. Proposed Formation Mechanism of Rodlike Polysiloxane with Hexagonal Phase

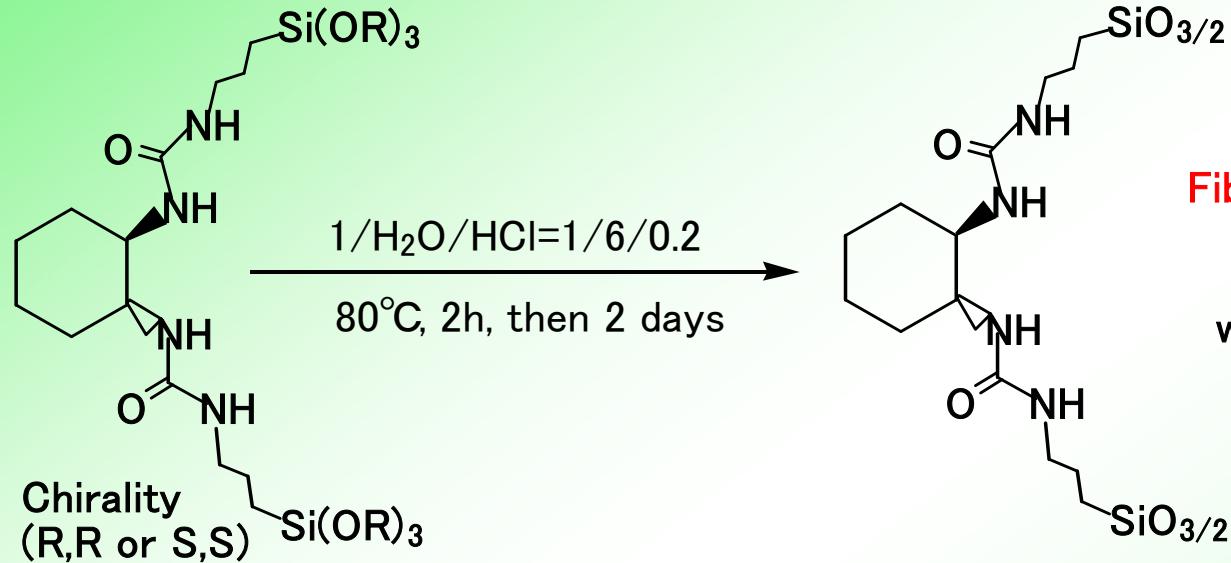


Hexagonal SiO₂ with a helical structure



6) Hybrid fibers with helical structure

J. E. Moreau, et al., J. Am. Chem. Soc., 2001, 123, 1509-1510; Chem. Eur. J. 2003, 9, No.7

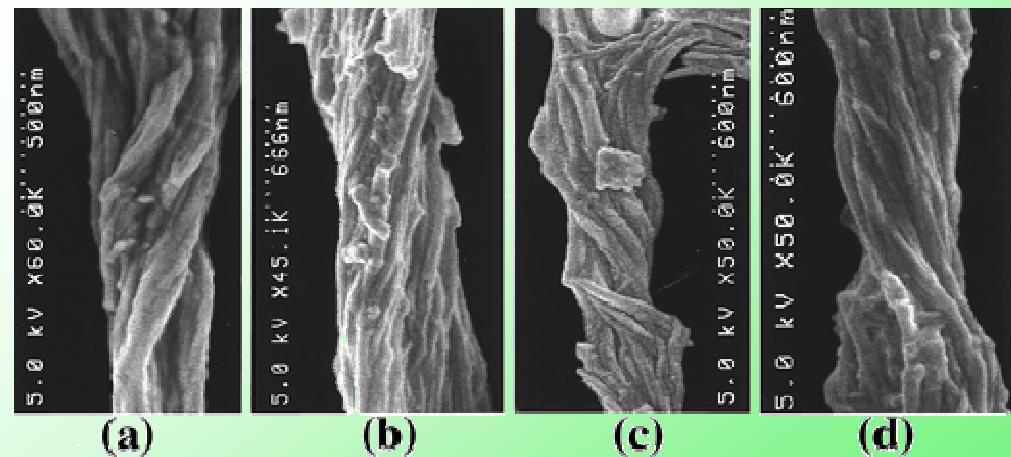


Fibers with helical structure:

Right handed helix from R,R
Left handed helix from S,S

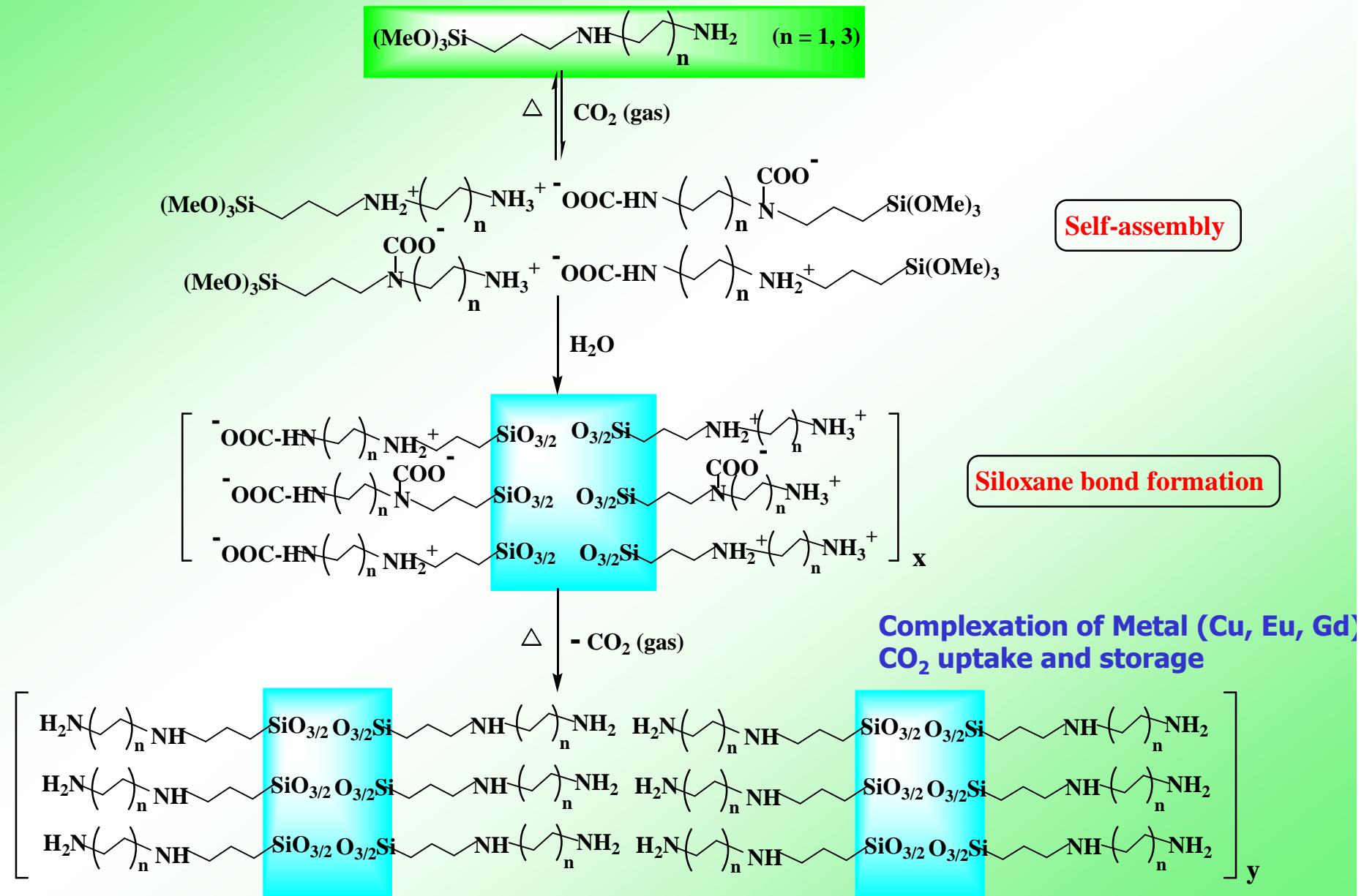
with width: $0.3-1 \mu\text{m}$ length: $15 \mu\text{m}$

A left and right handed helix are self-assemble via H-bonding mediated hydrolysis, according to the configuration of starting material structure.



7) Silica hybrids with lamellar structure by self-assembly (1)

J. P. Corriu, et al., JACS, 2005, 127, 11204

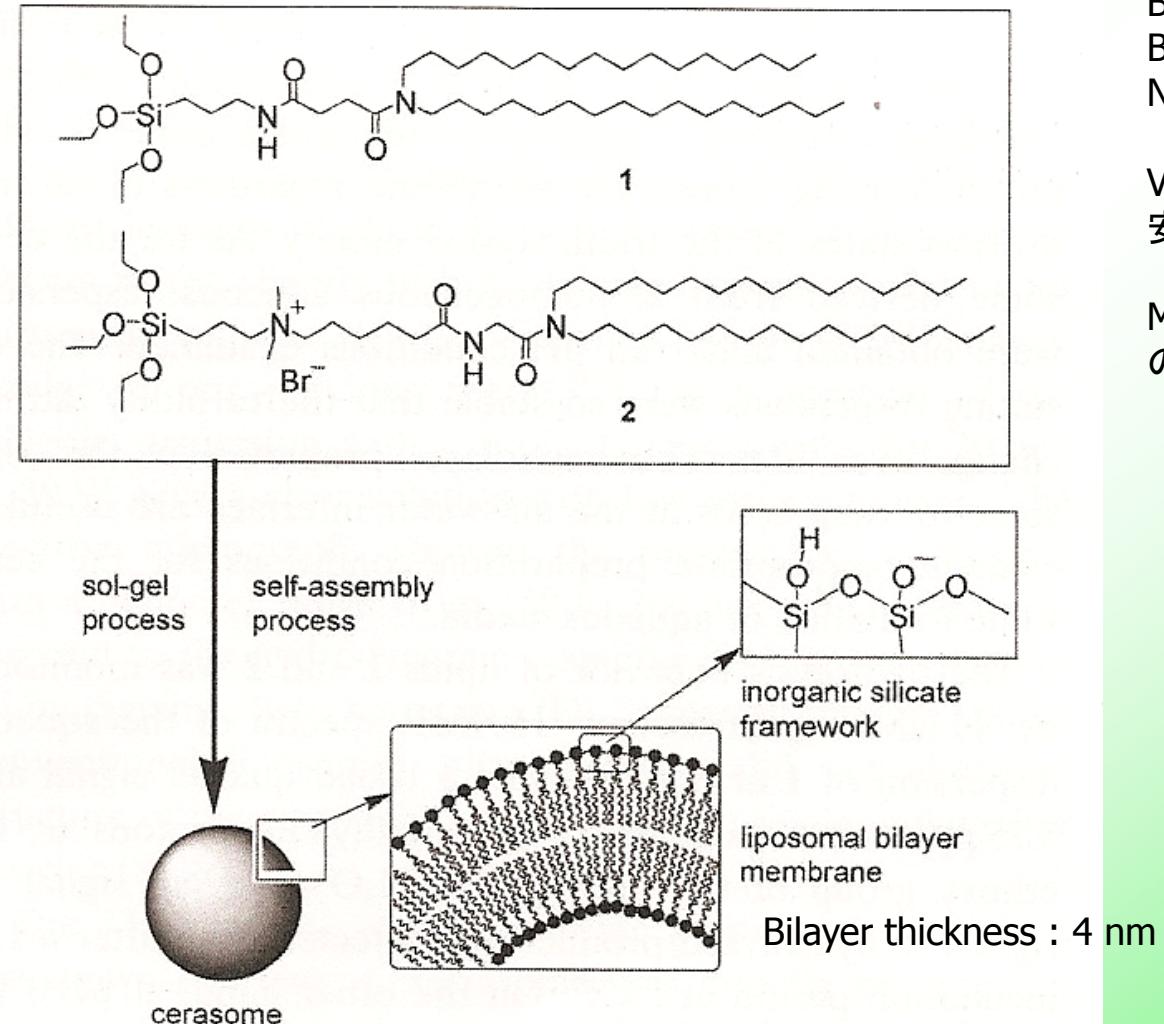


5) Cerasome : bilayer vesicles covered outside with siloxane network

Kiyohumi Katagiri, Jun-ichi Kikuti , et al., Chem. Eur. J. 2007, 13, 5272-5281; J. Am. Chem. Soc., 2002, 124, 7892-7893

Ceramic
+
Liposome
↓
Cerasome

Diameter :
1 : 70-300 nm
2 : 20-100 nm



Biomimetic membranes
Biomembranes
Nanocapsules

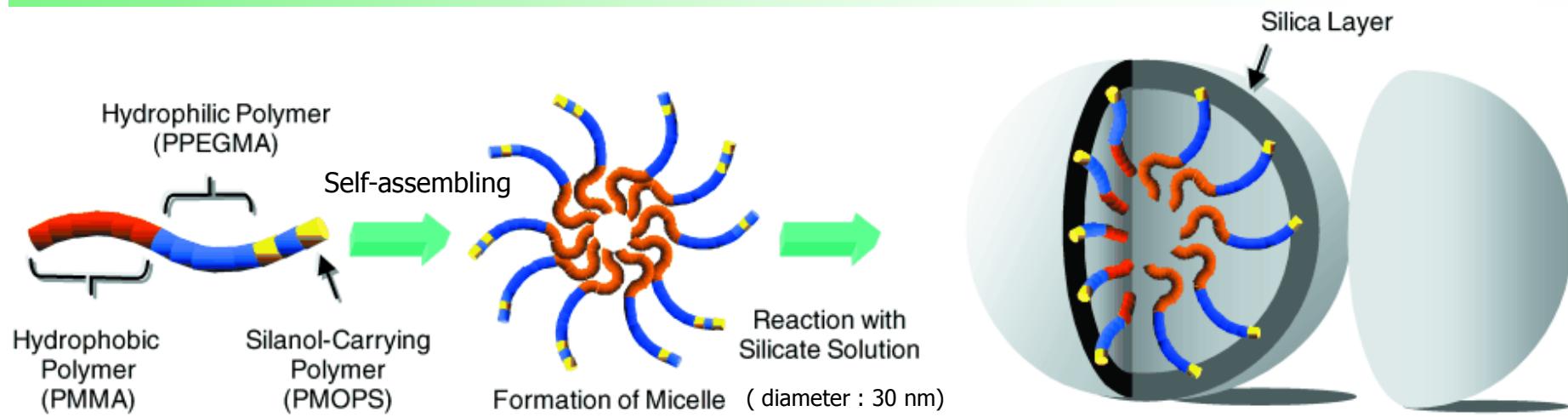
Vesicle: 崩壊、融合
安定化 : silica-support

Monomerによりcapsule
の構造制御可

Figure 1. Molecular structures of the cerasome-forming lipids (1 and 2) and schematic drawing of the cerasome.

9) Hybrid nanocapsules with Si-OH functional micelle template

T. Fukuda, et al., Angew. Chem. Int. Ed. 2003, 42, 4194



Synthesized by ATRP method

PMMA-*b*-PPEGMA-*b*-poly(PEGMA-*r*-MOPS) Methacryloxypropyltrimethoxysilane

$M_w = 20900$ $M_w/M_n = 1.16$

PMMA-*b*-PPEGMA

$M_w = 15500$ $M_w/M_n = 1.11$

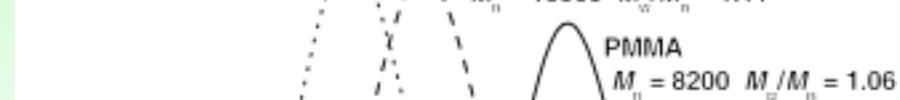
Methacryloxypropyltrimethoxysilane

Poly(ethylene glycol) methyl ether methacrylate

$M_w = 8200$ $M_w/M_n = 1.06$

PMMA

$M_w = 8200$ $M_w/M_n = 1.06$

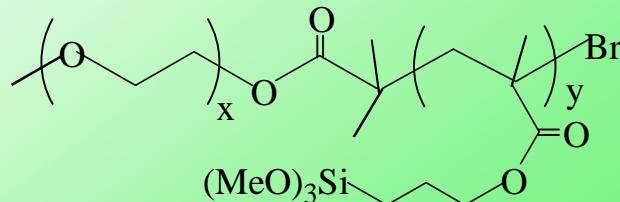


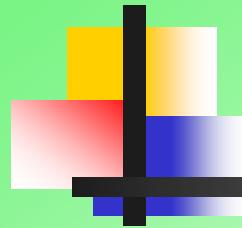
With stable and confined nanoscale cavity

Encapsulation by :

- 1) Molecular assemblies (micelles, liposomes, vesicles, hollow spheres)
- 2) Gel wrapping

Related paper: JACS., 2003, 125, 14710
and the reference cited herein.





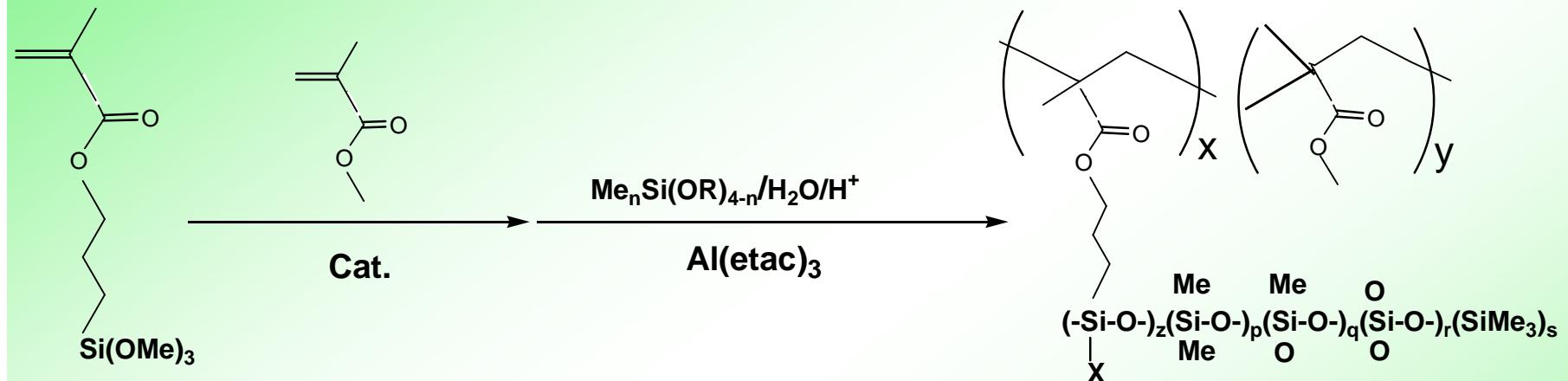
4. 新材料開発の現状

- 1) 有機・無機ハイブリッドコート剤グラスカ (JSR)
- 2) 有機・無機ハイブリッド樹脂コンポセラ(荒川化学)
- 3) 包装材料用ガスバリアフィルム(凸版印刷)
- 4) ガラス用コーティング剤(麒麟ビール)
- 5) HPLC用カラム充填剤 (京大、中西)
- 6) 光硬化及び超耐熱性シリセスキオキサン
- 7) PPE/siloxane hybrids
- 8) Cellulose PPSQ hybrids
- 9) 粘土鉱物一ナイロン6ハイブリッド(豊田中研)
- 10) Nylon, PNIPA/clay hybrid

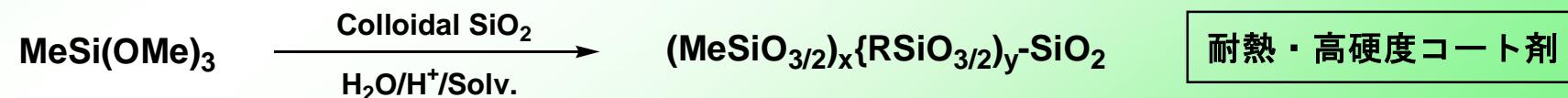
	製品	有機成分	無機成分	反応方法	特徴	企業
	コート剤	MMA	3-MAPS $\text{Me}_n\text{Si}(\text{OMe})_{4-n}$	付加重合 Sol-gel	柔軟、耐光、 耐熱	JSR
	コート剤 (硝子)		TMOS, $\text{Ti}(\text{OPr}^i)_4$, 3-MAPS, VTES	Sol-gel	耐摩耗性、高機 械特性、軽量化	麒麟 ビール
	樹脂	P. amido, PMMA, BPA Phnol res.	$\text{RSi}(\text{OMe})_3$	付加重合 縮合 Sol-gel	耐熱性 電気特性	荒川化学
	薄膜	PVA	TEOS	Sol-gel	耐酸素透過性 耐水性	凸版印刷
	HPLC 充填剤	PEG, EtOH	TEOS	Sol-gel	細孔制御 分離機能	京大
	膜材料		$\text{RSi}(\text{OMe})_3$ (R= H, Vi, Epoxy.)	Sol-gel 附加	光硬化、 超耐熱性	東亞合成
	改質PPE	PPE	Linear, ladder, & cube siloxanes	Mixing	耐熱、耐発火、 高成形性	旭化成
	膜材料	Cellulose	Cube siloxanes	Mixing	低軟化点、高硬 度、高成形性	KRI
	膜材料	Nylon	Clay	Mixing	機械的強度 高熱変形温度	豊田中研
	樹脂、 膜材料	NIPA	Clay	Mixing	高伸縮性、高破 壊弾性、機械強 度、水吸脱着	川村理研

1) 有機・無機ハイブリッドコート剤の開発 (JSR、山田)

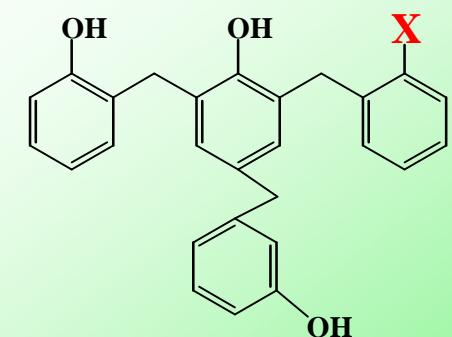
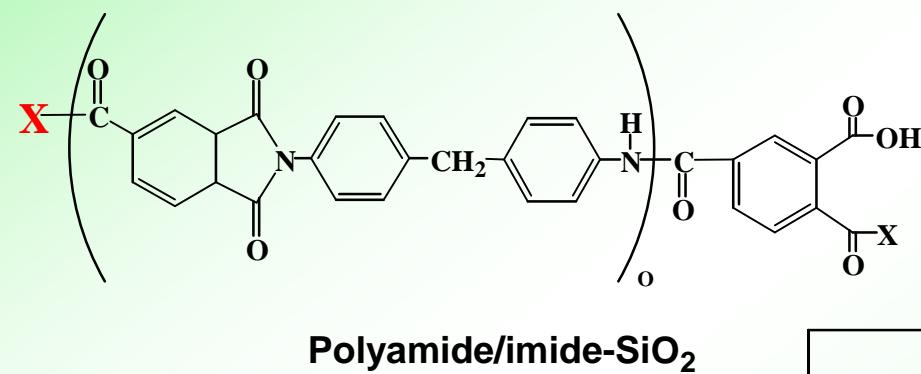
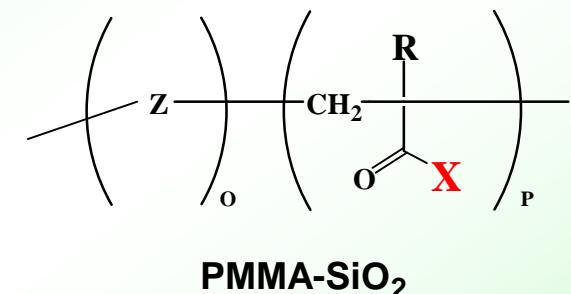
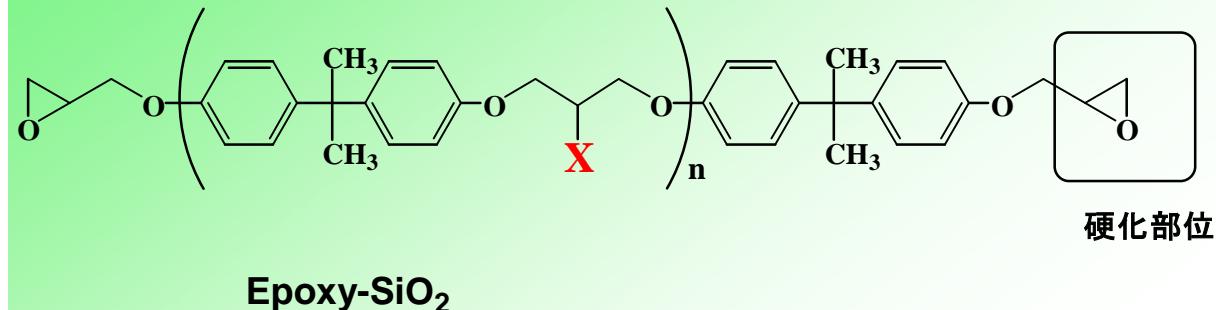
(グラスカ)



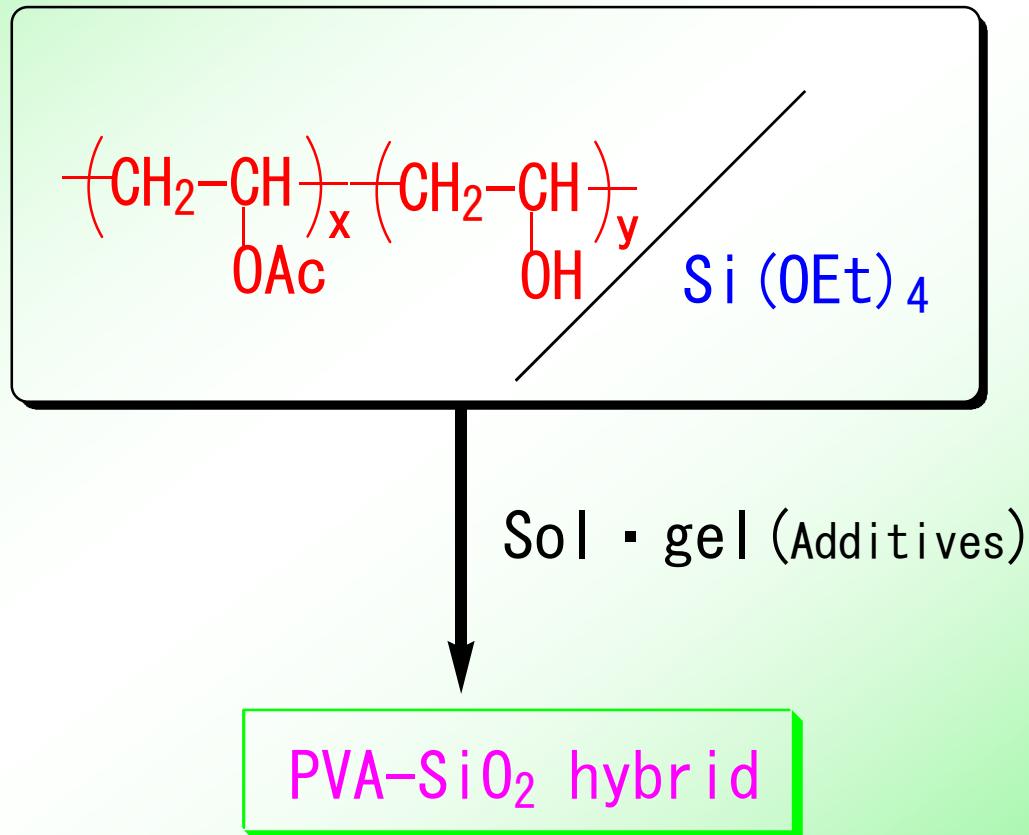
柔軟性、耐光性、耐アルカリ性
耐汚染性、光沢保持率
低水蒸気透過性（シロキサン、アクリル）



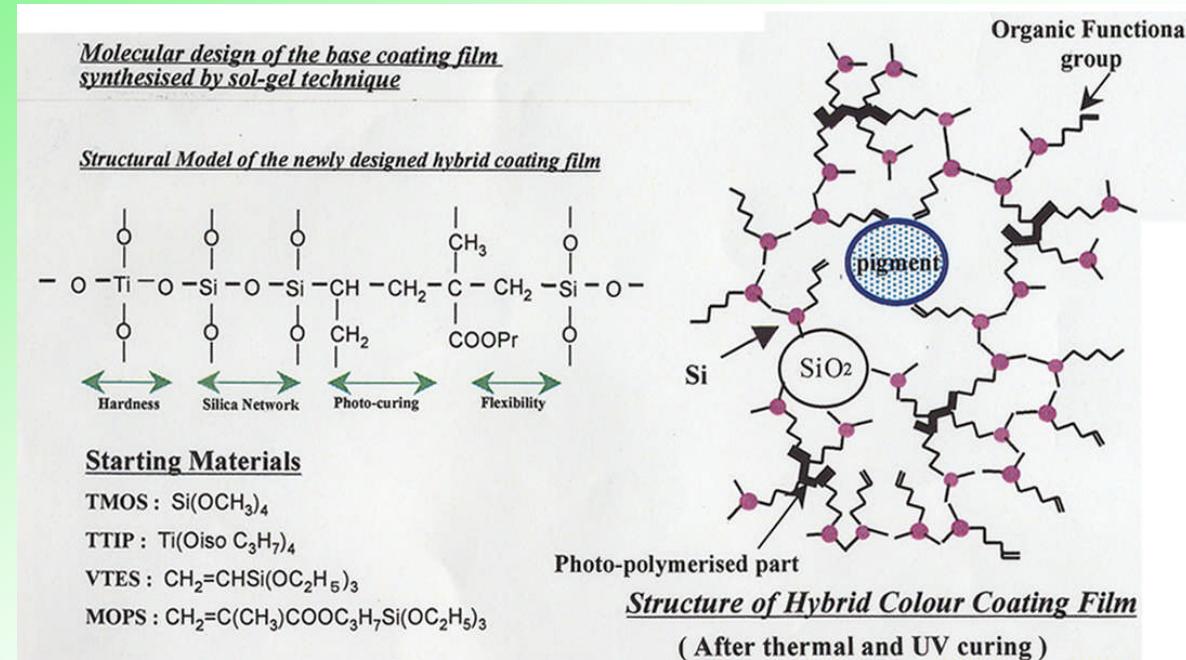
2) 有機・無機ハイブリッド（荒川化学、合田）：コンポセラシリーズ



3) 包装材料用ガスバリアーフィルム

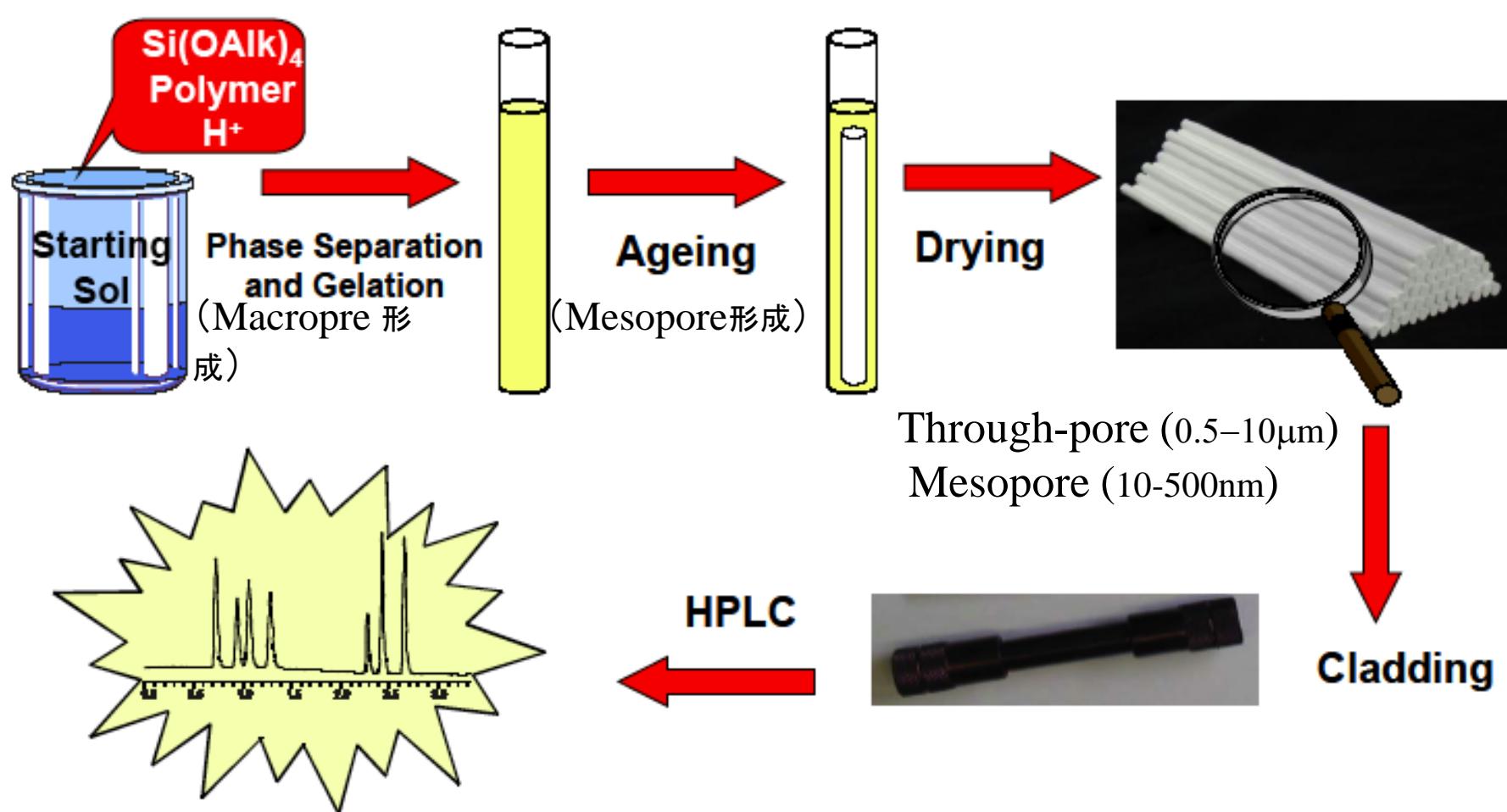


4) ガラス用コーティング剤 (麒麟ビール：白倉)



5) HPLC用モノリス型カラムの開発 (京大、中西)

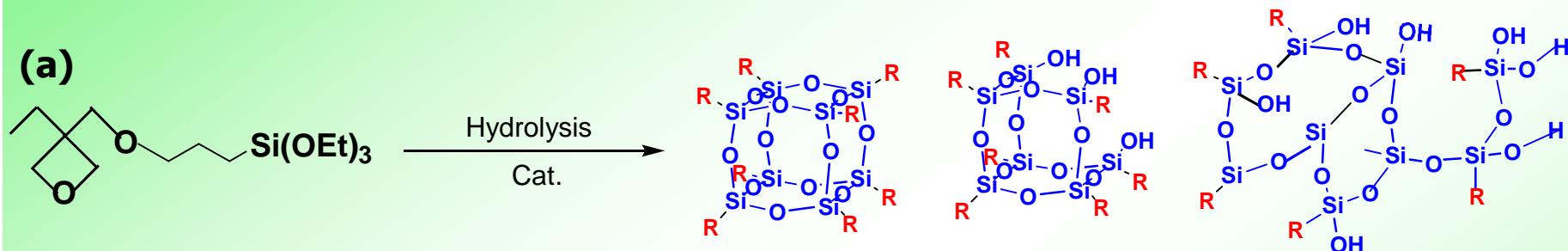
(2000、10月発売)



Sol/gel process : Si(OEt)₄/PEG/EtOH/H⁺

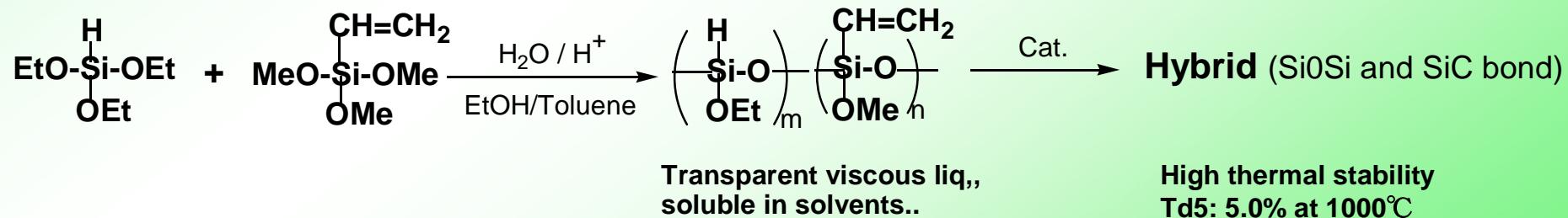
6) 光硬化性(a)および超耐熱性シリセスキオキサン(b)

鈴木 浩、東亞合成株 *Photoinitiated Polym., ACS Symposium Series, 847, 306(2003)*



無色透明光カチオン硬化剤(混合物、Mn 2000)として製品化
エポキシモノマーとの硬化膜: 5H~6H, アセトン耐性良好

(b)



7) Siloxanes / PPE hybrids (to improve low processability)

(Polyphenylene ether(**PPE**) has excellent thermal stability and good inflammability)

池田 正紀、旭化成株

目的:PPEの耐熱性を維持しつつ、溶融流動性(成形性)を改善し、かつ難燃性の向上を図る

各種添加剤によるPPEの特性改善

	(PPE)	添加剤(5 wt %)			
溶融流動	--	--	--	-·-·-	+
難燃性	--	-	--	+	-·-·-

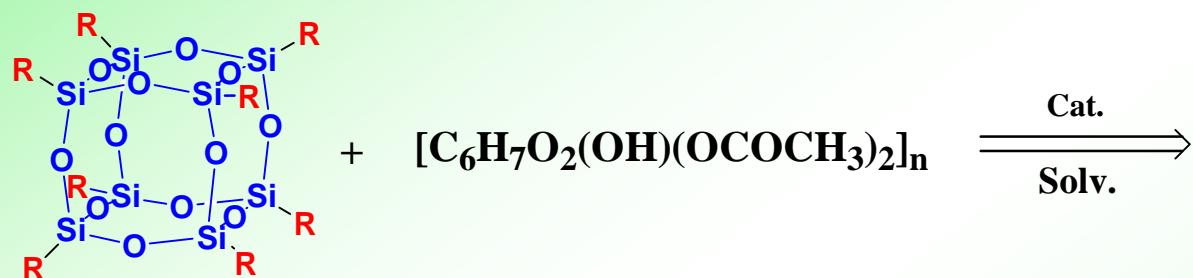
(キューブはPPEの耐熱性(熱変形温度)をほとんどそこなうことはない。)

PE, Nylon 6,6, PBT に対する T_g^{Bu-i} の添加効果はない。
(R. L. Blansky, et al., Nanocomposites 2001 (Chicago))

8) Cellulose/PSSQ hybrid as protecting films

K. Obata, et al., KRI Co. Ltd

As a transparent protecting films



(R=(CH₂)₃-epoxy, (CH₂)₃OCH₂-epoxy)

Amount added : 20, 30 wt%

20 wt%, 30 wt%

Softning temp. 249°C → 205, 193°C

Pencil hardness 1H → 2H , 3H

Young modulus(MPa) 2992 → 2569, 3151

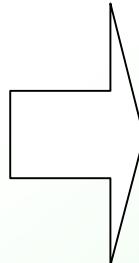
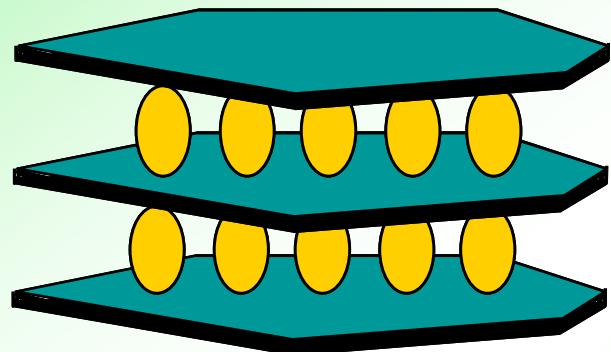
9) 層間重合法による粘土鉱物/ナイロン-6ハイブリッドの生成

(豊田中研 白杵、岡田、加藤、長谷川, 1993)

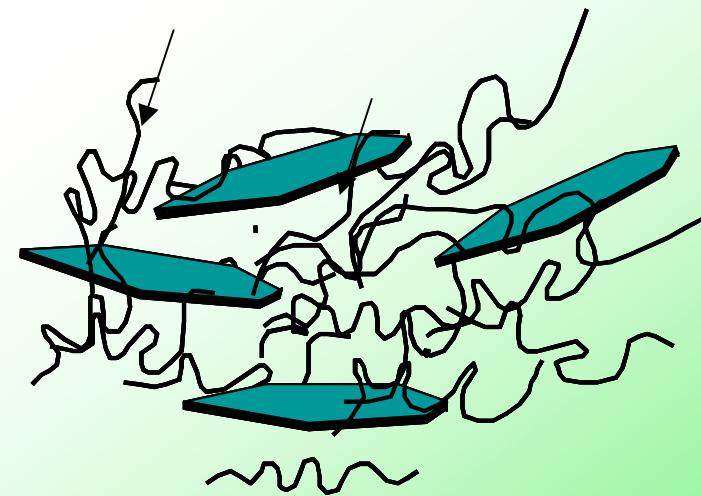
分散型ハイブリッド

Silicate layer

Polymerization



Nylon 6 シリケート層



○ : ε -caprolactam

NCH
(Nylon6-Clay Hybrid)

Properties of NCH

Specimen	Montmorillonite (wt %)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Heat Distortion Temperature (°C at 18.5kg/cm ²)
NCH 5 (層間重合による)	4.2	97	1.9	152
NCC 5 (混合系による)	5.0	61	1.0	89
Nylon 6	0	69	1.1	65

Clay-PP(MAH, Extrusion), Polystyrene(oxazoline), Polyacrylate(Intercalation), Polyimide(Solubilization with solv.)等のハイブリッド系も開発されている。

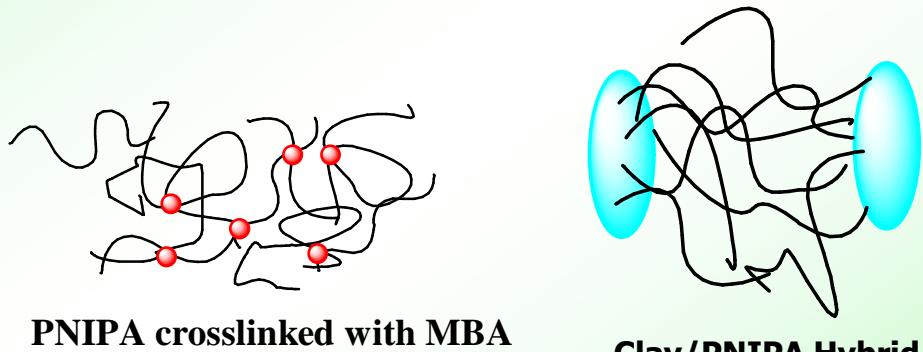
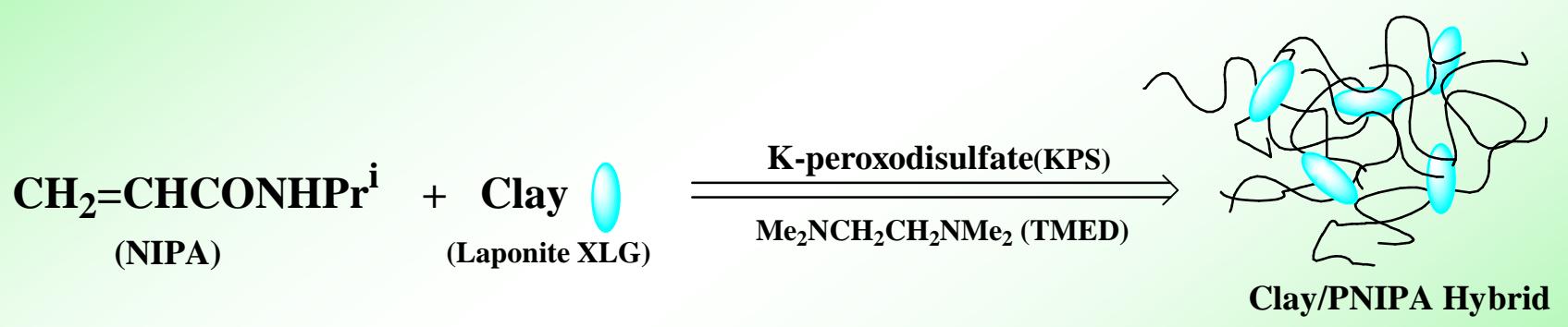
10) PNIPA / Clay hybrids by in situ polymerization (2)

Kazutoshi Haraguchi, et al., Macromol, 2007, 40, 2299, 4287, & 5526;
Adv. Mater., 14, 1120 (2002)

Polymer hydrogels : High H₂O absorption & diffusion rate,
soft mechanical properties, high transp.,
wet surface, good biocompatibility

PNIPA : Stimuli sensitive, etc.

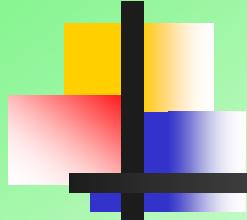
Their disadvantages: Poor mechanical, structural, & absorption
properties due to networks with cross-linkage



Characteristics of Clay/PNIPA :

- 1) Ultra-high elongation (1000%)
- 2) Higher fracture energy (3300 times) than PNIPA gels
- 3) Controlled modulus & strength
- 4) Superb swelling & deswelling

(CH₂=CH-COOCH₂CH₂OMe – Clay system)

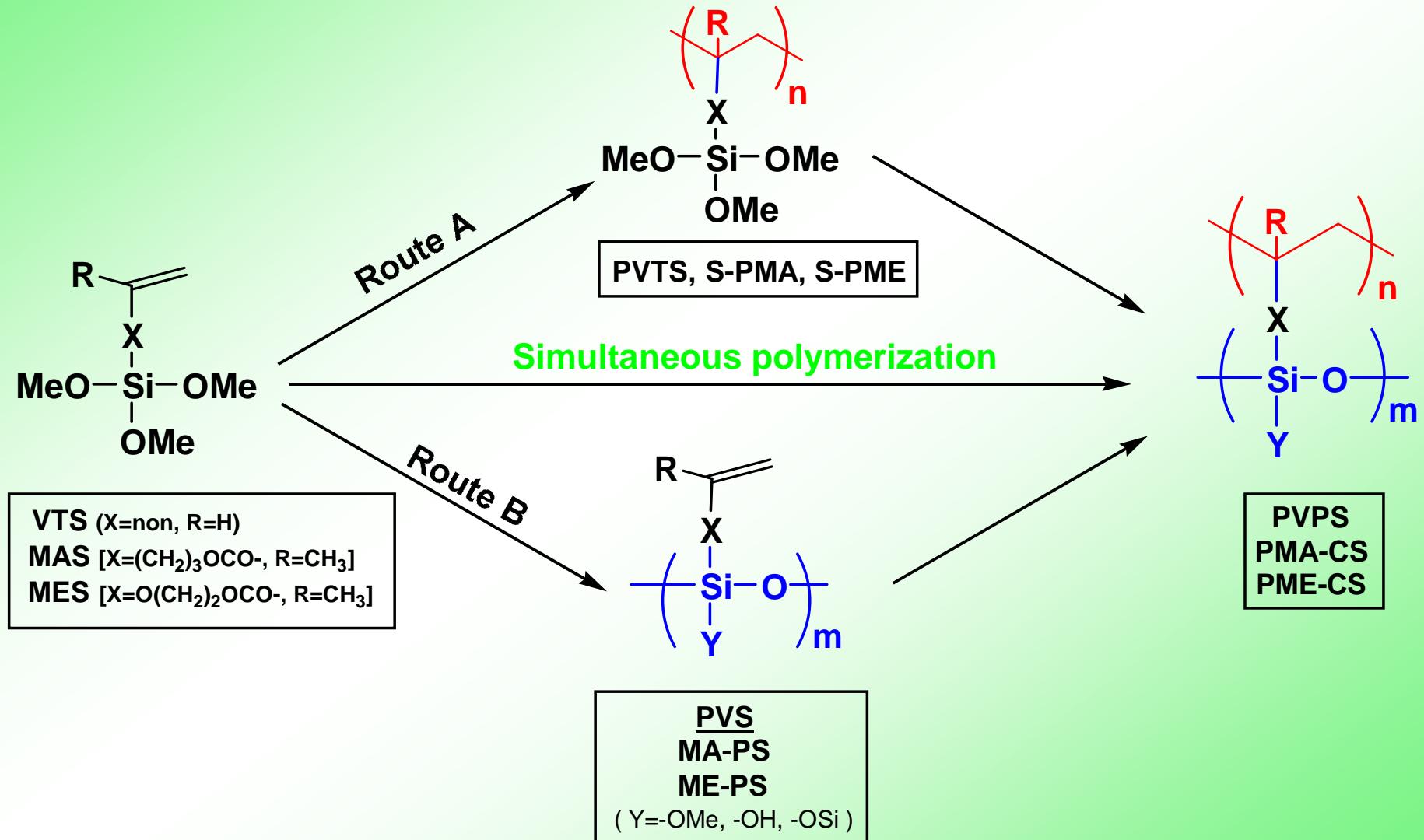


5. ハイブリッドに関する我々の研究

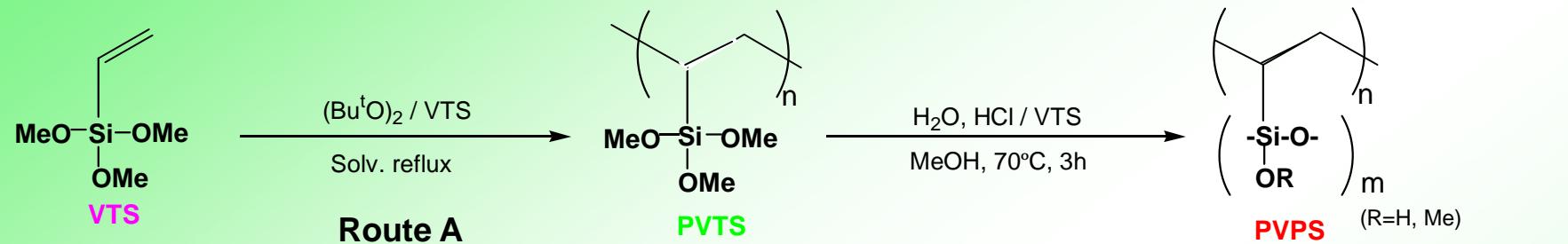
Synthesis of new material :

- 5. 1) Hybrids from VTS, 3-MAS, 2-MES
- 5. 2) Polyalkoxysiloxanes PAOS by sol-gel process of $\text{Si}(\text{OR})_4$
- 5. 3) Oligo- & polysilsesquioxanes

5. 1) Hybrids from VTS, MAS, MES



Synthesis of hybrids from VTS by routes A and B



- 1) Proc. of Colour Mats. (Tokyo), 46-9 (2002).
- 2) Appl. Organometal. Chem., 17, 580-588 (2003).
- 3) J. Sol-Gel Sci. and Tech., 33, 9-13 (2005).

$H_2O, HCl / VTS$

Route B

PVTS	PVPS
D.P. ($M_w \times 10^{-2}$)	$M_w \times 10^{-4}$ (DC%)
76 (113)	8.0 (7.0)
50 (74)	1.7 (9.0), 5.0(9.3), 8 .6(10.3), 17.0(13.3)
22 (32)	1.3(15.9), 2.0(17.2), 4.0(18.1), 13.2(19.0)
13 (18)	1.4(17.3), 2.5(21.4), 4.4(22.8), 14.0(23.3)
4 (6)	0.5(26.1), 1.1(32.6), 3.8(57.5), 5.0(65.2)

$(Bu^tO)_2 / VTS = 0.05 - 0.2$, Solv. : Non, Toluene, Benzene*, : AIBN was used.

Molar ratio : $H_2O / VTS = 0.13 - 0.29$ (* 0.08, 1.00), $HCl / VTS = 0.0002$ (* 0.040 - 0.056)

Table 2 Preparation of VPSQ by hydrolytic polycondensation of VTS ^{a)}

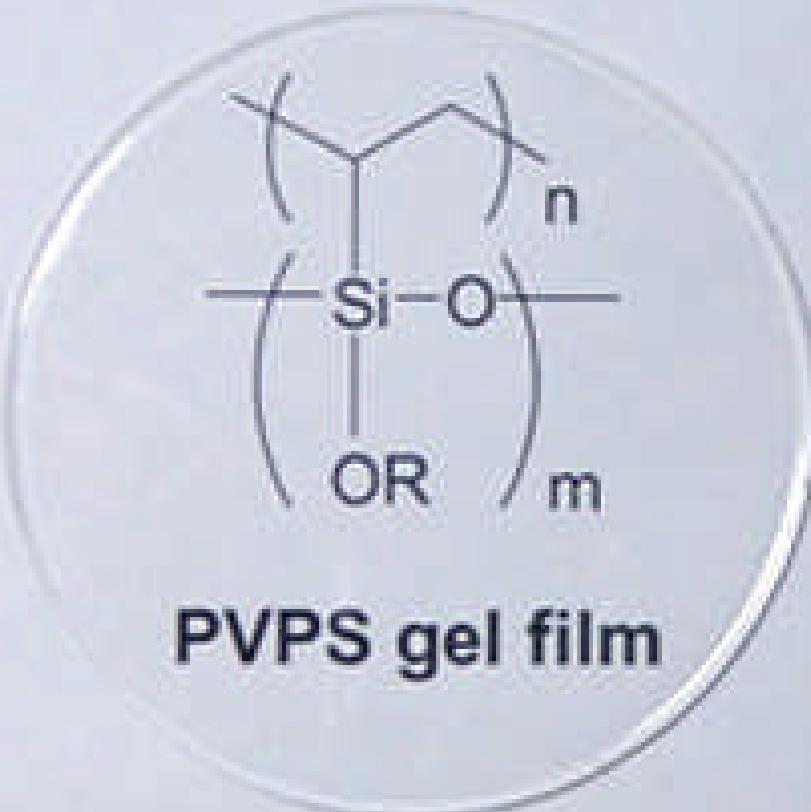
No.	Molar ratio H_2O/Si	GPC		Ratio of siloxane unit			DC (%)
		$M_w \times 10^{-3}$	M_w/M_n	T ¹	T ²	T ³	
7	1.1	1.1	1.4	11	48	41	77
8	1.3	2.1	2.1	3	39	58	85
9	1.45	6.4	2.7	0	28	72	90

a) VPSQ used : 0.0167 mol as Si, $HCl/Si=0.105$, solvent: methanol 14 ml, Temp.: $70^\circ C$, Time: 3 h,
stirring rate: 150 rpm, N_2 flow rate: 360 ml/min.

Free-standing films
Coating films
 $\text{SiO}_2\text{-SiC-C Ceramics}$

4) J. Sol-Gel Sci. & Technol., 16, 227(1999)

Organic-Inorganic Hybrid Gel Film



PVPS gel film



Properties of hybrids PVPS from VTS by routes A and B

	Hybrids by	
	Route A	Route B
Decomp. /°C (DC%)	262–271 (24–25)	320–430 (70–85)
Weight loss/%(1400°C)	45–54 (DC 25%)	22–27 (DC 85–89), 9 (DC 93%)
T%(500 nm)	>93	
R. Index	1. 44	
Tensile strength /MPa (Young's modulus)	1(6) - 14(567)	6(380) - 12(1320)
Adhesion	10(glass), 4-8(nylon)	
Hardness	6B - 7H	
Expansion (ppm/°C)	20	
ϵ	3.8	

Simultaneous polymerization of VTS

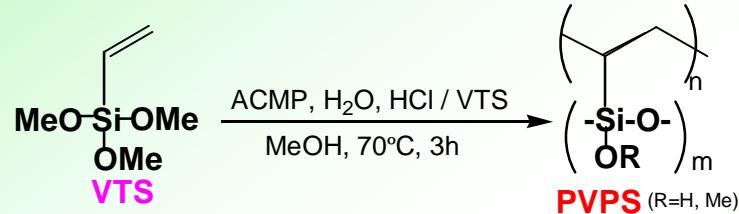


Table 3 Results on the simultaneous polymerization of VTS^{a)}

No.	Solv.	(ml)	Molar ratio			GPC ^{b)}		Yield (%)
			ACMP/VTS	H ₂ O/Si	HCl/Si	Mw	Mw/Mn	
12	—	—	0.05	0.110	0	150000	6.8	33
13		2		0.222	0.028	100000	6.1	55
14	Ethyl lactate	5	0.05	0.444	0.056	135000	5.1	65
15		7		0.600	0.075	114000	5.8	67
16		12		0.955	0.120	120000	5.5	82

a) VTS : 0.1mol ,Stirring rate : 150rpm, Time: 3 h, Temp.: 130 °C, N₂ flow: 50 ml/min.

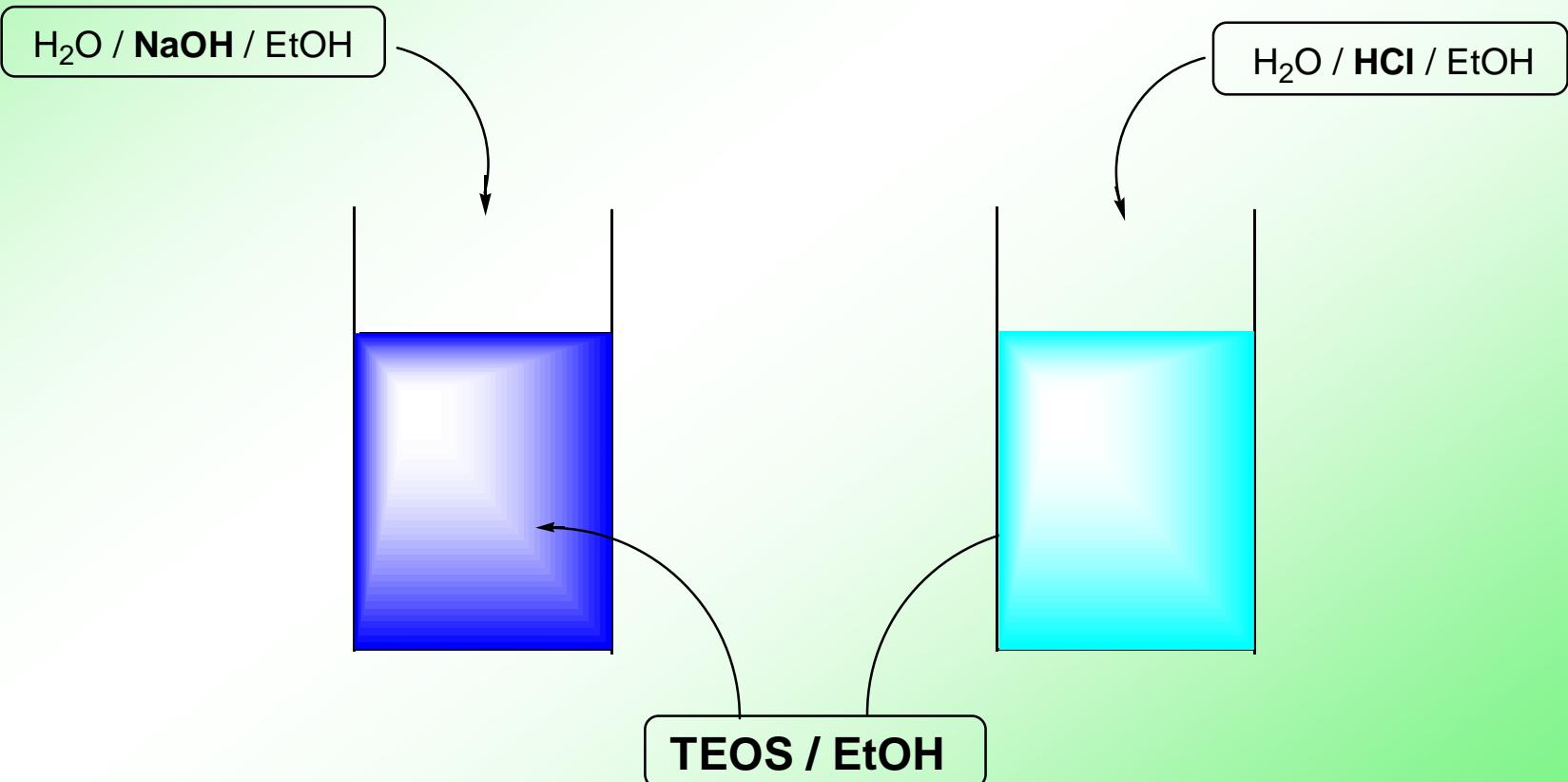
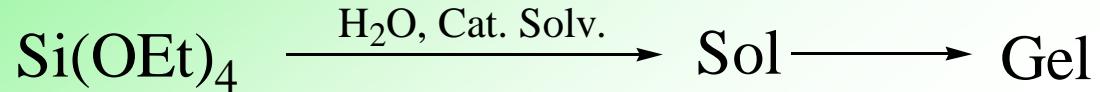
b) Based on polystyrene

Table 5 Reactivity of simultaneous polymerization of VTS

No.	Radical polymerization (%)	²⁹ Si NMR (%)				DC ^{a)} (%)
		T ⁰	T ¹	T ²	T ³	
12	95	90.0	10.0	0	0	3.3
13	91	81.9	13.1	5.0	0	7.7
14	75	71.4	17.1	11.5	0	13.4
15	67	68.7	13.7	11.6	6.2	18.5
16	57	56.4	10.2	19.8	13.6	30.2

a) Degree of condensation of siloxane bonding.

5. 2) 目で見るゾルゲル反応



5. 2) Synthesis of PAOS by Sol-gel process of Si(OR)₄

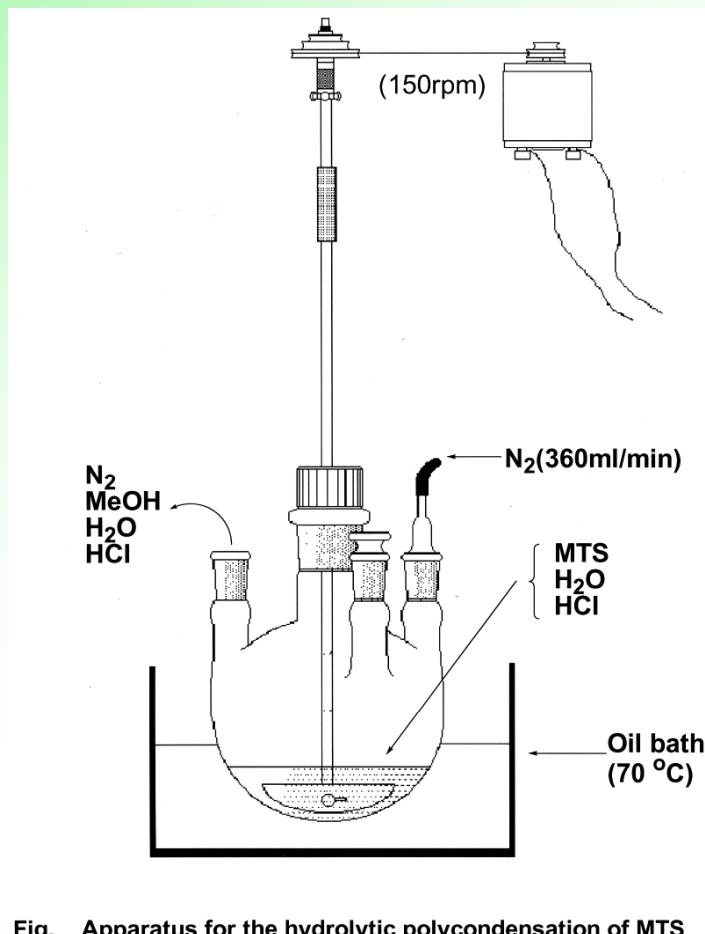
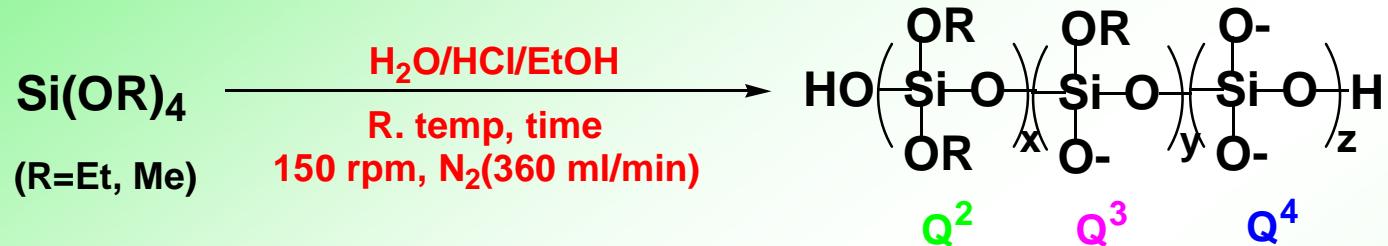


Fig. Apparatus for the hydrolytic polycondensation of MTS

PAOS

Stability to self-cond.
Soluble in solvents
High molecular weight
Spinnability
Adherent

構造制御 : Q²
Q³

市販工業材料との比較

・市販工業材料

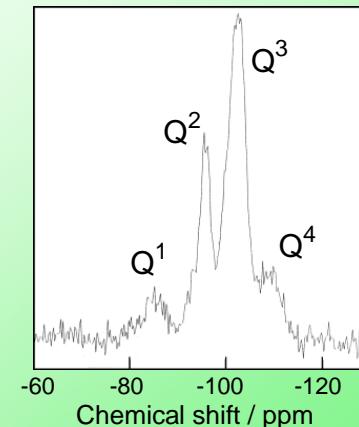
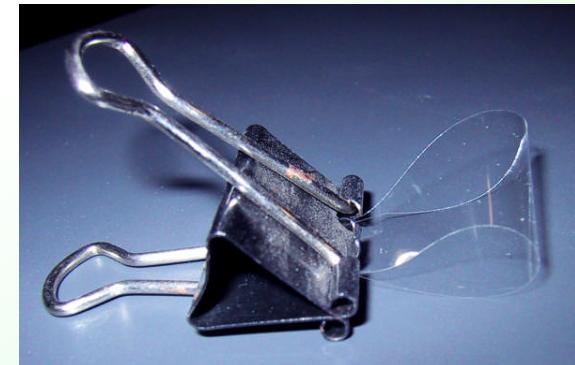
	Mn	SiO ₂ %
SE40 :	700 – 1,200	40 (TEOSと溶媒を含む低分子量体の混合物)
HAS :	~ 2,000	50 (TEOSとTEMOSの共縮合物)

・Polyalkoxysiloxanes (Et, Me)

	Mw (Mw/Mn)	SiO ₂ %
Et :	1,700 – 11,700 (1.2~3.8)	60<
Me :	2,700 – 31,000 (1.7~8.2)	70<

縮合に対し安定
有機溶媒に可溶
高い付着力
柔軟な自己支持膜の形成
主な構造単位: Q³ (55~65%)
Q² (30~20%)

H ₂ O/TEOS	1.6 - 1.8
Tensil s. (MPa)	1.6 - 5.2
Young's m. (MPa)	34 - 156



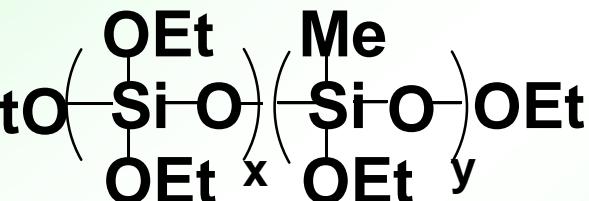
²⁹Si CP / MAS NMR spectra of PEOS

共重合体の合成



TEOS

MTES



As confirmed by:

- $x/y = 1$ (^1H NMR, ^{29}Si NMR)
- T^3 : shift to lower field vs PMSQ
- No signal shift after reprecipitation
- GPC (unimodal)

- TEOS/MTES=1, 1.5, 2.3
- $M_w : 3,000 \sim 10,000$ (M_w/M_n 1.7~2.9)
- Stable to self-condensation
- Soluble and spinnable
- Free-standing and coating films (~6H)

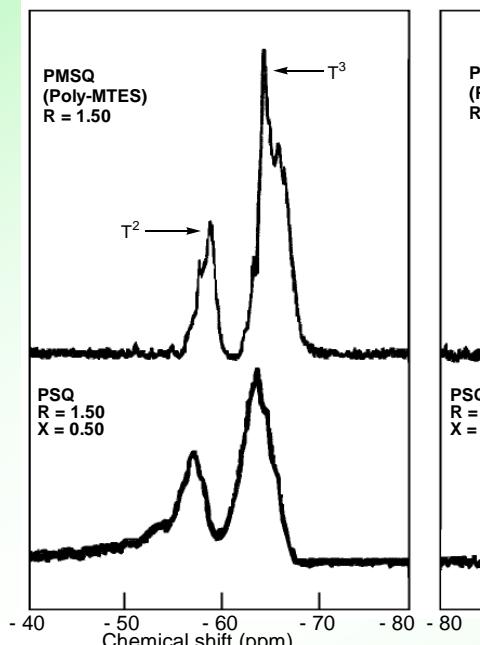


Fig. 5 ^{29}Si NMR spectra of Poly-MTES and Poly-(MTES/TEOS) on T-area
 $R = \text{H}_2\text{O} / (\text{TEOS} + \text{MTES}), X = \text{MTES} / (\text{TEOS} + \text{MTES})$

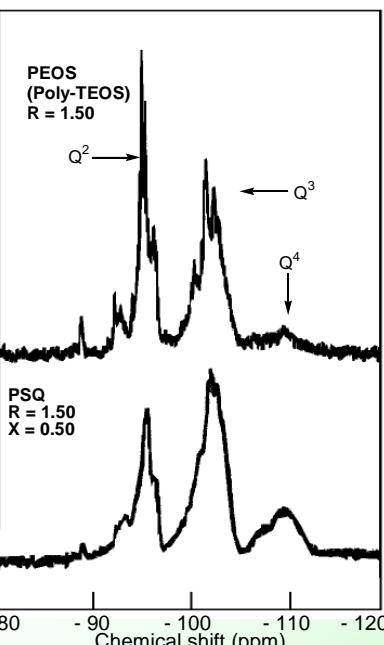


Fig. 6 ^{29}Si NMR spectra of Poly-TEOS and Poly-(MTES/TEOS) on Q-area

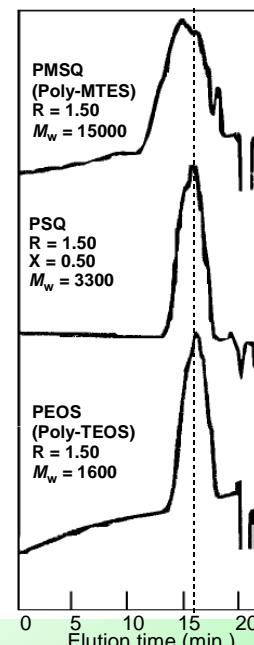
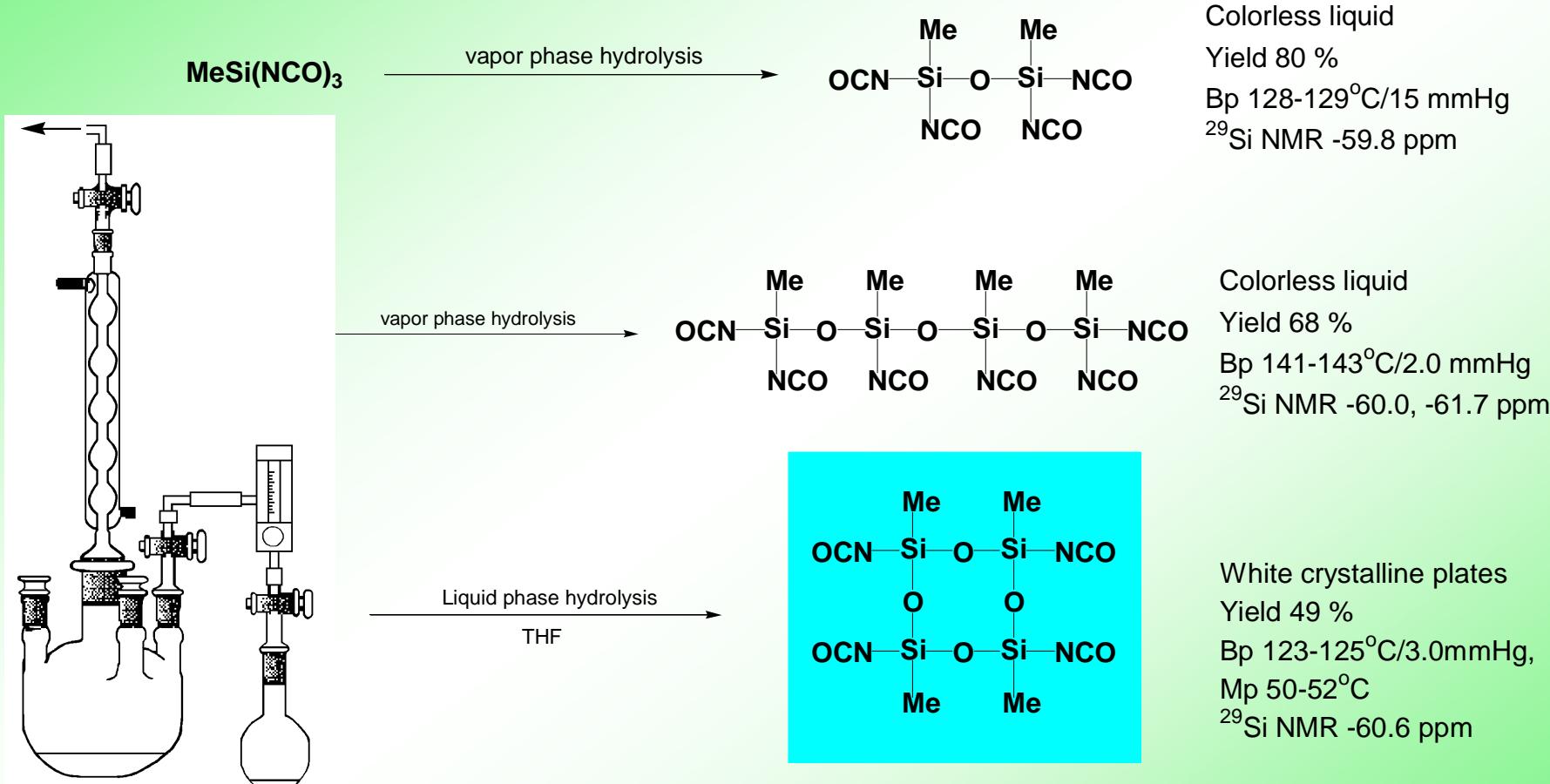


Fig. 7 GPC traces of polymers



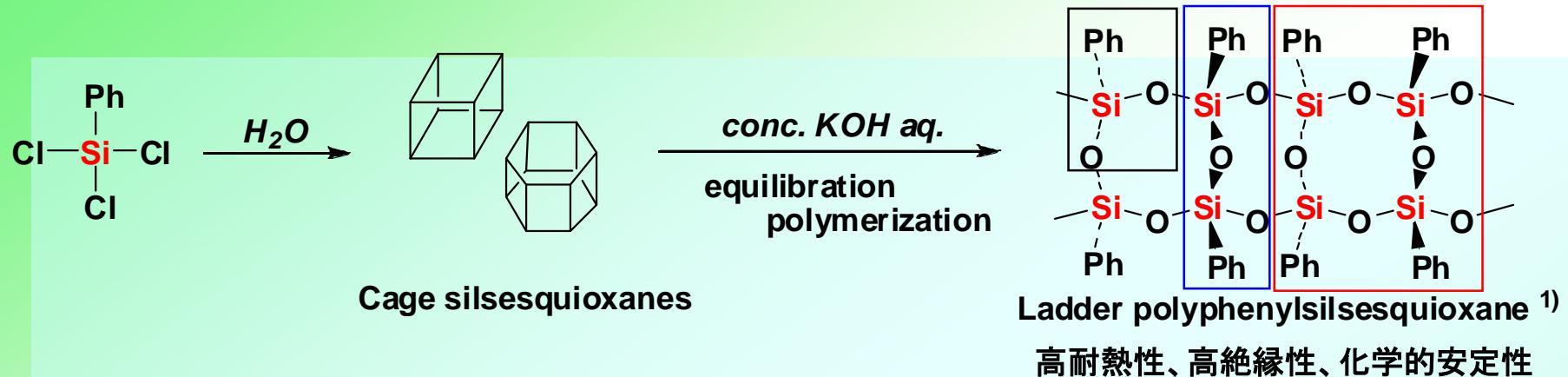
Fig. 9 Gel film prepared from PSQ

5. 3) Oligo- & polysilsesquioxanes

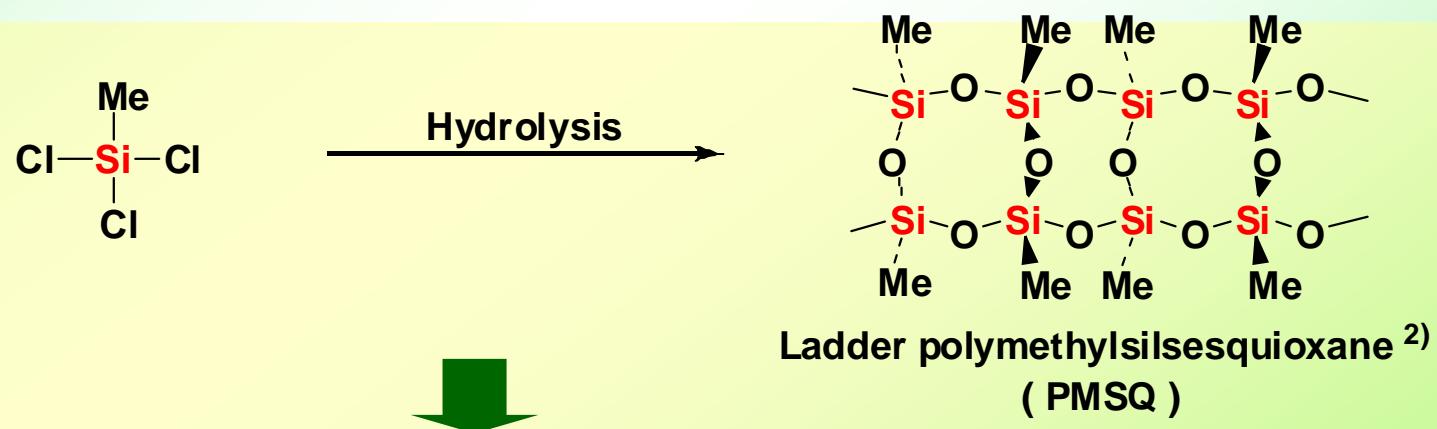


Abe, Y. et al. *Chem. Lett.* 2006, 35, 114.

- Vapor phase hydrolysis provides a very convenient method to prepare sila-functional oligosilsesquioxanes.
- The silane **4** is a potential building block. In order to obtain **4** in good yields, there are the key factors to be considered: 1) Intramolecular condensation from 3 to 4. 2) Molar concentration of substrate on the reaction.



背景



3官能性シランからラダー性の高いPMSQは得難い

1) Brown, J. F. et al., *J. Am. Chem. Soc.* **1960**, 82, 6194.

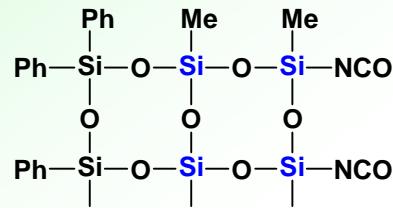
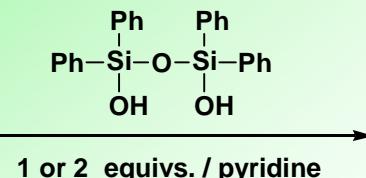
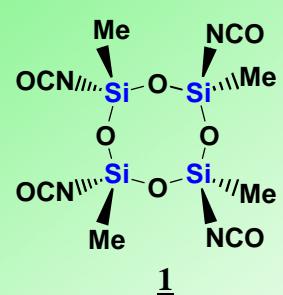
2) Merrill, D. F. *Canadian Patent*, 868996, 1971.

3) Itoh, M. *Silicon Chemistry Japan* **2001**, 15, 19.

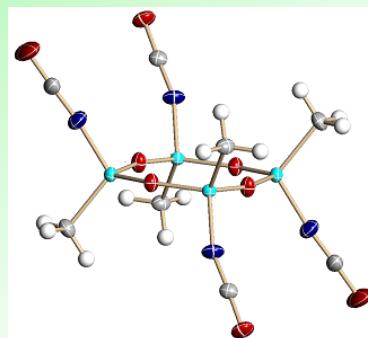
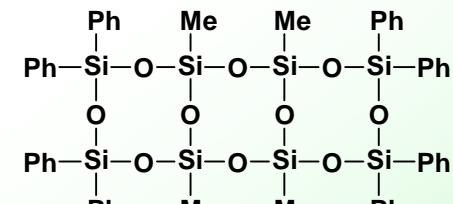
Synthesis of ladder oligosilsesquioxanes

(to obtain spectral data for the structure of perfect ladder polysilsesquioxanes)

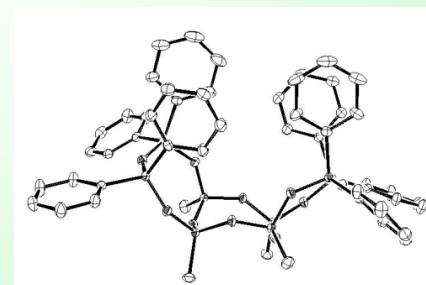
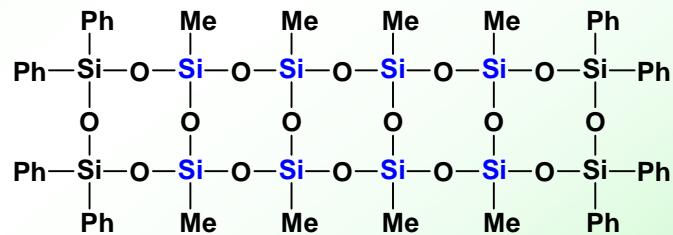
Seki, H. et al., *J. Organomet. Chem.*, in press.



or

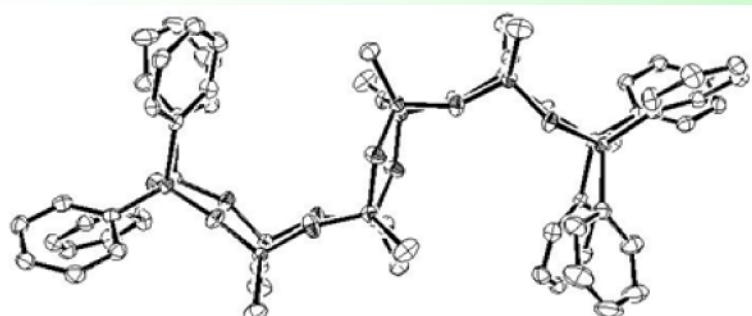


cis,trans,cis-configuration



syn-configuration

Abe, Y. et al. *Chem. Lett.* 2006, 35, 114.

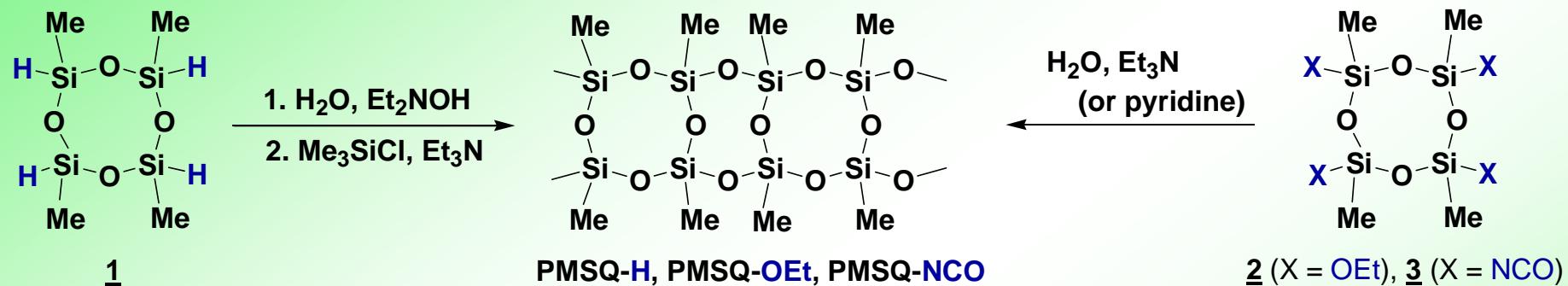


syn,anti,syn-configuration

Seki, H. et al., *Chem. Lett.*, under contribution.

Synthesis of polymethylsilsesquioxane

(with controlled ladder structure has never been obtained.)



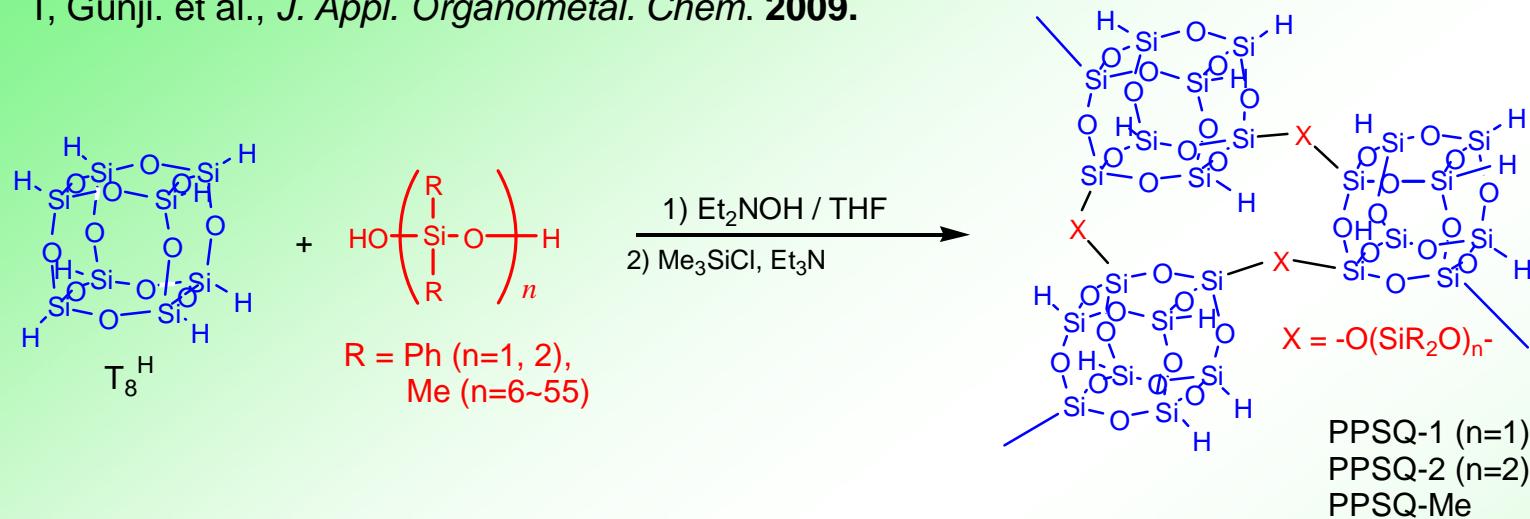
Results on synthesis of PMSQs and the data to estimate ladderness

x	State	Yield, %	M_w	M_w/M_n	a	$\Delta_{1/2}$	T^3/T^2
H	W. pow.	97	42,000 ^{a)}	2.7	0.38	190	3.6
OEt	Vis. liq.	56	55,000	5.8		184	1.3
NCO	W. pow.	72	70,000 ^{b)}	2.1	0.53	118	8.9

a) 214,000 b) 285,000

Synthesis of polyhedral polysilsesquioxanes (PPSQ)

T. Gunji. et al., *J. Appl. Organometal. Chem.* 2009.



	Diol / T_8^H	State	Mw	Mw/Mn
PPSQ-1	2	White powder	45000	2.0
	4	White powder	11000	1.5
PPSQ-2	2	White powder	27000	1.8
	4	White powder	9000	1.6
<hr/>				
		550	White powder	45000
PPSQ-Me	1100	H.viscous liq.	41000	3.2
	4200	H.viscous liq.	9000	2.7

- Gels were formed in Diol / $T_8^H = 1$ (PPSQ-1 & -2)
- PPSQs were soluble except for MeOH and C_6H_{14} for PPSQ-1 & -2)

Synthesis of PPSQ-H from T_8^H

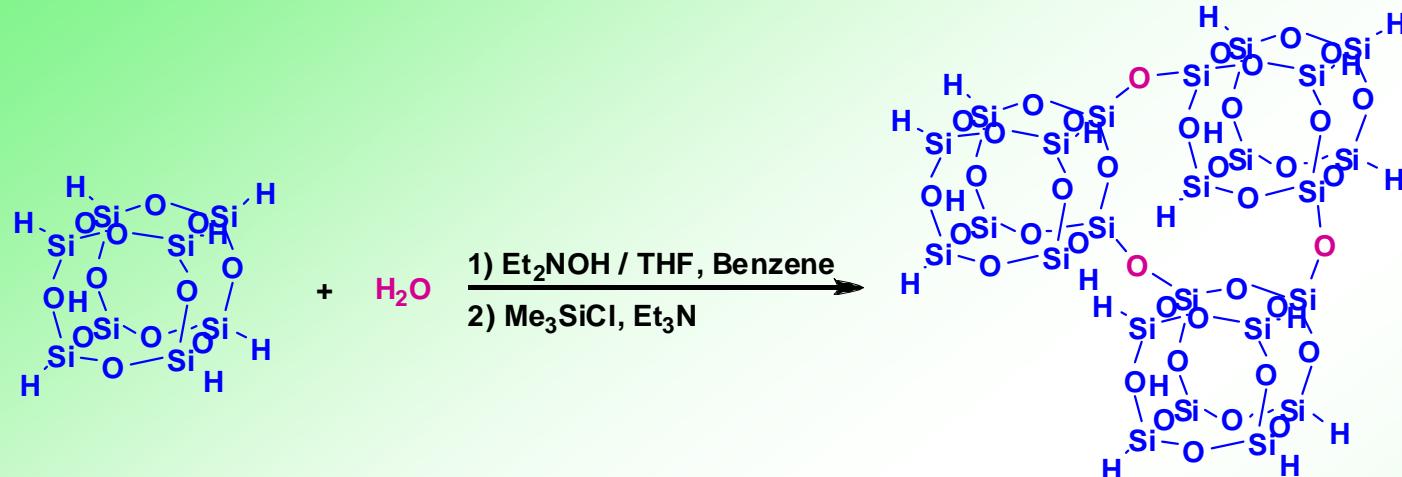


Fig. Free standing film

	H_2O / T_8^H	State	Mw	Mw/Mn
PPSQ-H	1	Gel		
	2	White powder	29000	2.0
	4	White powder	15000	1.9

• PPSQ-H were soluble in organic solvents except for MeOH

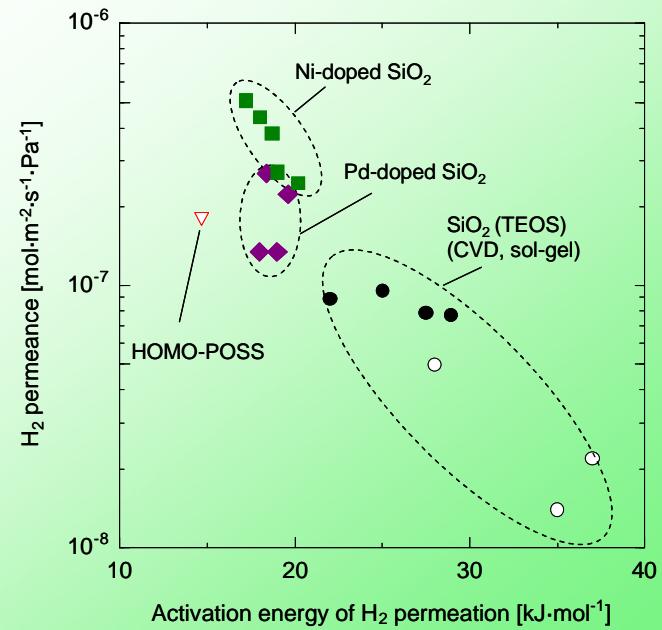


Fig. He/H₂ permeance ratio at 500°C

おわりに

1. これまでの約40年間にわたる研究により多くの貴重な成果が得られるとともに、若手研究者の著しい進出があり、これらが今後の研究推進の原動力になると期待される。
2. 自己組織化および粘土鉱物-有機高分子系の複合化領域で、新材料の創製と製品の上市も実現されつつある。
3. ここ数年包装材料、コート材の上市があり、エレクトロニクス、封止、添加物材料の技術開発も具体化されつつある。
4. 医薬、医療、生体関連材料創製における新展開が期待できる。
5. この分野に研究開発と材料の製品化に大きな可能性と期待が寄せられている。