Hierarchically Porous Monoliths
Preparation and Application to Separation Sciences

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Outlines

• Preparation of hierarchically porous monolithic silica via sol-gel accompanied by polymerization-induced phase separation

• Advantages of monolithic silica columns in HPLC separations

• State-of-the-art performance and perspectives
Outlines of Sol-Gel Method

14 Uniform Particles

2 3 Sol

4 Gelation

5 Evaporation

6 Gel

8 Solvent Extraction

9 10 Aerogel

13 Evaporation of Solvent

11 Heat

11 13 Dense Film

(11) Films: AR Sensor

14 Glass Ceramics

Catalytic Sealing Glasses

Dielectric Catalyst Supports

Protective Fiber Optic Preforms

Controlled-Pore Glasses

Dense Ceramic

Sol–Gel Reactions of Silica

Hydrolysis:

$$\text{Si(OR)}_4 + n\text{H}_2\text{O} \rightarrow \text{Si(OR)}_{4-n}(\text{OH})_n + n\text{ROH}$$

$$(n = 1 \sim 4)$$

Polycondensation:

$$\equiv\text{Si–OR} + \text{HO–Si} \equiv \rightarrow \equiv\text{Si–O–Si} \equiv + \text{ROH}$$

$$\equiv\text{Si–OH} + \text{HO–Si} \equiv \rightarrow \equiv\text{Si–O–Si} \equiv + \text{H}_2\text{O}$$
GOAL

To Prepare Oxide Gel Materials with ...
Precisely Controlled
Pore Volume
Pore Size
Size Distribution
in Discrete Size Ranges
Control of Macropores through Polymerization-Induced Phase Separation
Preparation of Hierarchical Macro- & Mesoporous Monoliths

Starting Sol → Phase Separation and Gelation → Aging and Solvent Exchange → Evaporation Drying

Si-Alkoxide
Water
Acid Catalyst

+ Water-Soluble Polymer
Surfactant
Polar Solvent

Meso- & Micropores

Interconnected Macropores

Volume: <1.5 cm³g⁻¹
Diameter: 0.1 - 10 μm

Volume: 0.2 - 2 cm³g⁻¹

Heat-Treatment (up to 600°C)

Double Pore Silica

Sintering (>1000°C)

Porous Silica Glass
What drives the system to separate into phases?

- Gibbs free energy change on mixing

\[ \Delta G = \Delta H - T\Delta S \]

- Lowering temperature
- Decreasing entropy (polymerization)
- Increasing enthalpy (repulsive interaction)

Any change that increases \( \Delta G \) destabilizes the system.
Phase Separation Induced by $T\Delta S$ Term

Comparison between

Physical and Chemical Cooling

Diagram showing a comparison between physical and chemical cooling processes, with temperature on the y-axis and composition on the x-axis.
Transient structures of spinodal decomposition are spatially arrested by sol-gel transition as a permanent morphology.
Time Evolution of Phase Domains by Spinodal Decomposition

height = 230mm

230mm

146mm

shortly after gelation

after aging

230mm

230mm

230mm

230mm
Relation between Composition and Resultant Morphology

- **Solvent**
  - Macroscopic Phase Separation

- **Silica**
  - Smaller Pore Size

- **PEO**
  - Higher Pore Volume

- **No Macropores**
Independent Controls of Pore Diameter and Pore Volume

Constant Pore Size

Pore Volume, $V_p / \text{cm}^3\text{g}^{-1}$

Pore Diameter, $D_p / \mu\text{m}$

Constant Pore Volume

Pore Volume, $V_p / \text{cm}^3\text{g}^{-1}$

Pore Diameter, $D_p / \mu\text{m}$
Tailoring Mesopores by Aging Process

Without Affecting Macropores
Preparation of Hierarchical Macro- & Mesoporous Monoliths

Starting Sol → Phase Separation and Gelation → Aging and Solvent Exchange → Evaporation Drying

Si-Alkoxide Water Acid Catalyst + Water-Soluble Polymer Surfactant Polar Solvent

Meso- & Micropores

Volume: <1.5 cm³g⁻¹

Interconnected Macropores

Volume: 0.2 - 2 cm³g⁻¹ Diameter: 0.1 - 10 μm

Heat-Treatment (up to 600°C)

Double Pore Silica

Sintering (>1000°C)

Porous Silica Glass
Relation between Surface Curvature and Solubility  
(Ostwald Ripening)

Gibbs–Thomson Eqn.

\[ S = S_0 \exp\left(\frac{2\gamma_{SL}V_m}{R_g T r}\right) \]

- \( S \) : Solubility of interface with radius of curvature, \( r \),
- \( S_0 \) : Solubility of flat interface (\( r = \infty \)),
- \( \gamma_{SL} \) : Solid–liquid interfacial energy
- \( V_m \) : Molar volume of solid, \( R_g \) : Gas constant,
- \( T \) : Temperature, \( r \) : radius of curvature

- Average pore size increases
- Specific surface area decreases
Temperature & pH Dependence of Solubility of Silica

The graph shows the solubility of amorphous silica in ppm as a function of pH for different temperatures. The solubility increases with increasing pH and temperature. For example, at 0°C, the solubility is lower compared to 200°C. The graph indicates that the solubility is significantly higher at higher pH values, especially at elevated temperatures.
Structural Evolution during Aging in Weakly Basic Condition

Small-Angle X-ray Scattering

Scattering Intensity (a.u.)

$10^8$
$10^6$
$10^4$
$10^2$
$10^0$

Scattering Vector, $q / \text{nm}^{-1}$

$0.1$
$1$

$1.61$
$2.66$
$3.35$
$3.53$
$4.00$
$120h$

$1h$
$4h$
$12h$

$2^9\text{Si-NMR}$

Chemical shift / ppm

Changes in $2^9\text{Si NMR}$ spectra of sol-gel-derived silica gel immersed in 1 mol dm$^{-3}$ NH$_3$ aqueous solution at 40 °C
Mesopores after Basic Aging and Calcination

Differential Pore Volume, \( \frac{dV_p}{d(\log D_p)} / \text{cm}^3 \text{g}^{-1} \)

Pore Diameter, \( D_p / \text{nm} \)

- 0.1M 25°C
- 0.1M 40°C
- 1M 40°C
- 1M 60°C
- 1M 80°C
Distribution of Hierarchical Macropores and Mesopores

Cumulative Pore Volume, $V_p / \text{cm}^3\text{g}^{-1}$

Differential Pore Volume, $dV_p / d(\log D_p) / \text{cm}^3\text{g}^{-1}$

Pore Diameter, $D_p / \mu\text{m}$
Monolithic Silica as a Separation Medium for HPLC (Including Silica-MSQ Hybrid)
Liquid Chromatography (Twett 1907)

Chromatographic Process

Distribution: 
\[ K = \frac{C_s}{C_m} \]

Elution through the Column

Chromatogram
LC separation and theoretical plates

Number of theoretical plates
\[ N = 16\left(\frac{t_r}{\omega}\right)^2, \quad N = 5.54\left(\frac{t_r}{\omega^{1/2}}\right)^2 \]

Height equivalent to Theo. Plate
\[ H = \frac{L}{N} \] (L: column length)
Particle-packed vs. Monolithic Columns

- Smaller Particles
- Higher Efficiency
- Column Pressure
- Thinner Gel Skeleton
- Continuous Macropores
- Continuous Skeletons
- Higher Efficiency
- Higher Permeability
- Higher Mech. Stability
Van Deemter Curve (Plate Height vs. Linear Velocity)

\[ H = A + B/u + Cu \]

A: Eddy (Multi-path) Diffusion
B: Longitudinal Diffusion
C: Mass Transfer between stationary and mobile phases + within S.P.

\[ H = \frac{L}{N} \]

L: Column Length
N: Plate Number

\[ H = \frac{1}{C_e d_p} + \frac{1}{C_m d_p^2} u + \frac{C_d D_m}{u} + \frac{C_{sm} d_p^2}{D_m u} \]

Lower Plate Height (\( H \)) means Higher Efficiency (\( N \))
Van Deemter Curves of Monolithic and Particulate Columns

Solute: amylbenzene, mobile phase: 80 % methanol, temperature: 30 °C.
Mobile phase: 80% methanol, temperature: 30 °C.
The pressures were normalized to the column length of 83 mm.
Separation Impedance (time and pressure dependence)

\[ E = \left(\frac{t_0}{N}\right) \left(\frac{\Delta P}{N}\right) \left(\frac{1}{\eta}\right) \]

Solute: amylbenzene, mobile phase: 80 % methanol.
Ultra-fast HPLC Separation with Monolithic Column

Retention Time (sec)

Alkylbenzenes
\( u = 11.5 \text{ mm/s} \)
\( N = 3000 \text{ plates} / 3 \text{ cm} \)
Chromolith™ - applications

Separation of Cromakalim

LiChroCART 250-4
ChiraDex

Mobile phase: methanol / water 20:80

* surface modification with β-cyclodextrin
Column Connection Generates Higher Plate Numbers


4.6mmID x 10 cm

1 column

N: 11 000  \( \Delta P: 13 \text{ kg/cm}^2 \)

10 columns

N: 81 000  \( \Delta P: 85 \text{ kg/cm}^2 \)
Fast Analysis by Combined Solvent- and Flow-Gradient

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>H$_3$PO$_4$ (%)</th>
<th>ACN (%)</th>
<th>Flow Rate (ml/min)</th>
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</thead>
<tbody>
<tr>
<td>0.0</td>
<td>65</td>
<td>35</td>
<td>3</td>
</tr>
<tr>
<td>1.8</td>
<td>54</td>
<td>46</td>
<td>3</td>
</tr>
<tr>
<td>2.5</td>
<td>20</td>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td>4.0</td>
<td>20</td>
<td>80</td>
<td>5</td>
</tr>
</tbody>
</table>

Solutes:
1. phenol
2. 2-chlorophenol
3. 2-nitrophenol
4. 2,4-dinitrophenol
5. 4-chloro-3-methylphenol
6. 2,4-dinitro-6-methylphenol
7. 2,4,6-trichlorophenol
8. pentachlorophenol

Column 4.6mm ID x 10 cm
High Throughput Analysis

• Thinner (narrower bore) columns
• Mass spectrometry detection (LC/MS)
• Microfabricated flow system
• Two-dimensional HPLC
• Pre-treatment of analytes in small amounts
Capillary Columns (Second Generation)

(a) MS(100)-T1.0-B

(b) MS(100)-T1.4-BII

(c) MS(100)-T1.4-BIII

Anal. Chem. 2006
Very Long (>10 m) Capillary Columns Generate >1M Plates!

Figure  Separation of polynuclear aromatic hydrocarbons. Mobile phase: acetonitrile–water (80/20). Detection: 254 nm. Temperature: 30 C. Sample: 16-PAHs primary pollutants designated by the EPA.
Micro-analysis using MEMS Chips
MSQ Gels in a Microgroove Template
Schematic Presentation of Two-Dimensional HPLC

HPLC conditions
System 1: column 1: F-R, Mobile Phase: 70% CH$_3$OH, Flow rate: 0.4 ml/min, Detection 254 nm
System 2: column 2: PBB, Mobile Phase: 80% CH$_3$OH, Flow rate 8.0 ml/min, Detection 254 nm
System 3: column 3: C$_{18}$, Mobile Phase: 80% CH$_3$OH, Flow rate 5.0 ml/min, Detection 254 nm
2D-PAGE vs. 2D-HPLC (analysis of biomolecules)
DNA Purification Tool (GL Sciences Inc.)

『MonoFasシリーズ』の特長

1. 表面積が大きい ➔ 高回収率
2. 多孔質シリカ連続体なので、通液性が良い ➔ 早い処理時間
3. 一体型なので、フィルターが不要 ➔ 高精製

シリカモノリス

均一なスルーポア 硬い骨格

モノリスタイプ

粒子タイプ

シリンガモリス

他社製品（例）
Protein Digestion Tool with Immobilized Trypsin
(GL Sciences Inc.)

Ovalbumin
In solution at 37°C

Transferrin
Monolith-Based SPE Tools

MonoTrap™ and MonoTip™ (GL Sciences Inc.)

**MonoTrapTMDSC18, RSC18 (w/o AC, ODS)**
Moderate hydrophobicity for general purposes

**MonoTrapTMDCC18, RCC18 (w/ AC, ODS)**
Dispersed activated carbon acts as efficient adsorption sites for polar substances, VOCs and aromatic compounds.
Recent Progress by Refined Structure Control

- Analytical columns with $N > 200,000 /m$
- Preparative columns up to 1 L scale
Lab-made Monolithic Column with a Polymer Clad

Φ2.0-4.6mm Monolithic Silica

- Effective Column Length: 83mm
- Thermo-Shrinking PTFE
- Macro/ Mesoporous Silica
- Epoxy-Resin
- Polycarbonate Cylinder
- PTFE End-fitting

Used with a Radial Compression Module (WATERS Corp.)
Semi-Micro Column 2-3 mm Thick with Glass Clad

Silica monolith was heated in a borosilicate glass tube to be tightly fit on the side wall. Diameter of monolithic silica: 2.4 mm
Thickness of glass clad: 0.35 mm
Macropore Heterogeneity in Outermost Part of Monolith

Enthalpy-Driven Phase Separation
Higher Macroporosity
Significant Coarsening before Gel

Entropy-Driven Phase Separation
Lower Macroporosity
Less Coarsening before Gel
Separation of Alkylbenzenes by Semi-Micro Column

- Pressure: 15.1 MPa
- Column: 2.4 mmID × 100 mm
- Flow rate: 0.6 ml/min

<table>
<thead>
<tr>
<th>time (min)</th>
<th>N/m</th>
</tr>
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<tbody>
<tr>
<td>0.398</td>
<td>111,300</td>
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<tr>
<td>0.963</td>
<td>138,800</td>
</tr>
<tr>
<td>1.285</td>
<td>146,100</td>
</tr>
<tr>
<td>1.593</td>
<td>153,900</td>
</tr>
<tr>
<td>2.222</td>
<td>157,300</td>
</tr>
<tr>
<td>3.176</td>
<td>157,600</td>
</tr>
<tr>
<td>4.655</td>
<td>157,600</td>
</tr>
<tr>
<td>7.010</td>
<td>153,500</td>
</tr>
</tbody>
</table>

Conditions:
- Column: ODS modified
- Mobile Phase: acetonitrile / water = 65 / 35 (v / v)
- Temperature: Ambient
- Detection: UV 210 nm
- Sample: Alkylbenzenes ($C_6H_5(CH_2)_nH$, \(n=0-6\))
Comparative $H-u$ Curves of Particle-Packed and Monolithic Silica Columns

Height Equiv. to Theor. Plate, $H$ / µm

- 5µm Particle-packed
- 3µm Particle-packed
- 2µm Particle-packed
- Chromolith 3-50mm

Linear Velocity, $u$ / mm s$^{-1}$

- 1616-800 (Mesoporous)
- 1356H (HPAA)
Using an optimized aging process, silica monolith was successfully fabricated in a large scale up to 1000 mL.

(Upper right) Φ50 × 120mm
(center) Φ50₀ₒₒ × 10₁₁ᵢᵢ × 180mm (Radial flow type)
(Left below) Φ4 × 80mm and FRISK®
SEM Images of Large Silica Monolith with Enlarged Mesopores

(a) Macropore:

(b) Mesopore:
Hierarchically porous MSQ for separations

MSQ monolith

Column preparation
- Monolithic gel
- Column for HPLC
- Epoxy resin
- Plastic tube
- End-fitting

HPLC separation in normal phase

1. Urasil
2. Methylbenzoate
3. Naphthalene

Mobile phase:
ACN/H₂O = 60/40
Flow rate: 1.0 mL/min
Pressure
M13.0-U: 4.8 MPa
M13.0-T: 4.1 MPa

Pore diameter, \( D_p/\text{nm} \)

1  2  3  4  5  10  15  20  25  30  35  40  45  50

0.5  0.4  0.3  0.2  0.1  0.0  0.6

0  1  2  3  4

Time/min

Macropores & Mesopores

5 µm
### MOx Macroporous Gels (from Metal Salts)

<table>
<thead>
<tr>
<th>1\textsuperscript{st} Metal</th>
<th>2\textsuperscript{nd} Metal</th>
<th>Crystalline Phase</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>–</td>
<td>γ-Alumina, Corundum</td>
<td>PEO</td>
</tr>
<tr>
<td>Al</td>
<td>Y</td>
<td>Garnet</td>
<td>Co-hydrolysis</td>
</tr>
<tr>
<td>Al</td>
<td>Mg</td>
<td>Spinel, LDH</td>
<td>Co-hydrolysis</td>
</tr>
<tr>
<td>Al</td>
<td>Si</td>
<td>Mullite</td>
<td>+Si(OR)(_4)</td>
</tr>
<tr>
<td>Al</td>
<td>Si, Mg</td>
<td>Cordierite</td>
<td>+Si(OR)(_4)</td>
</tr>
<tr>
<td>Cr</td>
<td>–</td>
<td>Cr(_2)O(_3), CrN, Cr(_3)C(_2)</td>
<td>PAAm</td>
</tr>
<tr>
<td>Fe</td>
<td>–</td>
<td>Magnetite, Fe, Fe(_3)C</td>
<td>PAAm</td>
</tr>
<tr>
<td>Fe</td>
<td>Zn</td>
<td>Ferrite</td>
<td>PAAm</td>
</tr>
<tr>
<td>Ni</td>
<td>–</td>
<td>NiO, Ni</td>
<td>PAAm</td>
</tr>
<tr>
<td>Cu</td>
<td>–</td>
<td>CuO, Cu</td>
<td>PAAm</td>
</tr>
<tr>
<td>Zn</td>
<td>–</td>
<td>Zn(OH)(_2), ZnO</td>
<td>HPAA</td>
</tr>
</tbody>
</table>
# Phosphate-based Macroporous Monolith

<table>
<thead>
<tr>
<th>1st Metal</th>
<th>2nd Metal</th>
<th>Crystalline Phase</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>–</td>
<td>DCPA, Apatite, TCP etc.</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>Fe</td>
<td>Li</td>
<td>Olivine</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>–</td>
<td>Tridymite-type</td>
<td>PAAm</td>
</tr>
<tr>
<td>Zr</td>
<td>–</td>
<td>Layered</td>
<td>PAAm + PEO</td>
</tr>
<tr>
<td>Ti</td>
<td>–</td>
<td>Layered</td>
<td>PAAm + PEO</td>
</tr>
</tbody>
</table>
Various Porous Polymer Monoliths

divinylbenzene (DVB) + trimethylolpropane trimethacrylate (Trim) + 1,3-glycerol dimethacrylate (GDMA) + \( N,N\)-methylenebis(acrylamide) (BIS)

Poly(dimethylsiloxane) trimethylsiloxy-terminated (PDMS) + Poly(ethylene oxide) (PEO) + Poly(ethylene oxide) (PEO) + Poly(ethylene oxide) (PEO)

PDVB PTrim PGDMA PBIS

General Conclusions

• Structure control of hierarchically porous monoliths has now been established not only for pure silica but MSQ-silica, metal oxides and phosphates, as well as highly crosslinked organic polymers.

• Monolithic columns and analytical devices are available from capillary to preparative scale, offering widespread applications.

• Decreased porosity can suppress the undesired local deformation as well as heterogeneity, giving rise to improved efficiency with increased pressure drop.
Thank you for your attention...

We welcome you at Department of Chemistry, Graduate School of Science, KYOTO UNIV.

Acknowledgments
Grants from NEDO, JST, MEXT, Japan
XVIII International Sol-Gel Conference

Looking forward to seeing you in KYOTO, JAPAN

Save the dates

6 – 11 September, 2015

Sol-Gel 2015
From Solution, via Wet and Dry Gels to Dense Glass

図4.4 ゾル-ゲル法によるシリカ乾燥ゲル体および石英ガラスの作製。
Gibbs energy of a system containing polymerizing species

**Flory–Huggins' Formula**

\[
\Delta G = R T \left[ \left( \frac{\phi_1}{P_1} \right) \ln \phi_1 + \left( \frac{\phi_2}{P_2} \right) \ln \phi_2 + \chi_{12} \phi_1 \phi_2 \right]
\]

- \(\phi_i\) : volume fraction of component \(i\)
- \(P_i\) : degree of polymerization of component \(i\)
- \(\chi_{12}\) : interaction parameter
- \(R\) : gas constant
- \(T\) : temperature
Miscibility Windows at Varied Degrees of Polymerization

Phase Diagram of Polymerizing System

\[ \phi_{2c} = \left(1 + \sqrt{P_2/P_1}\right)^{-1} \]

for Solvent–Polymer, \(P_1 = 1\)

\[ P_2 \text{ increases} \]

\[ \text{TEMPERATURE} \]

\[ \text{SOLVENT} \quad \phi_{c, \text{poly}} \quad \phi_{c, \text{mono}} \quad \text{POLYMER} \]
Fig. 5.79  Two-liquid immiscibility. (a) to (e) show a sequence of Gibbs free energy curves corresponding to the phase diagram shown in (f). (a) \(T = T_1\); (b) \(T = T_2\); (c) \(T = T_3\); (d) \(T = T_4\); (e) \(T = T_5\). (From T.P. Seward, in *Phase Diagrams*, Vol. 1, Academic Press, Inc., New York, 1970.)
Figure 3. (A) Schematic phase diagram of a binary system. The solid curve is the binodal line and the broken curve is the spinodal line. $\phi$ is the volume fraction of one component. $\phi_C$ is the volume fraction of the critical composition where spinodal decomposition occurs at $T = T_1$. $\phi_N$ is the volume fraction of an off critical composition where nucleation and growth occurs at $T = T_1$. (B) The free energy on mixing for a binary system at $T = T_1$ in (A). $\phi_{S,i} (i = 1$ or $2)$ are the volume fractions of spinodal points where $d^2\Delta G / d\phi^2 = 0$. $\phi_{B,i}$ are those of binodal points, which are the contact points of the common tangent to $\Delta G(T = T_1)$, where $d\Delta G / d\phi|_{\phi B_1} = d\Delta G / d\phi|_{\phi B_2}$. In $\phi_{S1} < \phi < \phi_{S2}$, $d^2\Delta G / d\phi^2 < 0$. 

Miscibility Window in Binary System
Concentration fluctuation is NOT energetically favored.

Nucleation and Growth (activation energy required)

Fig. 5.80  (a) For a composition $C_o$ which lies outside the spinodal but within the miscibility gap, a small fluctuation in composition about the mean value to the limits $C_A'$ and $C_B'$ raises the free energy of the system (path 1). A larger fluctuation, to the compositions $C_A''$ and $C_B''$, is able to lower the free energy (path 2), leading to a lowering of free energy when the equilibrium compositions $C_A$ and $C_B$ are reached (path 3).
Phase Separation in Unstable Region

Concentration fluctuation grows spontaneously.

Spinodal Decomposition

Fig. 5.80  (b) A composition $C_o$ which lies within the spinodal will immediately undergo a decrease in free energy with a small fluctuation in composition about the mean value. The free energy decreases continuously with further compositional separation until the equilibrium values $C_A$ and $C_B$ are reached. This composition is *unstable* against fluctuations in composition, whereas the composition in (a) is only *metastable*. 
Difference between Spinodal Decomposition and Nucleation & Growth

Fig. 12. Schematic representation of time evolution of concentration fluctuation for (A) spinodal decomposition and (B) nucleation & growth. Time elapses in the order of (A), (B), and (C). $\phi_C$, $\phi_N$ and $\phi_{B_i}$ ($i = 1$ or $2$) are the same as in fig. 11. $\Lambda$ represents the wavelength of the most dominant mode of concentration fluctuation.
Figure 4. The onset and time evolution of coarsening of phase separating domains which occurs at various locations in the unstable region.
Composition vs. Macroporous Morphology

Macroscopic Phase Separation

Solvent

Higher Pore Volume

No Macropores

Smaller Pore Size

Silica

PEO
HPLC column: from particle to monolith
Chromolith™ - applications

Separation of β-Blockers*

Application

* mobile phase: acetonitrile/ 20mM phosphoric acid (20/ 80;V/V)
Structure Optimization Principle for Better HPLC Separation Medium

- Sharpen size distribution of macropores.
- Arrange gel skeletons and macropores as regularly (in 3D space) as possible.
- Avoid generating locally disturbed structures.

- All these contribute to homogenize the sample liquid flow through columns.

- Influence of mesopore structures can be discussed after fulfilling the above conditions.
Monolithic Capillary Columns in SiO$_2$-MSQ
Long Monolithic Capillary Columns

Separation of polynuclear aromatic hydrocarbons. Mobile phase: acetonitrile-water (80/20). Detection: 254 nm. Temperature: 30°C. Sample: 16-PAHs primary pollutants designated by the EPA. Peak numbers: 1, naphthalene; 2, acenaphthylene; 3, fluorene; 4, acenaphthene; 5, phenanthrene; 6, anthracene; 7, fluoranthene; 8, pyrene; 9, chrysene; 10, benz(a)anthracene; 11, benzo(b)fluoranthene; 12, benzo(k)fluoranthene; 13, benzo(a)pyrene; 14, dibenz(a,h)anthracene; 15, indeno(1,2,3-cd)pyrene; and 16, benzo(g,h,i)perylene.

(a) Column: MS-100H-C18 (5KK), effective length 133 cm. $\Delta P$ = 4.7 MPa. $u$ = 1.03 mm/s.

(b) Column: three monolithic silica C18 columns connected in series, MS-100H-C18 (8KM, 9KM, and 10KM), effective length 1238 cm (total length 1244 cm). $\Delta P$ = 46.6 MPa. $u$ = 1.31 mm/s. Detection: 210 nm. Temperature: 30°C.

Miyamoto et al., Anal. Chem., 2008, 80 (22), 8741-8750.

>1 million plates with 12.4 m monolithic capillary column
CFD Simulations of Pillar Array with Heterogeneity
Local Deformation of Macroporous Structure by Interfacial Wetting

MTMS(Tri-Functional) Capillary Columns

Phase separation in confined spaces are influenced by the container walls to cause wetting and local deformation. This leads to the decreased homogeneity through the column.
Optimized capillary columns perform at least 2-3 times better than commercially available particle-packed columns.

Figure van Deemter plots obtained for ODS-modified monolithic silica columns and a silica-C₁₈ packed column with ethylbenzene (a) and hexylbenzene (b) as solutes. Mobile phase: acetonitrile/water = 80/20. Temperature: 30°C. The symbols are the same as in the next Figure for the columns.
Monolithic columns can perform faster or higher efficiency separations that are impossible by particle-packed columns. (Forbidden Region)
Semi-Micro Column 2–3 mm Thick (Future Direction)

Columns with decreased domain (skeleton + pore) size and decreased porosity performs much better than existing products.
Columns with decreased domain (skeleton + pore) size and decreased porosity performs almost similarly to those packed with 2-3 µm particles but analysis time is shortened.
Formation of Cylindrical Mesopores with Rod-like Skeletons

Supramolecular Templating

Polymerization-Induced Phase Separation

- Rod-like skeletons (Fig. 1)
- 2-D hexagonally arranged mesopores in each skeleton (Fig. 2)
Structures of Monolithic Macroporous Silica with Templated Mesopores

Dependence on Starting Composition

10 mM Acetic Acid (mL)

Amount of Surfactant P123 (g)

TMOS 2.5 mL with Urea
Calcined at 600°C

Plate Number, Asymmetry Factor
Mesopores are eliminated at higher T

Nearly isotropic shrinkage is recognized at higher T.
HPLC Separations by Macroporous Silica with Templated Mesopores

Column length: 83 mm
Mobile phase:
ACN/water=70/30 (v/v)
Pressure: 12.6 MPa

N=140 000/m
H=7 µm

Fig. Chromatogram showing the separation of alkylbenzenes $C_nH_{2n+1}$ (n=0-6) using ODS modified 1616-800 stationary phase.
Lower Pressure Drop and High Performance should be compromised...

- Higher porosity leads to more deformed structure in the vicinity of container wall.
- Decreased porosity can suppress the undesired deformation as well as heterogeneity, but pressure drop increases.
- Higher porosity without deteriorating structural homogeneity is ideal conditions for ultimate speed and performance.
Potential Materials Processing for Optimized Separation Media

• Packing of Monodispersed Particles

• Monolithic Macroporous Gels by Phase Separation
  – Distributed as product for 14 years. Independent control of skeleton thickness and macropore diameter. Elimination of local heterogeneity is required for next generation performance (partially available).

• Top-down Microfabrication
  – Ideal structures such as micro-pillar arrays can be fabricated. Gradual penetration into analytical field will occur accompanied by reduced costs.
Fabrication process

Homogeneous solution: water, acetic acid, tetramethoxysilane, PEG10k, and Urea in a litter scale

Gelation and Aging

Hydrothermal treatment

Drying:
Drying process without solvent exchange was possible due to the enlarged mesopore by the hydrothermal treatment. However, supercritical drying is preferable.

Calcination
Direct calcination of wet gel is possible for 100 nm pore.

(upper left) Φ90 × 150mm (1L)
(upper right) Φ50 × 150mm (300mL)
(center) Φ8 × 150mm and Φ4mm column