

Formation Process and Liquid Transport
of Sol-gel Derived Monolithic Porous Silica

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GENERAL INTRODUCTION

High performance liquid chromatography (HPLC) is a form of column, and it is also sometimes referred to high-pressure liquid chromatography. HPLC is a technique to separate components of a mixture by using a variety of chemical interactions between the analyte and the chromatography column [1]. The application of HPLC covers a lot of ground: environmental investigation [2] and bioscience [3–5] and drug development [6] are some of the representative examples. Nowadays the application of HPLC is not restricted in the single application, but the combinations with other analysis systems are intensively studied: mass spectroscopy (LC–MS) [7–8], another HPLC system (two dimensional–LC) [9], solid phase extraction [10], etc.

Recent progress in bioscience is represented by genome–projects, which are scientific endeavors that ultimately aim to determine the complete genome sequence of an organism. The genome projects have now entered a rapid production phase with complete genome sequences and complete gene catalogues already available for a number of organisms [11–13]. In addition the new DNA and protein chip technologies can produce functional data about genes such as gene expression profiles at a rapid rate [14–16]. There is therefore a large and ever increasing amount of data about genes and molecules. However, there is still a huge gap between information at the molecular level and information at the level of integrated biological systems. It is the gap that is addressed in Post-genome Informatics. Post-genome informatics is the analysis of biological functions in terms of the network of interacting molecules and genes with the aim of understanding how a biological system is organized from its individual building blocks [17–19]. Therefore the importance of fast and efficient analysis system is required.

Realization of high performance at high flow rate has been an ultimate objective also for separation analysis. In the field of HPLC, numbers of efforts have been done from two kinds of standpoints: one is from mechanical equipments [20] and facilities, and the other is from designs of chromatographic support [21–22].

Since its first appearance in the field of HPLC, macroporous silica monolith has been attracting attention as a highly efficient separation media worth noting for more than a decade [23–26]. The most remarkable characteristics of silica monolith is continuous network of silica, which replaces the conventional particulate packing. This allowed the external macropore porosity to increase, and resulted in respectable performance at much higher flow rate compared to standard packed bed column [27–29].

The continuous networks in silica monolith are derived from spinodal decomposition [30–32], one of the phase separation mechanisms. Phase separating structure between polymerizing silica and solvents is frozen by sol–gel transition and the following removal and drying of solvent result in the co-continuous macropore structure. The principal factor which produces the macropore structure is the timing of phase separation and sol–gel transition [33]: Premature freeze of the phase separating structure leads to micro–mesoporous silica and too late freeze leads to particulate aggregation, or macroscopic two phases. Both rates of sol–gel transition and phase separation have to be adjusted to obtain continuous network structure.

This sol–gel transition is a transformation of a polymerizing system from “sol” to “gel”, which can be recognized by a formation of an infinitely large cluster in the length scale of the reaction vessel [34]. The time evolution of the polymerizing cluster size can be interpreted as a kind of percolation process [34], however the exact description of the sol–gel transition in detailed time and space domains is difficult since the time–evolution of cluster size exhibits

non-linear behavior.

Phase separation has been studied for long and the structural evolution through its process is predictable on the composition, physical properties of the two phases, interaction between the phases and the reaction temperature [32]. The combination of sol-gel reaction and phase separation, however, ingenerates further complexity: both compositions and physical properties of the separating phases keeps changing during the progression of sol-gel reaction.

The complexity in the formation mechanism of macroporous monolith has posed obstacle to the optimization of its macropore structure as a support, and it took nearly ten years for significant improvements of separation performance in monolith [35]. There arises necessity for the knowledge of the relation between macropore structure, separation performance and the formation process.

In Chapter 1, reviewed is the method for structural definition of co-continuous macropore using laser scanning confocal microscopy (LSCM), which provides cross-sectional images [36–39]. Further image processing on the obtained series of LSCM images provides three dimensional reconstructed image of co-continuous macropore, and the following image analysis yields structural parameters: macropore size, gel skeleton thickness, macropore porosity, surface curvature of macropore, etc.

In Chapter 2, the relation between liquid transport and macropore structure is reviewed. The macropore structures were analyzed using LSCM as described in Chapter 1, and experimental liquid transport behavior was evaluated by dimensionless flow resistance, which had been calculated from permeability and skeleton diameter. The mutual consistency between flow resistances in simulated and measured systems was examined in terms of the obtained structural parameters.

In Chapter 3, the time evolution of phase separating structure in sol-gel

systems is reviewed. The co-continuous macropore structure formation was investigated in two different representative systems using LSCM and studied the influence of starting composition on the structural formation mechanism.

In Chapter 4, the difference of macropore structures synthesized from different mechanisms of structural evolution was observed using LSCM and studied the influence of phase separation dynamics on the obtained macropore structure was examined. The influence on the separation efficiency is discussed on the observed difference.

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Chapter 1: Three Dimensional Structural Analysis

1. Introduction

Co-continuous macroporous silica has been applied to separation media in the field of high performance liquid chromatography for over a decade and has been gathering attention [1–11]. In the field of separation science, the needs for separation media with both high performance and high permeability are raising increasingly because the post-genomic analysis needs vast numbers of chromatographic analyses and fast and efficient analysis is needed. There are two kinds of strategy for fast and efficient analysis. One is to improve mechanical settings, for example, increasing mechanical strength of pipe-fittings or improvements in pumps. The other is to devise the core of the separation system; the structure of stationary phase.

Co-continuous macroporous silica, so-called monolith because of its monolithic substance, has been studied for over a decade, but the relation between structure and separation efficiency is still poorly understood. Moreover, the efficiency of silica monolith as separation media is tested for only limited range till now. It is expected that monolith has still possibility for improvements in permeability and separation efficiency. At this point, important problem arises for improvement: what is the ideal structure for separation media?

Computational fluid dynamics (CFD) simulation has been successfully applied to separation science for several yeas and has proven the irrefragability and reliability of the method itself [12–14]. It is expected that the study using CFD on reasonable model will provide the strategy for ideal macropore structure, which needs extraction of structural parameters from real structure.

There are several methods to observe and analyze macropore structure; scanning electron microscopy (SEM), mercury porosimetry, etc. Laser scanning confocal microscopy (LSCM) among them is gathering intensive attention as a novel method [15–18]. The more detailed analysis is expected to be possible since the LSCM images can be reconstructed in three dimension (3D) and be provided for the calculation of geometrical and topological parameters.

In this chapter macropore structure with different porosities and macropore sizes is observed and analyzed using several methods: scanning electron microscopy (SEM), mercury porosimetry and laser scanning confocal microscopy (LSCM), which is attracting attention as a novel method for three dimensional observation. Structural characteristic of co-continuous macropore are discussed in order to provide reasonable model for computational fluid dynamics (CFD) simulation.

2. Experimental

2.1 Material Preparation

In a first place, poly(ethylene glycol) (M.W. 100,000), PEO10, and D-sorbitol were homogeneously dissolved in 1M nitric acid. Then, 6.5g of tetraethoxysilane (TEOS) was added under vigorous stirring in an ice-cooled condition. The weight ratio of starting composition was TEOS: 1MHNO₃: PEO10: D-Sorbitol = 1: 1.23~1.54: 0.12~0.16: 0~0.08. Actual compositions are listed in Table.1.1. After 30 minutes of stirring, the resultant homogeneous solution was transferred into a polypropylene tube (i.d. 6mm, 20cm long) and allowed to gel at 40°C in a closed condition. After aging at the same temperature for 10 h, the resultant gel was immersed in water for 3 hours in order to remove residual acids, and solvent-exchanged with 1M urea aq for 3 h.

Table 1.1

An overview of starting compositions of real monoliths.

	1MNH ₃	PEO10	D-Sorbitol	TEOS
A	7.0	0.90	0.0	6.4
B	7.0	0.90	0.8	6.4
C	8.0	0.90	0.4	6.4
D	8.0	0.90	0.0	6.4
E	8.0	0.90	0.6	6.4
F	9.0	0.90	0.0	6.4
G	9.0	0.90	0.8	6.4
H	9.0	0.90	0.2	6.4
I	10.0	0.90	0.2	6.4
J	10.0	0.97	0.0	6.4
K	9.0	0.90	0.0	6.4
L	10.0	0.95	0.0	6.4

The following hydrothermal treatment took 5h at 110°C in 1.5M urea aq. After 2 hours of solvent exchange with water, obtained gels were dried and heat treated at 600°C for 5 h in order to remove residual organics.

The obtained silica gels were further sliced into 2mm pieces and immersed in a mixture solution of formamide, benzyl alcohol, and fluorescein. The weight ratio was formamide: benzyl alcohol: fluorescein= 1: 3: 0.05. These chemicals were chosen since they do not swell the silica gel and not change the macropore structure.

2.2 Structural Observation

The structures and geometrical properties of obtained gels were observed by a scanning electron microscope (SEM) (S-2600N, Hitachi, Japan), a laser scanning confocal microscope (LSCM, LSM5 PASCAL, Carl Zeiss, Germany). A mercury intrusion apparatus (PORESIZER 9320, Micromeritics, U.S.A.) was used to determine the size distribution of pores larger than 7nm in diameter.

2.2.1 Scanning Electron Microscope Observation

The obtained silica gels were cut into pieces with 2mm thickness, covered with Au ion using ion coater and observed with SEM.

2.2.2 Mercury Intrusion Method

The principle and measurement procedures of mercury intrusion method are well known, however the principle of this method is confirmed for the following disussion.

In mercury intrusion method, porosity, ϵ , is estimated by the ratio (mercury intrusion volume)/(total sample volume) and pore diameter, d_p , is estimated

with the Washburn's equation,

$$d_p = -4\gamma \cos \theta / P \quad (1.1)$$

where surface tension of mercury, γ , contact angle between mercury and silica, θ , and intrusion pressure, P . Note that cylindrical shape of the macropores and mesopores are assumed in this equation. By increasing the intrusion pressure continuously and recording an incremental intrusion volume at each pressure, pore size distribution can be obtained with the above Washburn's equation and the median pore diameter is determined from the probability based distribution.

2.2.3 LSCM Observation

As a preparation for LSCM observation, the obtained monolithic silica gels were cut into 2.5mm thickness, and immersed in a mixture of formamide, benzyl alcohol and fluorescein solution (1:3:0.05wt) which has the same refractive index as that of gel skeleton. This process is needed to allow the laser light to transmit the sample and to obtain a better contrast.

A laser with 488 nm wavelength was used to excite fluorescein [Figure 1.1]. A long pass filter (LP505) was installed in front of photomultiplier in order to detect only the fluorescent light (approximately 519 nm) and oil-immersed 63 $\times$, 100 $\times$ /NA=1.40 (Plan-Apochromat, Carl Zeiss) objective were employed. The increment along the optical axis of the microscope perpendicular to the focal plane, Δz , used for observation was 0.35 μm or 0.30 μm depending on the objective magnification. The lateral and axial resolutions, R_{lateral} and R_{axial} were approximately 0.18 μm and 0.46 μm , respectively. The difference in the axial and lateral resolution originates from "point spread" of laser light. The image of an ideal point objects would always spread, or elongated in the direction of incidence, and becomes comet-like, rotationally symmetrical shape. It results

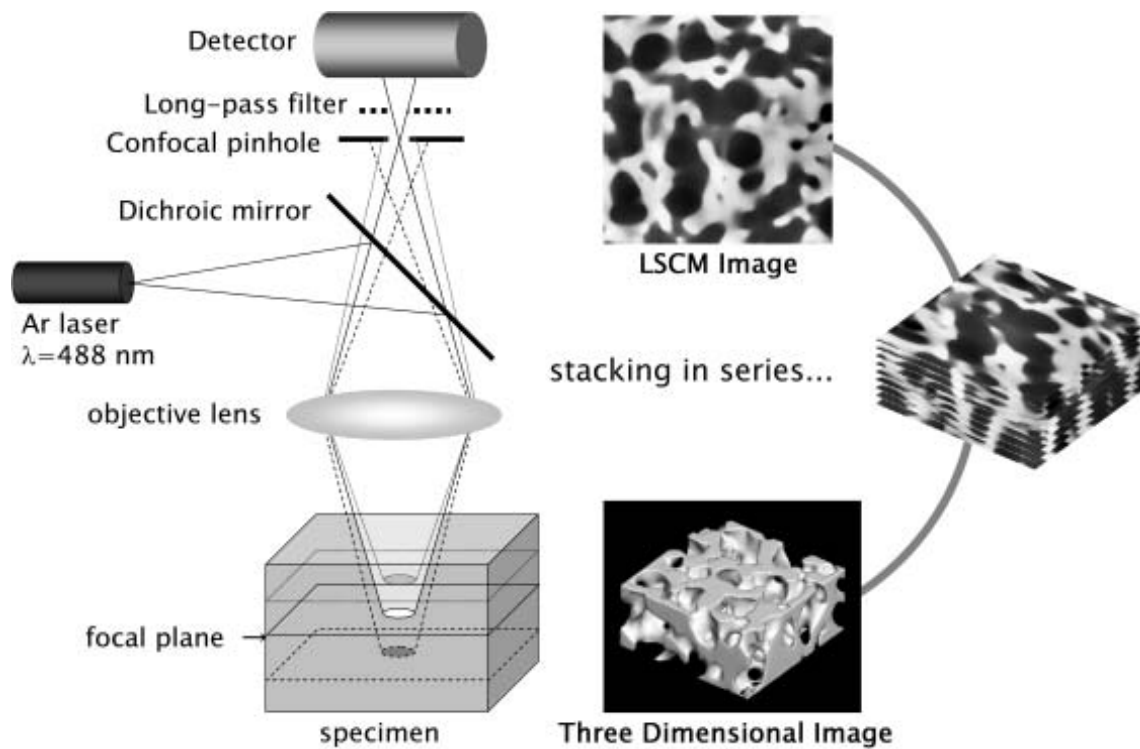


Figure 1.1

Schematic principle of LSCM and image processing. A long pass filter (LP505) was installed in front of photomultiplier in order to detect only the fluorescent light (approximately 519 nm) and oil-immersed $63\times$, $100\times$ /NA=1.40 (Plan- Apochromat, Carl Zeiss) and $40\times$ /NA=1.30 (Plan-Neofluar, Carl Zeiss) objective was employed.

in the difference in lateral and axial resolutions in LSCM. The laser was scanned in the lateral plane, measuring fluorescent intensity in a two dimensional optically sliced image composed of N^2 ($N=512$) pixel², where N is the number of pixels along the edge of the two dimensional image.

2.2.4 Image Processing

The LSCM images have to be binarized before reconstructions into 3D images and a proper threshold of brightness is needed for the binarization process. The raw LSCM images sometimes suffer from noises and spatial intensity variations (i.e. inhomogeneous illuminations and high-frequency noises) due to aberrations of the objective, which complicate the threshold determination. In order to remove the intensity variation, the LSCM images were further processed with “contrast variance enhancement (CVE)” method [19]. The CVE is a technique that makes all local regions of an output image have an equal variance in terms of their image intensities. The noises were removed by a median filter, a class of nonlinear spatial filter which was designed to remove outlier pixels whose intensities are completely inconsistent with their surrounding values. The thresholds were calculated on the processed images according to Otsu’s method [20]. The Otsu’s method depends on statistical calculations and determines the threshold so as to minimize the intra-class variance and to maximize the between-class variance. The binarized images were reconstructed with marching cube algorithm into 3D images [Figure 1.2]. Each of the reconstructed images has 512x512x100 voxels, which have black or white in color and the size was 0.285x0.285x0.35 μm^3 for those observed with 63x objective and 0.180x0.180x0.30 μm^3 for 100x objective. Other parameters were calculated by skeletonization [21]. The informal definition of the skeletonization is a line representation of an object that is 1) one-pixel thick, 2) through the middle of the object, and 3) preserves the

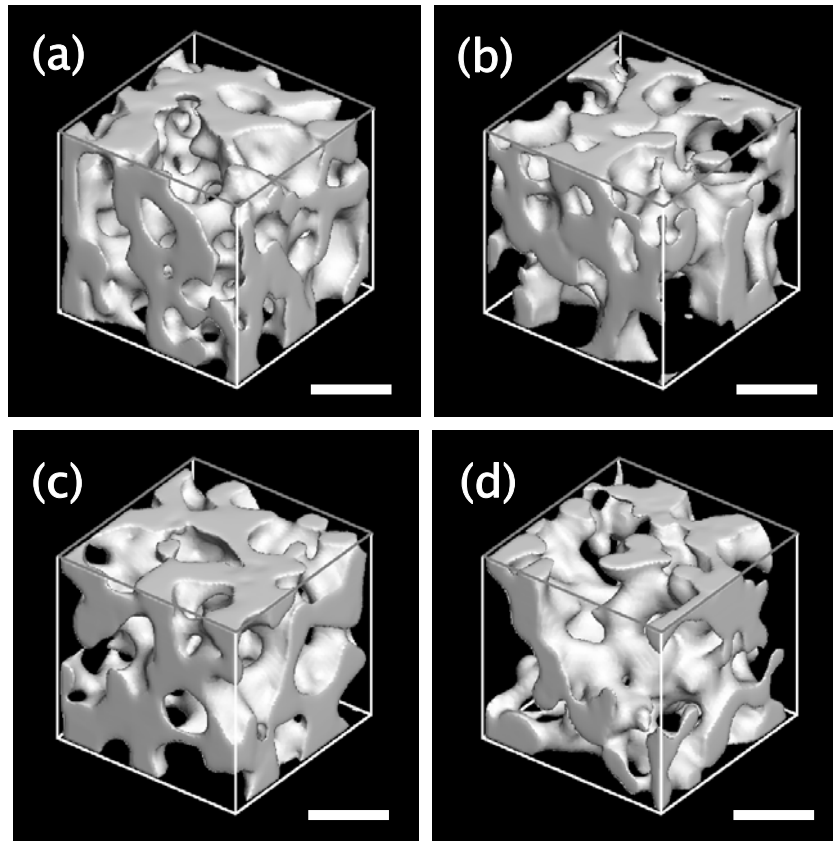


Figure 1.2

Overview of three dimensional structures reconstructed by image processing: (a) sample A, (b) sample C, (c) sample F, (d) sample K. The lengths of the bars are $5\mu\text{m}$.

topology of the object. By skeletonizing macropore/skeleton, the middle of the macropore/skeleton can be determined, and calculating the distances between the middle and the interface, the distributions of macropore size and skeleton thickness can be obtained. The skeleton thickness and macropore size were determined by further using the Gaussian fitting procedure on the distributions of those obtained from the skeletonization. The wavelength of periodic repetition of co-existing phases in the spinodal pattern was measured by the chord length method, in which lines in 341 directions were drawn in the obtained three dimensional image and the number of voxel for pore and skeleton sections were counted on every drawn line and the most probable values were taken by the Gaussian fitting.

The curvature of a site on a 1D arc is equal to the reciprocal of the radius of a circle best fit to the curve at the site (osculating circle). Similarly, local principle curvatures, κ_1 , κ_2 , on a 2D curved surface are defined as reciprocals of the largest and the smallest osculating circles at the same point [Figure 1.3]. Note the curvature is classified positive if the center of the osculating circle locates in the macropore region. The mean curvature, H , and the Gaussian curvature, K , are defined as,

$$H = \frac{(\kappa_1 + \kappa_2)}{2} . \quad (1.2)$$

$$K = \kappa_1 \cdot \kappa_2$$

The curvature distribution was calculated using sectioning and fitting method (SFM). The methodological details are found in [22].

3. Results and Discussion

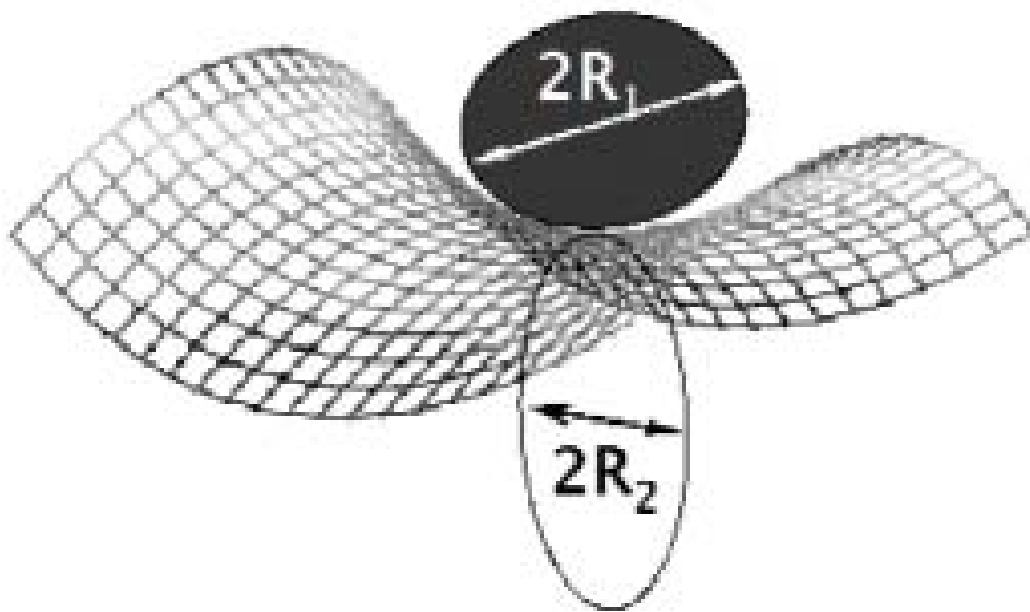


Figure 1.3

Overview of two osculating circles at curved surface.

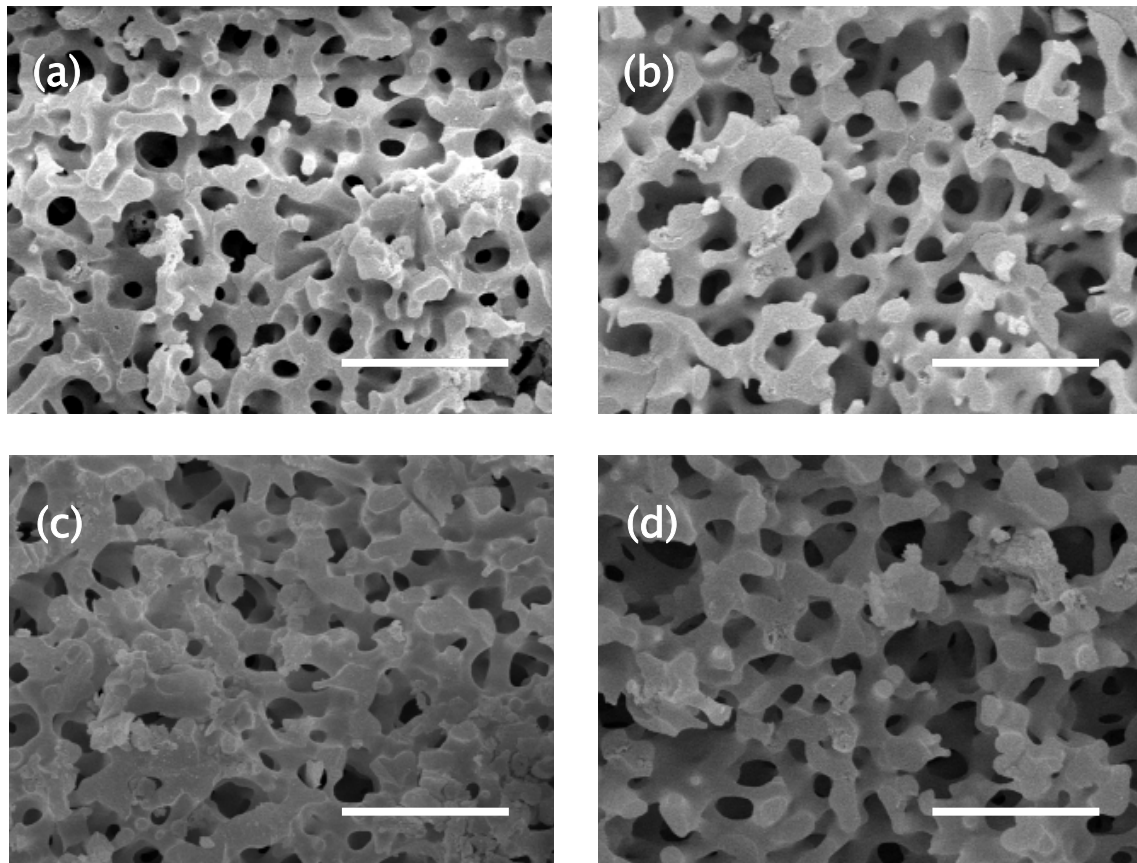


Figure 1.4

SEM images of macroporous. (a) sample A, (b) sample B, (c) sample C, (d) sample D. The length of the bars correspond to 20 μ m.

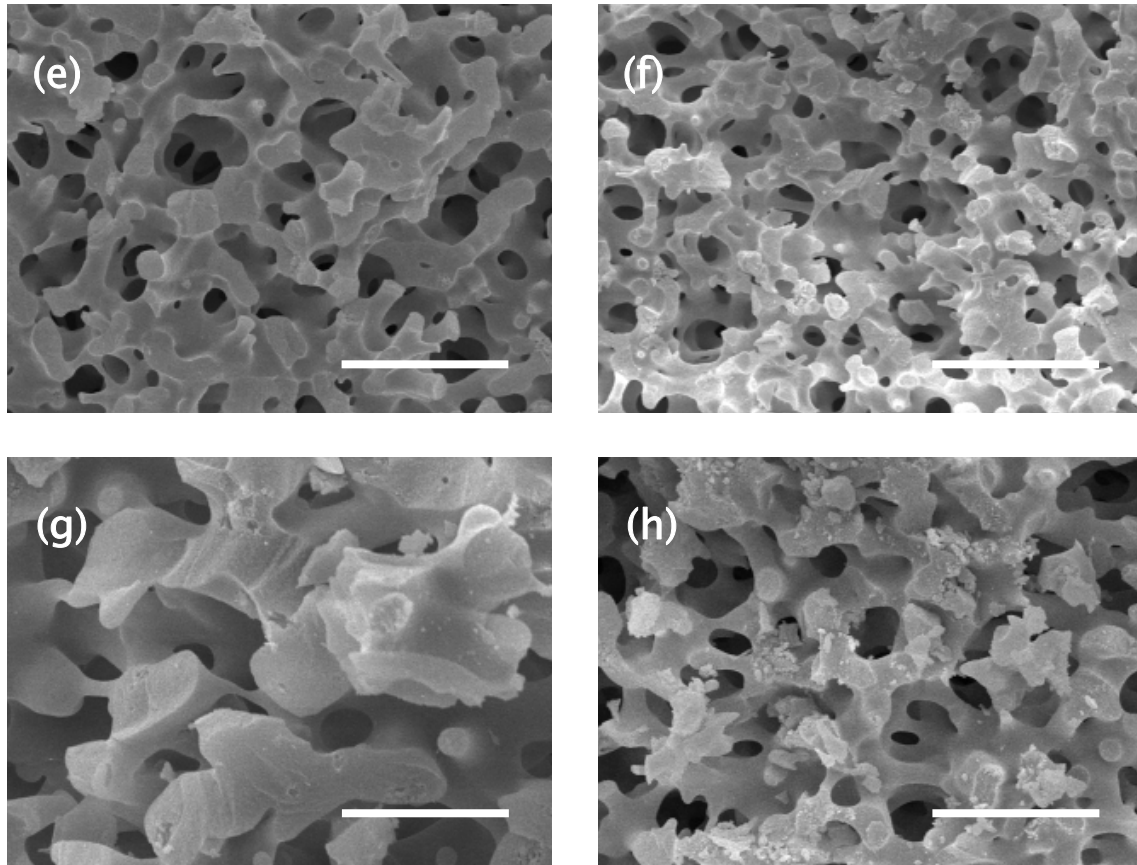


Figure 1.4

SEM images of macroporous. (e) sample E, (f) sample F, (g) sample G, (h) sample H. The length of the bars correspond to 20 μ m.

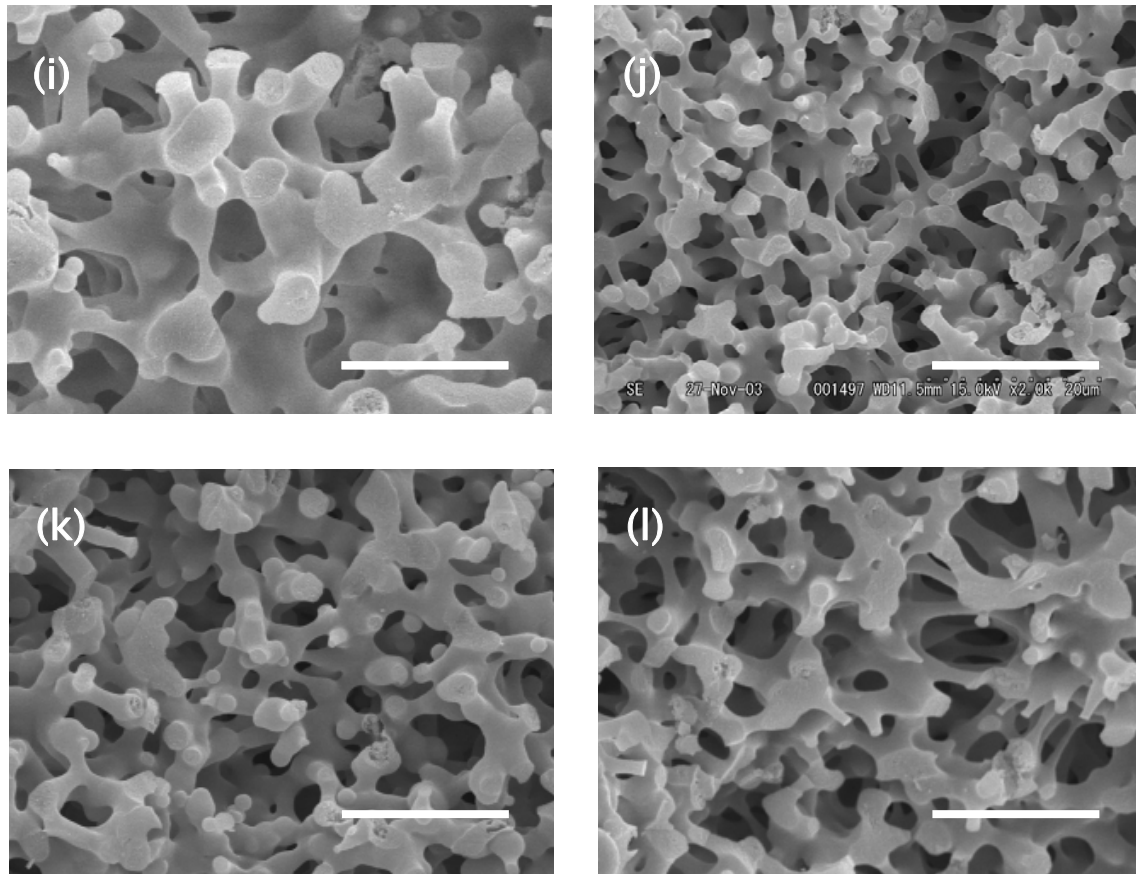


Figure 1.4

SEM images of macroporous. (i) sample I, (j) sample J, (k) sample K, (l) sample L. The length of the bars correspond to 20 μ m.

3.1 Observation by SEM

Figure 1.4 shows SEM images of the obtained silica gels. Macropore size decreased with increasing amount of PEO in the starting composition, and the apparent volume fraction increased with increasing amount of 1M nitric acid.

The morphologies of the co-continuous macropore also exhibited differences. The amount of PEO was observed to be related to the homogeneity of the macropore structure other than the size, the amount of 1M nitric acid was observed to be related to the feature of gel skeleton: smaller amount of 1M nitric acid is concerned with relatively thick and short skeleton, and larger amount is concerned with relatively long and fibrous gel skeleton. Further analysis and observation is not possible from SEM images and is left to the LSCM images and their analysis.

3.2 Measurement by Hg intrusion method

Figure 1.5 shows typical Hg intrusion profile obtained from macroporous silica gel (sample B). It exhibited sharp distributions of macropore size and also the existence of mesopores formed by hydrothermal treatment. The macropore size can be estimated from the peak positions of the distributions, and the macropore porosity was calculated from the mercury intrusion volume. The estimated macropore sizes and porosities are listed in Table 1.2. The total volume of the samples subjected to the measurements were around 0.1 cm³ and large enough to consider the data to be statistic.

3.3 Three dimensional Analysis Using LSCM

3.3.1 Macropore Porosities

Macropore porosity is an important parameter to consider porous structure

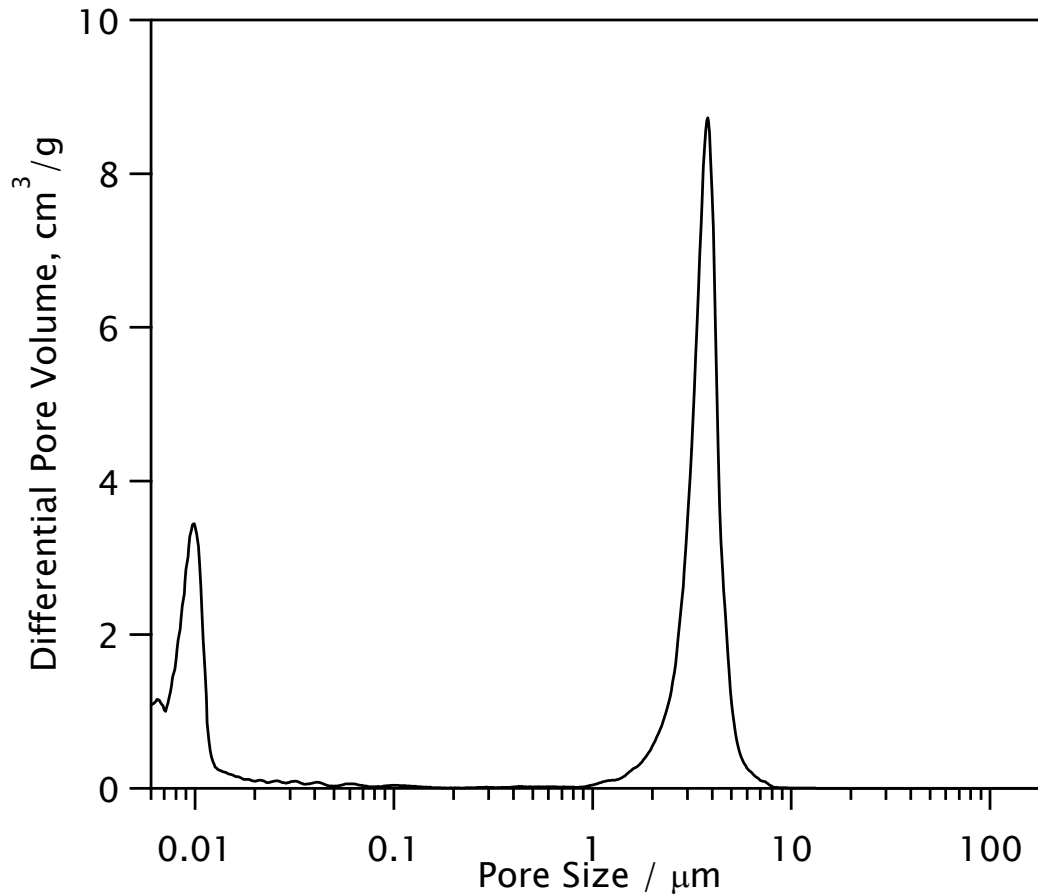


Figure 1.5

Hg intrusion profile of sample B is depicted. It exhibited sharp distributions of macropore size and also the existence of mesopores formed by hydrothermal treatment. The macropore size can be estimated from the peak positions of the distributions, and the macropore porosity was calculated from the mercury intrusion volume.

Table 1.2

An overview of porosities and macropore sizes obtained from Hg porosimetry

	ε	$d_{\text{pH}} / \mu\text{m}$
A	0.496	2.33
B	0.518	2.95
C	0.540	2.90
D	0.539	2.61
E	0.559	3.62
F	0.561	3.31
G	0.572	8.76
H	0.581	4.32
I	0.607	5.75
J	0.626	3.34
K	0.661	3.93
L	0.649	4.22

and is defined as volume fraction of pore space in porous material. Porosity has significant influences upon physical properties of porous materials, such as thermal conductivity, elasticity, mechanical strength, and liquid transport, which is the major concern in this study. There are several methods to measure porosity: traditional mercury intrusion method and image processing using LSCM. Table 1.3 shows porosity data obtained from these methods. Porosity obtained by mercury intrusion method, ϵ_H , took relatively smaller value compared to those obtained by LSCM and image processing method, ϵ_L . The discrepancy between ϵ_H and ϵ_L did not show distinct change with porosity [Figure 1.6].

Porosity estimation by mercury intrusion method and LSCM method each contain several drawbacks and advantages. Mercury intrusion method can measure larger volume at one time compared to LSCM method and the obtained data is less affected by macropore structure imperfection produced by air bubble, for example. Meanwhile, LSCM can measure the surface of macropore structure point by point in three dimension (3D), and the obtained data is regarded more accurate compared to mercury intrusion method for limited observation area.

The consistent inclination that ϵ_L shows larger value than ϵ_H suggests two possibilities: One is that there are large number of filled defect, and the other is that mercury intrusion method does not perfectly reflects real macropore structure. The former possibility is easily refuted since there were no such large numbers of filled defects observed by both SEM and LSCM. The latter is more possible since experimental failure can easily happen and it is often the case that all of the macropores are not filled with mercury even at the highest intrusion pressure. The inclination of the larger porosity measured by LSCM also suggests that the macropore structure can be regarded enough homogeneous on the whole to rely on LSCM method.

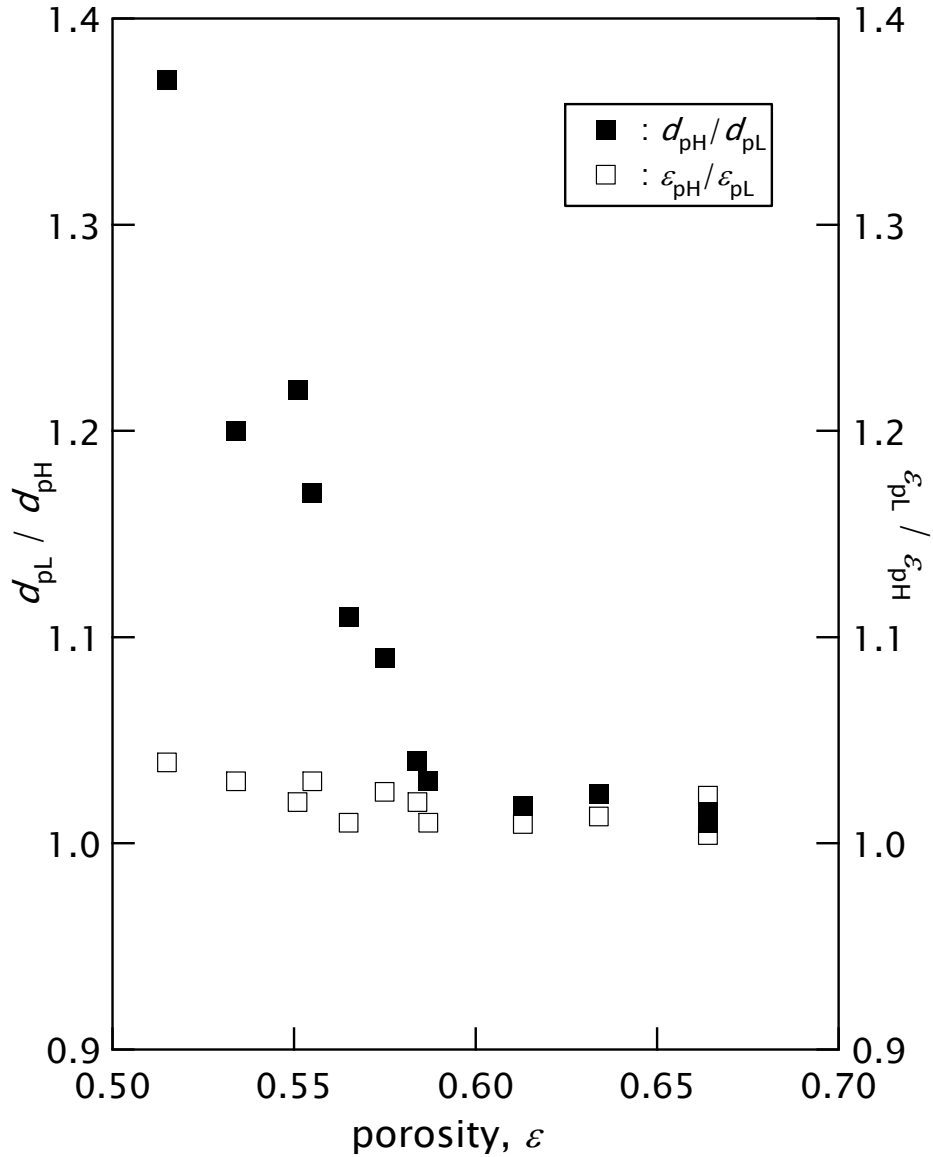


Figure 1.6

Porosity dependencies of d_{pL}/d_{pH} and $\varepsilon_L/\varepsilon_H$ are depicted. Regarding the porosity data, mercury intrusion method and LSCM method were in reasonable agreement and porosity data obtained from mercury porosimetry and LSCM, ε_H and ε_L respectively, were in reasonable agreement. Pore diameter data, however, exhibited increasing discrepancy with decreasing porosity.

Table 1.3

An overview of structural parameters of real monoliths.

	ε	$a / \mu\text{m}^{-1}$	$d_s / \mu\text{m}$	$d_p / \mu\text{m}$	$d_c / \mu\text{m}$	H^*	K^*
A	0.515	0.836	2.73	3.16	2.58	0.175	-1.241
B	0.534	0.762	3.45	4.17	3.40	0.183	-1.267
C	0.551	0.750	2.88	3.67	4.32	0.060	-1.569
D	0.555	0.841	2.55	3.20	3.46	0.038	-1.500
E	0.565	0.668	3.21	4.02	4.45	0.022	-1.624
F	0.575	0.668	3.13	4.03	5.63	-0.012	-1.672
G	0.584	0.280	7.41	9.37	9.62	0.006	-1.355
H	0.587	0.618	3.36	4.40	5.75	-0.064	-1.762
I	0.613	0.411	4.70	6.17	6.45	-0.162	-1.820
J	0.634	0.794	2.39	3.26	3.10	-0.174	-1.880
K	0.664	0.632	2.91	4.36	3.78	-0.314	-1.754
L	0.576	0.623	3.13	5.26	5.19	-0.129	-1.872

3.3.2 Surface area

Traditionally, structural dimension of co-continuous structure has been evaluated by the macropore size, however, macropore size is not always a reasonable measure for structural dimension. When comparing macropore structures with same macropore sizes and different porosities, structural dimensions are observed smaller with increasing porosity. One of the ways to compare structural dimension between non-homothetic structures is to compare specific surface area, a .

Volumetric specific surface areas calculated from reconstructed 3D images are listed in Table 1.3. These values are related to macropore sizes, porosities, however the investigation is left for the following discussion.

3.3.3 Macropore Size and Skeleton thickness

The distributions of macropore size and skeleton thickness were obtained from skeletonization [Figure 1.7]. Macropore size had broader distribution compared to skeleton thickness. The standard deviations calculated from the distributions are listed in Table 1.3. Each of the standard deviation was normalized with mean value in order to eliminate the influence of dimension.

The normalized standard deviation is plotted against porosity in Figure 1.8. The heterogeneity in skeleton thickness increased slightly with porosity, however the change is negligible. The heterogeneity in macropore size, on the other hand, took on steeper increase, suggesting that the structural deformation during phase separation is influenced by the volume fraction of siloxane phase: that is, the viscosity of siloxane phase is much higher than that of solvent phase and the decreased ratio of siloxane phase enhances the fluidity of the overall phase separating liquid. The macropores would be deformed by the minute flow that exists intrinsically, however, the connectivity of siloxane phase is conserved by its viscoelasticity and hence the heterogeneity in the skeleton

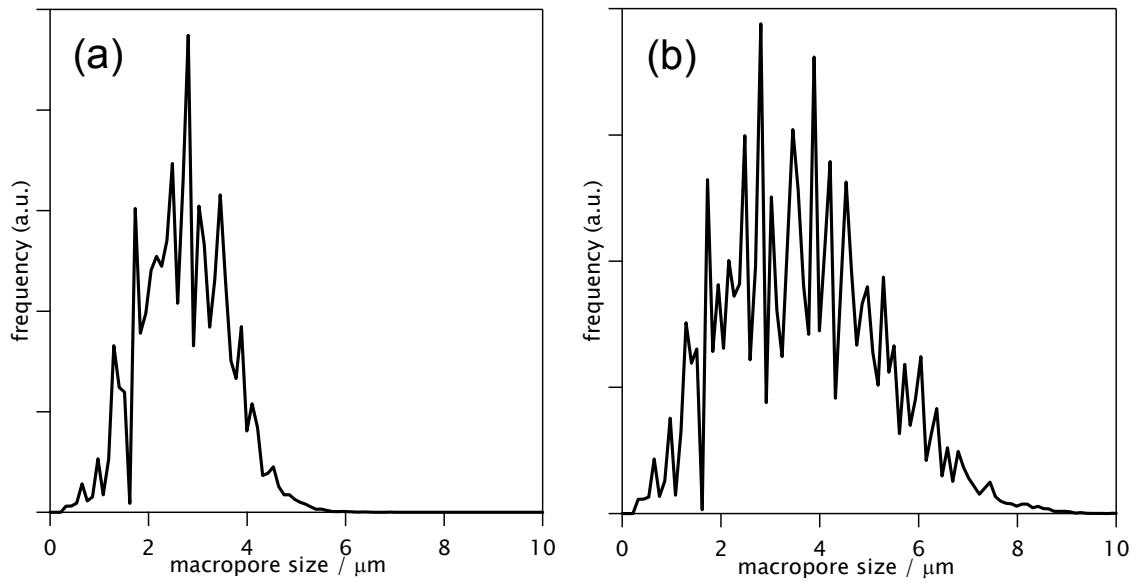


Figure 1.7

The distributions of (a) skeleton thickness and (b) macropore size are depicted. Macropore size had broader distribution compared to skeleton thickness.

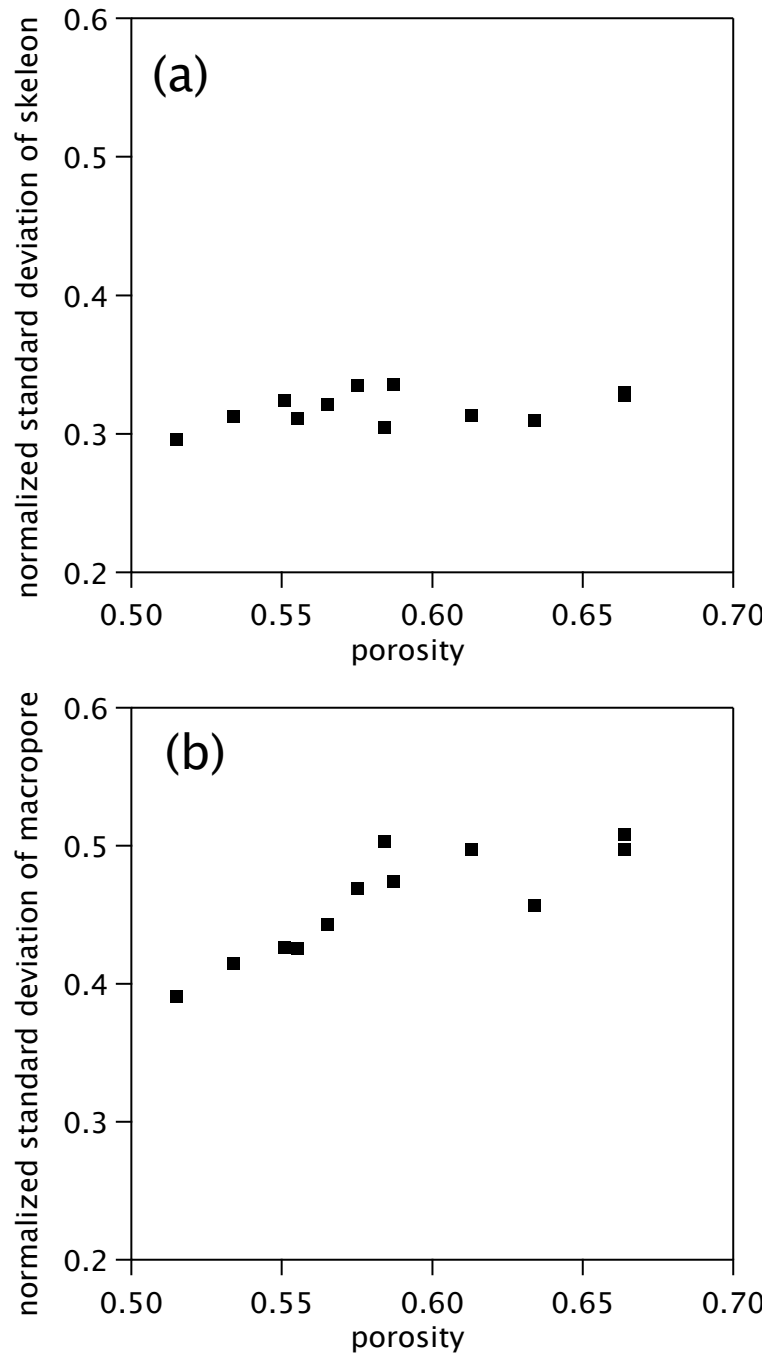


Figure 1.8

The normalized standard deviations of (a) skeleton thickness and (b) macropore size are depicted. The heterogeneity in macropore size increased with porosity while those of skeleton stayed around 0.3.

thickness hardly changes.

Macropore size obtained from Hg porosimetry and LSCM was compared here. The discrepancy between macropore sizes obtained from Hg porosimetry and those obtained from LSCM declined with porosity. For a sample with smaller porosity around 0.5, macropore size obtained from Hg porosimetry, d_{pH} has been smaller than that obtained from LSCM method, d_{pL} and d_{pH}/d_{pL} is ca. 0.8 while it is ca.1.0 for samples with higher porosity around 0.65 [Figure 1.6].

Taking a bottle neck type macropore for example, the total volume of the macropore is regarded to have diameter equal to its neck in mercury intrusion method since the pore diameter data reflects only the pressure at which mercury is intruded. Mercury will not be intruded until the pressure becomes high enough to penetrate the adjacent pore [Figure 1.9]. The same logic can be applicable to the case of through pores many necks, which are often observed in samples with lower porosity. Pore diameter data obtained from mercury intrusion method has been thus significantly affected by the pore morphology and we therefore adopt LSCM data for porosity, pore diameter and skeleton diameter in the following discussion.

3.3.4 Chord length

Chord length, d_c is also one of the measures for structural dimension besides specific surface area. The original definition of chord length is the distance between two intersections of a line and an arc, however the interpretation of chord length is extended to the distance between intersections of a line and a curved surface in the study of phase separating structure. The distance between two neighboring intersections is unable to become a reasonable measure for the structural dimension since the value is likely influenced by the porosity difference as discussed previously.

The most reasonable means among conceivable possibilities is to measure

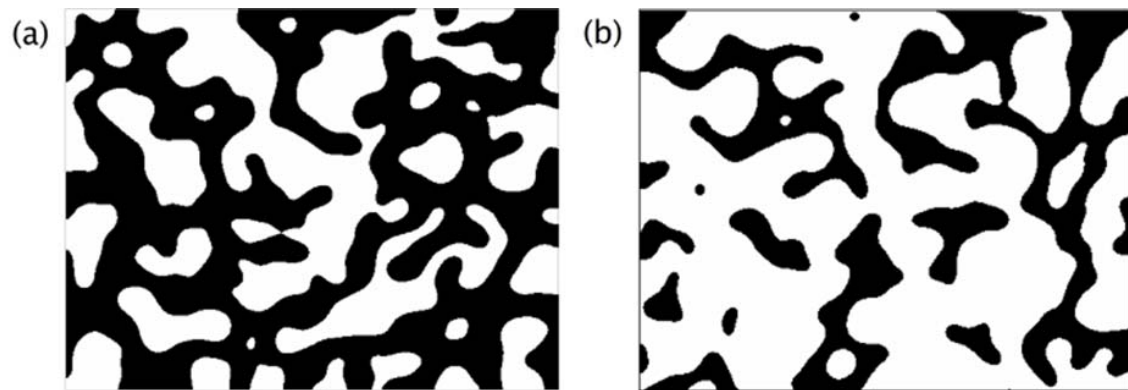


Figure 1.9

Schematic images of co-continuous structures are shown with (a) lower porosity and (b) higher porosity, in which black region corresponds to gel skeleton and white region to macropore domain.

the distance between second neighboring intersections since the influence of porosity is canceled out by adding the chord lengths of macropore and gel skeleton part.

Chord lengths were calculated from reconstructed images and listed in Table 1.3 and the values are plotted against specific surface area in Figure 1.10. The chord length increased proportionally to the specific surface area. It implies that the chord length can be a reasonable measure for structural dimension, however, it is difficult to comprehend what the chord length represents among the structural parameters of co-continuous structure: it is not macropore size, skeleton thickness, nor characteristic wavelength that is approximated by the summation of macropore size and skeleton thickness.

3.3.5 Mean Curvature and Gaussian Curvature

The curvature of a curved surface is the amount by which a geometric object deviates from being flat. The curvature of a site on an arc is equal to the reciprocal of the radius of a circle best fit to the curve at the site (osculating circle). Similarly, local principle curvatures, κ_1 , κ_2 , on a curved surface are defined as reciprocals of the largest and the smallest osculating circles at the same point. Mean curvature is defined as the mean of local principle curvatures and Gaussian curvature is defined as the product of local principle curvatures.

A parallel surface to the interface is formed by translating the original interface along its normal by an equal distance everywhere on the surface. The relation between the area of the infinitesimal patch at a point p , $da(0, p)$, and that of the parallel patch, $da(t, p)$, is

$$da(t, p) = da(0, p)(1 + 2H(p)t + K(p)t^2) \quad (1.3)$$

where $H(p)$ and $K(p)$ are, respectively, the mean and Gaussian curvatures at the

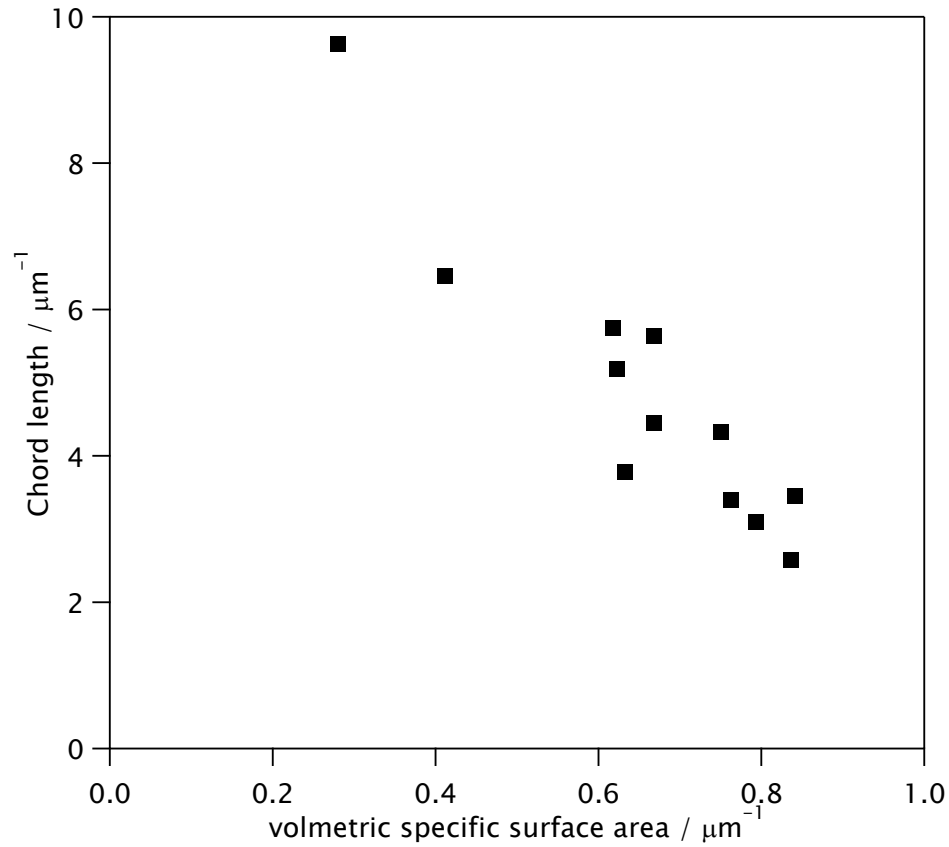


Figure 1.10

Chord lengths were calculated from reconstructed images and plotted against specific surface area. The chord length increased proportionally to the specific surface area. It implies that the chord length can be a reasonable measure for structural dimension.

point $\mathbf{p}$ and t is a signed displacement of the parallel surface from the interface: it is positive if the direction of the displacement points to one side of the surface, and negative otherwise. Summing equation 1.3 over the whole area of the interface by changing the position of the point of interest, $\mathbf{p}$, gives

$$A(t) = A(0) \left(1 + 2\langle H \rangle t + \langle K \rangle t^2 \right) \quad (1.4)$$

Where $A(0)$ is the total area of the original surface and $A(t)$ is that of the parallel surface with displacement t . Thus area averaged mean and Gaussian curvatures were calculated using equation 1.4.

In order to eliminate the influence of structural dimension, area averaged mean and Gaussian curvatures calculated by parallel surface method (PSM) have been further scaled by inverse of specific surface area, Σ^{-1} ($\Sigma = S/V$, S and V corresponds to total gel skeleton surface area and total sample volume, respectively). Inverse of specific surface area was employed to eliminate the influence of structural dimension.

Scaled area averaged mean and Gaussian curvatures, $H^* = \langle H \rangle \Sigma^{-1}$ and $K^* = \langle K \rangle \Sigma^{-2}$, respectively, were plotted against porosity, ϵ . The values of H^* had positive value at lower porosity, then decreased with increasing porosity and finally took negative value [Figure 1.11(a)]. The values of K^* , on the other hand, are located in $K^* < 0$ region for all samples [Figure 1.11(b)] and decreased with porosity.

At porosity around $\epsilon < 0.6$, H^* took positive values and K^* took negative values, which suggests that the macropore surface on an average is curved inward relative to the macropore side. Such kind of surface forms convexly curved macropores and on another front, the SEM and reconstructed 3D images show continuous macropores. Macropores, which meet both of the requirements, should have convexly curved domain for the most part and

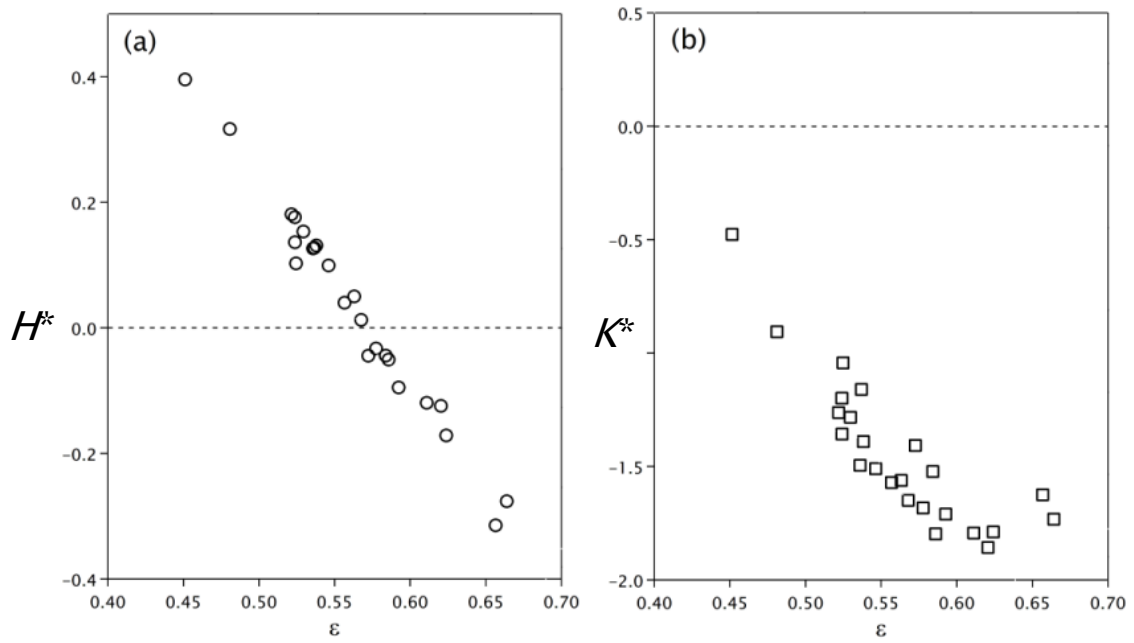


Figure 1.11

(a) Scaled mean curvatures, H^* , and (b) scaled Gaussian curvatures, K^* , have been plotted against porosity.

bottle-neck domain which connects the convexly curved part.

At porosity around $\epsilon=0.6$, H^* took values around zero and K^* took negative values, which suggests that the macropore surface on an average is curved evenly to both of the macropore and gel skeleton sides. The expectation from this kind of surface is symmetric properties between macropore and gel skeleton structure. Macropore surface is also expected to be evenly curved since the driving force of structural evolution during SD is decrease in interface energy, or interface area between polymerizing siloxane and solvent, which later on forms gel skeleton and macropore respectively. The size distribution of macropores with porosity around 0.6 is hence expected to be sharper when compared to those with porosity less than 0.6.

At porosity over $\epsilon>0.6$, H^* took negative value and K^* took negative values, which suggests that the macropore surface on an average is curved inward relative to the gel skeleton side or that the gel skeleton surface is curved outward relative to the macropore side. The strongly negative values of K^* represents that the macropore surface is not convex and hence the macropores are expected to have kind of structure generated by fiber-like gel skeletons.

The detailed discussion on the formation mechanism of such macropore structure is left to chapter 4.

3.3.6 Curvature Distributions

The Gaussian and mean curvatures exhibit the principal shape of surfaces, e.g. $K>0$ corresponds to an elliptic surface (such as sphere), $K=0$ to a parabolic surface (such as cylinder) and $K<0$ to a hyperbolic surface (like saddle-shape) and H is related to the symmetrical property of two co-existing phases. By plotting the probability density distribution of the combination of the mean and Gaussian curvatures, $P(H,K)$, the overall characteristic of the macropore surfaces can be examined.

3.3.6.1 Comparison between Different Porosities

For sample B, H and K, probability density distributions of local curvature is shown in Figure 1.12 (b), (d) and (c), respectively. The distribution area increased with porosity, suggesting that the surface geometry becomes more manifold with increasing porosity. The peak position at lower porosity located in $H>0$ region and eventually shifted to $H<0$ region with porosity. This is corroborative of the observation and discussion describe previously in 3.3.4.

At the same time, the tail on $H<0$ side grew following the $K=H^2$ curve. Mean and Gaussian curvatures related by $K=H^2$ represents spherical surface of gel skeleton. This suggests that the macropore structure at higher porosity is not simply constructed only by fiber-like gel skeletons. The origination of the sphere-like surface of gel skeleton can be the instability of cylindrical thread of fluid.

Cylindrical thread of fluid is known to be unstable to surface wave fluctuations whose length is greater than the circumference of the cylinder. The capillary wave fluctuations brought about in the thread builds up pressure gradients that drive the thread forming fluid from a thinner part to the thicker part. The thread is eventually broken up into a number of spherical droplets aligned along the thread. Once the breakups of the bridge occur, it is expected to split into a pair of elliptic surfaces, i.e., corns facing each other.

More detailed discussion on the origination of the formation process of macropores is however left to Chapter 4.

3.3.6.2 Comparison between Different Macropore Sizes

For sample H, sample L and G, probability density distributions of local curvatures are also shown in Figure 1.12 (d), (e) and (f), respectively. The peak position and distribution range is almost the same for samples H and D. This

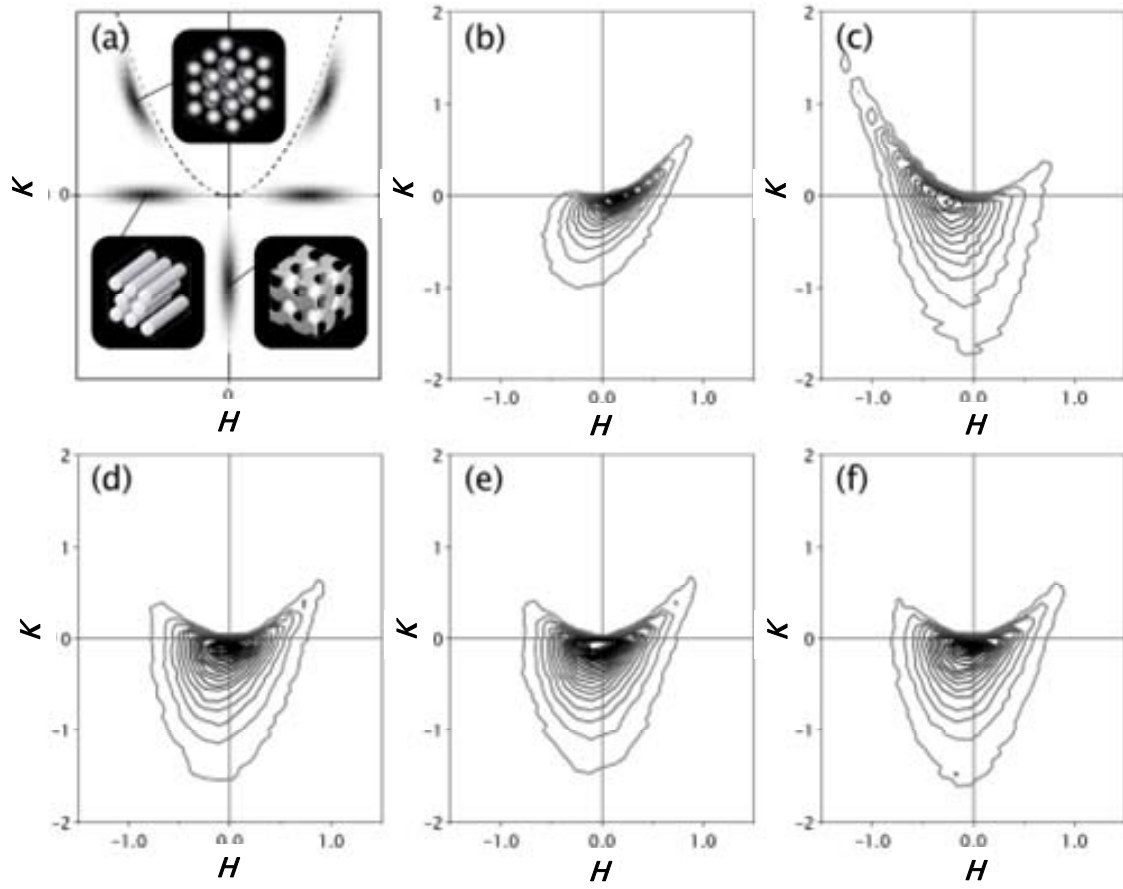


Figure 1.12

(a) Schematic distributions of local curvatures and the corresponding structures where M is scaled mean curvature and G is scaled Gaussian curvature.

(b) curvature distribution of sample B ($d_p=4.17 \mu\text{m}$, $\varepsilon=0.534$), (c) sample K ($d_p=4.36 \mu\text{m}$, $\varepsilon=0.664$) (d) sample H ($d_p=4.40 \mu\text{m}$, $\varepsilon=0.587$) (e) sample L ($d_p=5.26 \mu\text{m}$, $\varepsilon=0.576$) (f) sample G ($d_p=9.37 \mu\text{m}$, $\varepsilon=0.584$)

suggests the self-similar growth of phase separating structure during spinodal decomposition. The peak position for sample G is also located closely to those for samples H and D, but the distribution range has grown to smaller H direction following $K=0$. This suggests the existence of fibrous gel skeleton.

The comparison between sample with same porosity and different pore diameters is closely related to the time evolution of phase separating structure. Detailed discussion is hence preferable to be left to Chapter 4.

3.3.7 Structural Parameters as a Function of Porosity

Table 1.3 gives an overview of skeleton thickness, pore diameter skeleton length, volume specific surface area, a , which is equal to “surface area/total sample volume of monolith”, and porosity.

One of the methods to compare structural characteristics is to use shape factor. There are several known shape factors, and the one based upon porosity, surface area and skeleton thickness is adopted in this chapter since these parameters are significantly related to the liquid flow.

The adopted shape factor K_v is defined as

$$K_v = \frac{k_s}{k_v} \quad (1.5)$$

wherein surface shape factor, k_s is defined as the following using surface area of the solid phase, S ,

$$k_s = \frac{S}{d_s^2} \quad (1.6)$$

and volume shape factor, k_v is defined as the following using the volume of the

solid phase, V .

$$k_v = \frac{V}{d_s^3} \quad (1.7)$$

K_V was calculated by the following equation, actually.

$$K_V = \frac{(a/d_s^2)}{((1-\varepsilon)/d_s^3)} \quad (1.8)$$

Shape factor, K_V can be calculated for all kinds of structures with known volumes, surface areas and characteristic length, for example, $K_V=6$ for spheres and $K_V=3$ for cylinders. In order to compare macropore structure with well-known model, shape factor for tetrahedral skeleton model (TSM) were also calculated. TSM was constructed upon crystal lattice structure of a diamond in which each carbon atom is bonded tetrahedrally to its four neighbors, and has the feature of bonds in the lattice shown in Figure 1.13. One of the advantages of this model is that the structural parameters can be represented using two parameters: the skeleton diameter, d_s , and the skeleton unit length, l_s . Using geometrical considerations and Microsoft Excel based least-squares-of-error parameter fitting procedure, the following relations were established. Porosity, ε , is described in terms of l_s and d_s ,

$$\varepsilon = 1 - \frac{d_s^2(l_s/2 - d_s/5.27)}{4(l_s/2)^3} \quad (1.9)$$

and for specific surface area, a ,

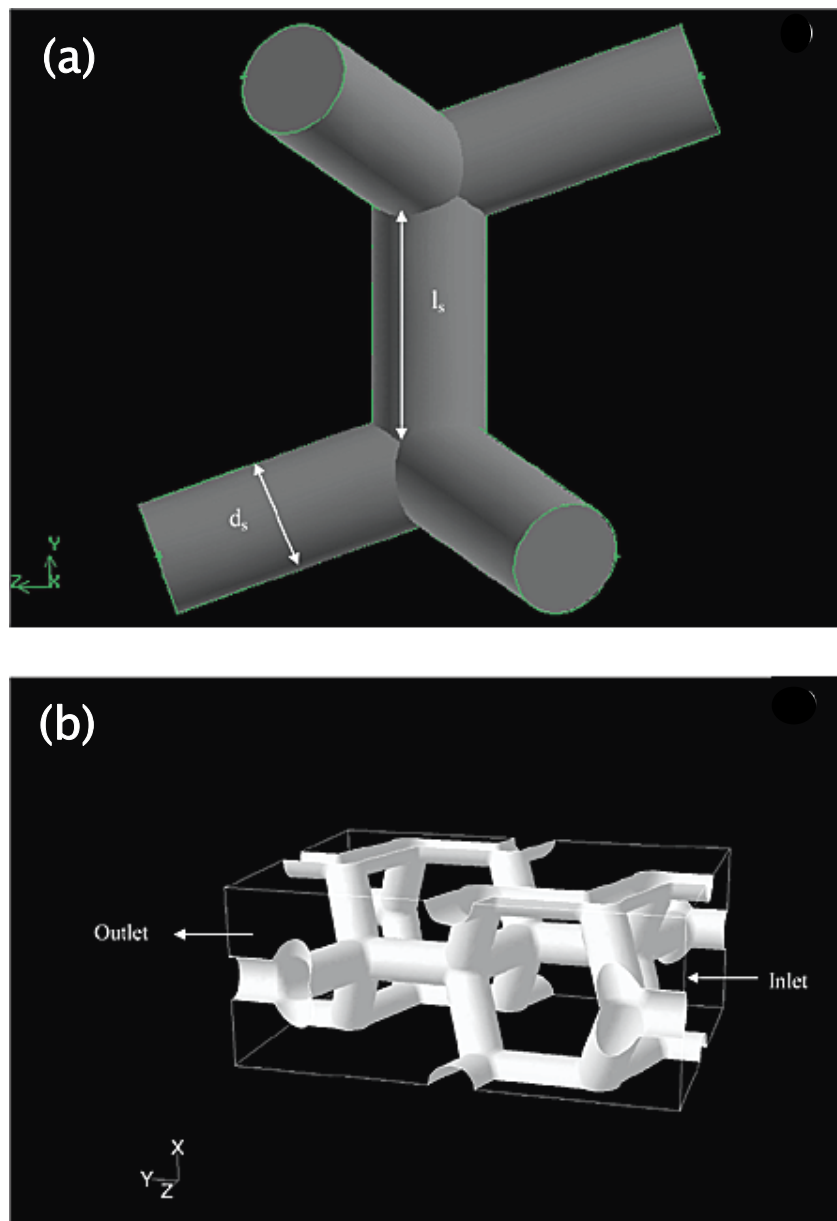


Figure 1.13

(a)Detailed view of skeleton structure and definition of the geometric parameters, d_s and l_s . (b) global view of unit cell of tetrahedral skeleton column.

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$$a = \frac{6\sqrt{6}\pi d_s(24l_s - \sqrt{2}d_s)}{(4\sqrt{2}l_s + 3d_s)^3} \quad (1.10)$$

The shape factors of real monolith and TSM are plotted against porosity in Figure 1.14. The difference in the magnitude of shape factor values calculated on structural parameters is mainly due to difference in surface area between real monolith and TSM. TSM skeleton has perfectly cylindrical shape, while real monolith does not. Let us consider the side surface area of a cylinder with uniform radius and a cylinder whose radius changes according to sinusoidal curve [Figure 1.15].

$$y = R\left(\frac{2}{\pi} + 1\right) - R\sin\left(\frac{\pi}{L}x\right), \quad 0 \leq x \leq L \quad (1.11)$$

The surface contour of the macropore of real monolith can be represented by more complicated function: the ideal structure of spinodal decomposition (the formation mechanism of macropore structure of real monolith) can be generated using trigonometric approximation as represented in the following

$$f(x, y, z) = \sin\left(\frac{2\pi}{L}x\right)\cos\left(\frac{2\pi}{L}y\right) + \sin\left(\frac{2\pi}{L}y\right)\cos\left(\frac{2\pi}{L}z\right) + \sin\left(\frac{2\pi}{L}z\right)\cos\left(\frac{2\pi}{L}x\right) \quad (1.12)$$

We adopted simpler function for the comparison with TSM model. Assuming that both of the cylinders have the length of L , the side surface area of a cylinder with uniform diameter R equals to $2\pi RL$ and that of a cylinder with varying diameter equals to ca. $2.52\pi RL$.

Since the volume of the cylinder also increases when the sinusoidal variation is introduced in the diameter, the shape factors were re-calculated and plotted against the re-calculated porosity [Figure 1.14]. By adding

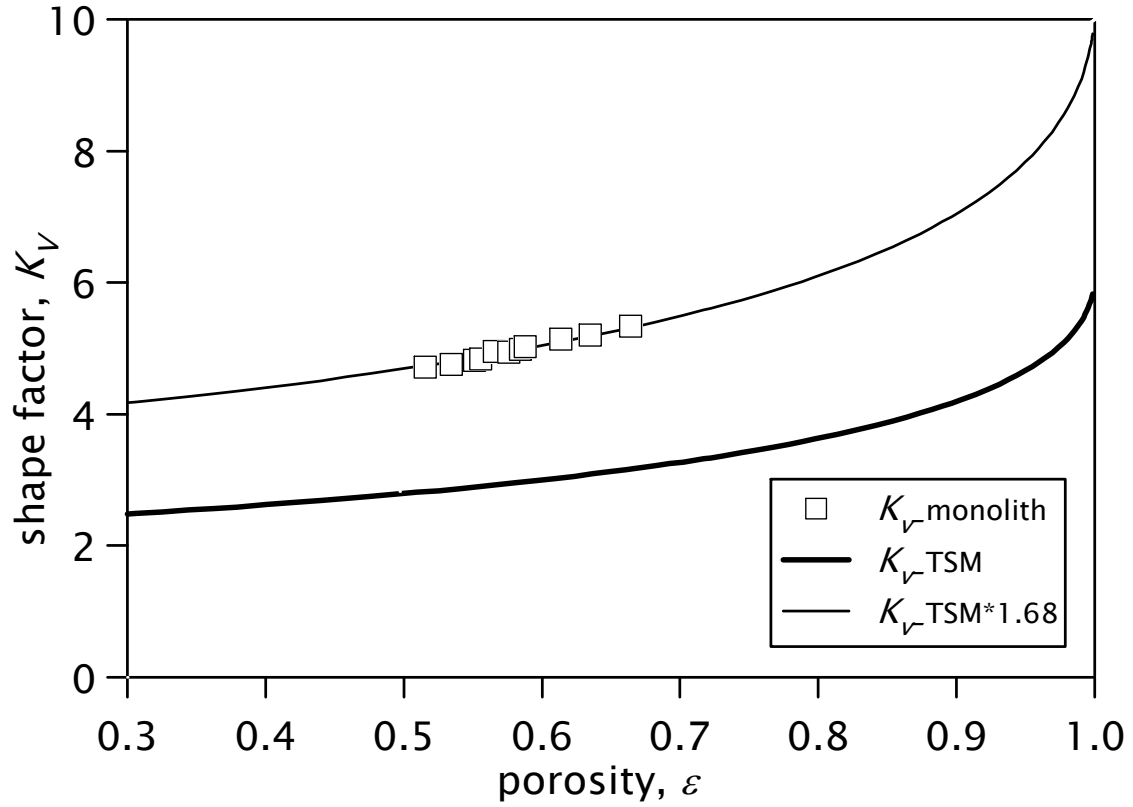


Figure 1.14

Shape factor K_v for real monolith and TSM are shown. The agreement between $K_{v_monolith}$ and $K_{v_TSM} \times 1.68$ well accounts for the similarity between real monolith and TSM on the basis of porosity, surface area and skeleton thickness.

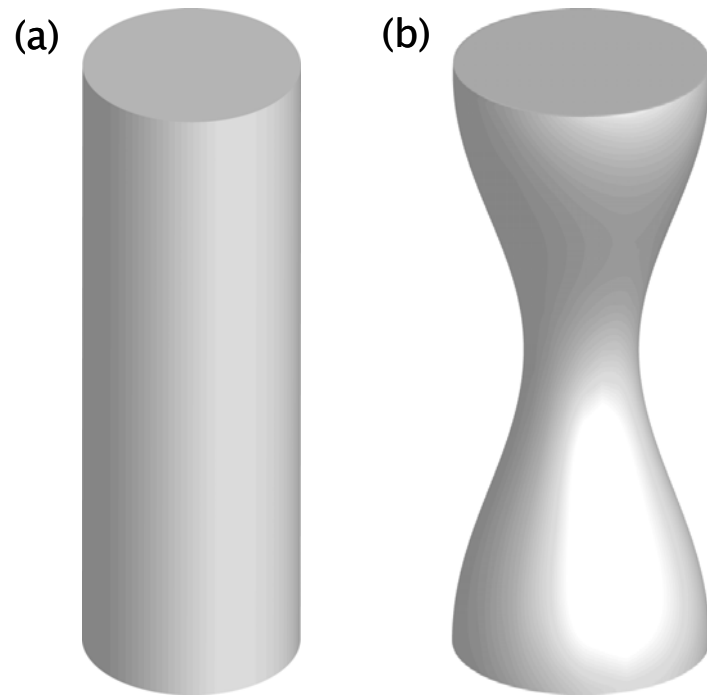


Figure 1.15

The G-surface is known to be the ideal structure for spinodal decomposition (a), cylinders with constant diameter (b) and that with diameter changes according to sinusoidal function.

heterogeneity in unit skeleton length, the overall surface area further increases. When a variation with standard deviation, σ , is introduced on the unit skeleton length, which is directly related to macropore diameter in TSM model, the surface area increased by a factor of ca. 1.04 when the standard deviation $\sigma=0.1$ and ca. 1.21 when $\sigma=0.2$.

Since the shape factor calculated using previous equation is a function of porosity, specific surface area and skeleton diameter, the increase in calculated shape factor of macropore structure compared to TSM is reasonably explained by assuming that the macropores are constructed by the cylinders with same mean diameter, different surface area and heterogeneity in length.

4. Conclusions

Macropore structure was observed in three dimension using laser scanning confocal microscope (LSCM). Following image processing extracted several kind of structural parameters. Since these parameters can be directly obtained from LSCM images, more accuracy can be expected than conventional methods, i.e., SEM, mercury intrusion method, etc. A comparison between mercury intrusion and LSCM methods actually confirmed that the way of mercury intrusion depends on the morphology of macropore. Together with the idea that SEM has thick focal plane, it can be concluded that LSCM method will a promising candidate for structural analysis methods for porous material.

By using structural parameters obtained from LSCM observation, the consistency between the structure of real monolith and TSM model was examined, and it was confirmed that TSM model well represents the structure of real monolith on the basis of surface area.

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Chapter 2: Mutual Consistency between Measured and Simulated Systems

1. Introduction

Co-continuous monolithic silica column has been commercialized and evaluated for more than five years, exhibiting noticeable properties; increased permeability and decreased plate height selectivity to that of comparable standard packed bed columns [1–11]. The comparison, however, can not be done straight away between monolithic and packed bed columns. It was shown in recent studies [12–13] that the comparison of minimal separation impedance alone can not account for the separation efficiency: while the minimal separation impedance of monolithic columns corresponds to higher plate numbers than that of packed bed columns, the E-number for a given separation (around $N=10000$) of the packed bed can have a smaller value than the monolith. More versatile normalization which enables the direct comparison between monoliths and packed bed are now in urgent need.

Flow behavior and separation behavior in macroporous monolith are naturally affected by the macropore properties (i.e. porosity and macropore size), as in the case of packed beads bed. These parameters can be easily controlled as to obtain best performance by a simple adjustment in preparation conditions (i.e. starting composition and temperature) [14–16]. The porosity change may raise a problem which has not considered before. The closely packed beds always have a porosity of around 0.4 and their geometry is similar independently of the particle size. The porosity of monoliths, on the other hand, can range from 0.45 to 0.85 and their geometries are not super imposable lost among monoliths with varied porosities. The liquid transport behavior is therefore

expected to change with the porosity increase, since the behavior is significantly affected by flow path details. The flow behavior and separation behavior in monoliths can no more be estimated accurately with familiar equations which have been designed for packed beads bed structure [17–19]. Additional independent parameters other than “particle diameter” and “porosity” need to be introduced.

In order to examine the relation between structural properties and flow or separation behavior, and to make the best use of silica monolith, a vast number of studies have been done [1–8, 20]. Among them, as a novel method, a series of validated computational fluid dynamics simulations has been performed on a simplified model structure, and it contributed to gain insight into the relation between the internal structure of a monolithic column and its flow behavior [21–23]. The model structure used for computational fluid dynamics, tetrahedral skeleton model [Figure 2.1], was constructed upon crystal lattice structure of diamond in which each carbon atom is bonded tetrahedrally to its four neighbors, as mentioned in Chapter 1.

Characteristic structure of monolithic silica, on the other hand, derives from spinodal decomposition (SD) [24], one of the well-known classical phase separation mechanisms [25–27]. By freezing the phase separating structure at an appropriate stage by a sol–gel transition, co-continuous macroporous structure of silica monolith can be obtained. A steep increase in viscosity of the gel phase significantly affects anisotropic deformation of continuous gel skeletons [28–32] near gelation point. Because of its structural complexity, the geometrical properties of resultant monolithic silica have only been evaluated by averaged parameters such as pore diameter or porosity measured by conventional methods such as mercury intrusion.

In this chapter, the geometrical properties on macropore surface structure were investigated by using laser scanning confocal microscopy (LSCM), of which

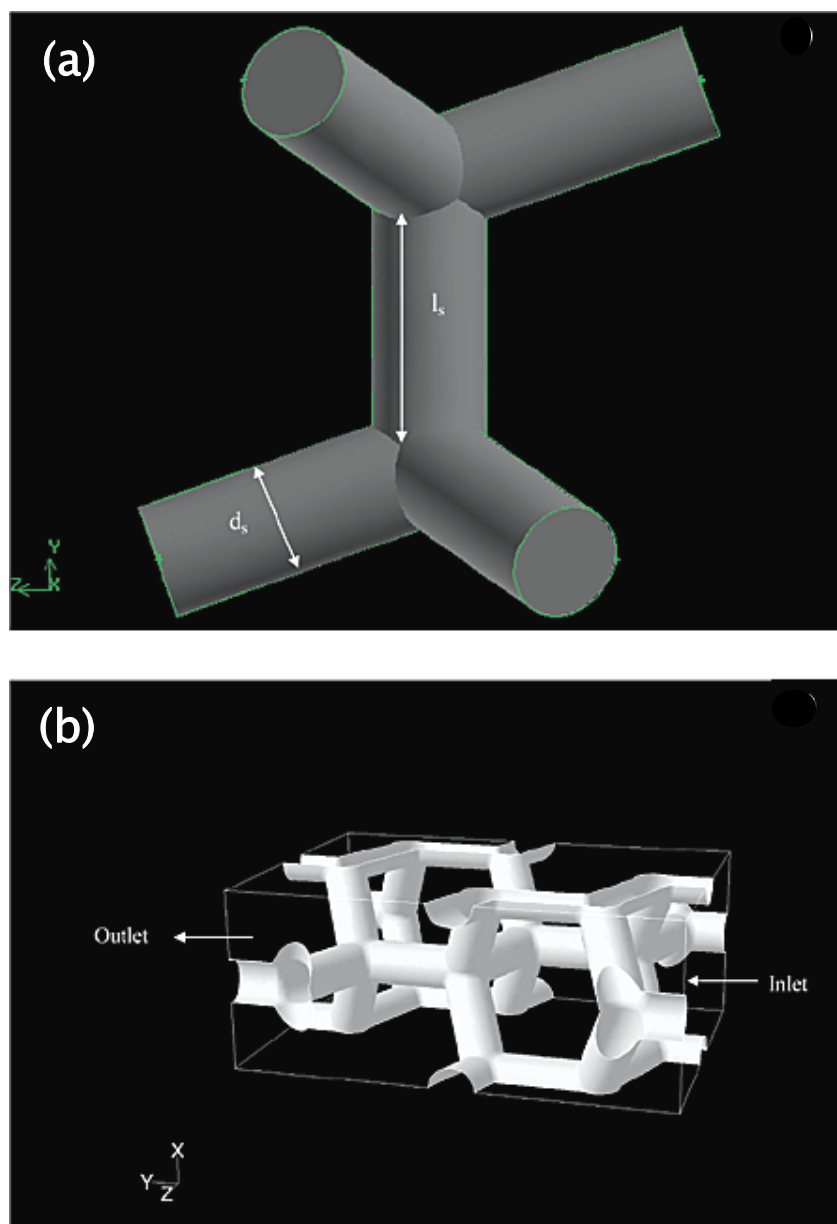


Figure 2.1

(a) Detailed view of skeleton structure and definition of the geometric parameters, d_s and l_s . (b) global view of unit cell of tetrahedral skeleton column.

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images can be reconstructed in three dimension (3D) and be provided for the calculation of geometrical and topological parameters [33–36]. Experimental liquid flow behavior was evaluated by dimensionless flow resistance calculated from permeability and skeleton diameter. The mutual consistency between flow resistances in simulated and measured systems was examined in terms of the obtained structural parameters.

2. Experimental

2.1 Sample Preparation

In a first place, poly(ethylene glycol) (M.W. 100,000), PEO10, and D-sorbitol were homogeneously dissolved in 1M nitric acid. Then, 6.5g of tetraethoxysilane (TEOS) was added under vigorous stirring in an ice-cooled condition. The weight ratio of starting composition was TEOS: 1MHNO₃: PEO10: D-Sorbitol = 1: 1.23~1.54: 0.12~0.16: 0~0.08. Actual compositions are listed in Table 2.1. After 30 minutes of stirring, the resultant homogeneous solution was transferred into a polypropylene tube (i.d. 6mm, 20cm length) and allowed to gel at 40°C in a closed condition. After aging at the same temperature for 10 h, the resultant gel was immersed in water for 3 hours in order to remove residual acids, and solvent-exchanged with 1M urea aq for 3 h. The following hydrothermal treatment was carried out for 5h at 110°C in 1.5M urea aq. After 2 hours of solvent exchange with water, gels obtained were dried and heat treated at 600°C for 5 h in order to remove residual organics.

2.2 Structural Observation

The structures and geometrical properties of obtained gels were observed

Table 2.1

An overview of starting compositions of real monoliths

	1MNH ₃	PEO10	D-Sorbitol	TEOS
A	7.0	0.90	0.0	6.4
B	7.0	0.90	0.8	6.4
C	8.0	0.90	0.4	6.4
D	8.0	0.90	0.0	6.4
E	8.0	0.90	0.6	6.4
F	9.0	0.90	0.0	6.4
G	9.0	0.90	0.8	6.4
H	9.0	0.90	0.2	6.4
I	10.0	0.90	0.2	6.4
J	10.0	0.97	0.0	6.4
K	9.0	0.90	0.0	6.4
L	10.0	0.95	0.0	6.4

by a scanning electron microscope (SEM) (S-2600N, Hitachi, Japan), a laser scanning confocal microscope (LSCM, LSM5 PASCAL, Carl Zeiss, Germany). A mercury intrusion apparatus (PORESIZER 9320, Micromeritics, U.S.A.) was used to determine the size distribution of pores larger than 7nm in diameter.

2.3 Pressure Drop Measurement

For the pressure drop measurement, the monolithic silica gels were shaped into cylinders of 83mm in length and 4.2mm in diameter, and clad with epoxy resin into liquid chromatography column.

The pressure drop measurement was performed with liquid chromatography pump (LP10, Shimadzu, Japan) and pressure transducer (TP-AR, TEAC, Japan). Columns were tightened by a radial compression module (RCM8×10) for the purpose of withstanding the pressure exerted from the mobile phase. Mobile phase adopted was pure water and pressure drop was measured with flow rate ranging from 0.1 ml/min to 2.0 ml/min at room temperature (20°C).

Linear velocity of mobile phase was calculated from dead time, t_0 , which was measured with water as mobile phase and thiourea as a non-retained solute. The Reynolds numbers calculated for the monolithic columns are well in the range of laminar flow.

3. Results and Discussion

3.1 Flow Resistance for Monolith and Tetrahedral Skeleton Model

The permeability of real monolith was calculated by the slope of measured ΔP vs u_0 plot, based on Darcy's law

$$K_0 = \frac{u_0 \eta L}{\Delta P} \quad (2.1)$$

where η is viscosity of the working fluid, and L is column length. In order to generalize the results, the obtained permeability was further generalized into flow resistance $\phi_{\text{Darcy},0}$, in order to eliminate the influence of dimension.

$$\phi_{\text{Darcy},0} = \frac{d_s^2}{K_0} \quad (2.2)$$

The flow resistance values of TSM obtained from computational fluid dynamics are described using porosity, ε , by the following correlation [21].

$$\phi_{\text{TSM},x} = 55 \left(\frac{1-\varepsilon}{\varepsilon} \right)^{1.55} \quad (2.3)$$

Another relationship is the Happel equation [42–43]. Happel equation was obtained on the basis that two concentric spheres can serve as the cell model for a random assemblage of spheres moving relative to a fluid [Figure 2.2]. The inner sphere, $r=\alpha$, comprises one of the particles in the assemblage and the outer sphere, $r=\beta$, consists of a fluid envelope with the frictionless surface, so-called “free surface”. The entire disturbance due to each particle can be thus confined to the cell of fluid and a closed solution of sedimentation can be obtained. Since it is presumed here that the effect of walls of the containing vessel is sufficiently small so that the two cases are mathematically equivalent where either the particles move and there is no average motion of the fluid or alternatively the particles remain more or less stationary and fluid passes around them.

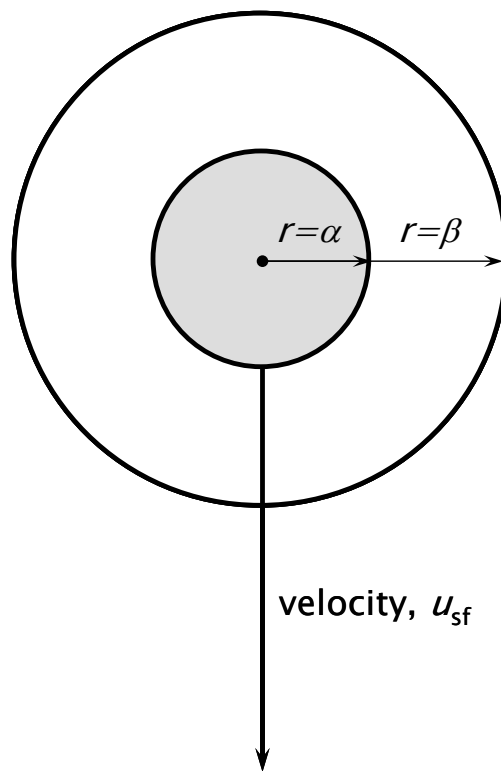


Figure 2.2

Schematic of “free surface cell model” proposed by J. Happel is shown. The inner sphere with a radius α is solid and the outer sphere of radius β is fluid, and the inner sphere is moving with velocity u_{sf} .

The drag on a sphere in a fluid cell moving in the x-positive direction is given by

$$W_x = -4\pi\eta \cdot \frac{\alpha u_{sf}(3 + 2\gamma^5)}{2 - 3\gamma + 3\gamma^5 - 2\gamma^6} \quad (2.4)$$

For the free-surface cell model, the drag divided by the cell volume, $(4/3)\pi\beta^3$ equals to the pressure gradient, $-\Delta P/L$. The use of this relation gives

$$u_{sf} = \left(\frac{2 - 3\gamma + 3\gamma^5 - 2\gamma^6}{3 + 2\gamma^5} \right) \cdot \left(\frac{2\alpha^2}{9\gamma^3\eta} \right) \frac{\Delta P}{L} \quad (2.5)$$

$$\phi_{Happel,x} = \frac{9}{2} \gamma^3 \cdot \frac{3 + 2\gamma^5}{3 - (9/2)\gamma + (9/2)\gamma^5 - 3\gamma^6} \cdot \varepsilon \quad (2.6)$$

where $\gamma = \alpha/\beta = (1 - \varepsilon)^{1/3}$. Happel equation is valid, in theory, over broad range of porosity for packed beads bed.

For real monoliths and in chromatography in general, the linear velocity is usually determined by the common practice of measuring the residence time of a non-retained tracer compound. These measurements assume that the tracer plug is never retained by the column packing material but does diffuse into the porous skeleton of the stationary phase material, thus having a zone retention factor k_0 does not equal to 0. Since the zone retention factor of the t_0 marker is not equal to 0, the average x-velocity of the tracer is lower than the average interstitial x-velocity. This also means that the theoretical correlations, which are based upon the use of the linear interstitial velocity, cannot be used directly for comparison with experimental data based upon u_0 . To allow direct use of theoretical correlations for comparison with experimental data, based upon u_0 , the obtained flow resistance correlation should be rescaled so that it is also based upon u_0 . Since the u_0 value can be written as

$$u_0 = u_x(1 + k_0) \quad (2.7)$$

and k_0'' can be calculated as

$$k_0'' = \frac{1 - \varepsilon}{\varepsilon} \varepsilon_{\text{int}} \quad (2.8)$$

the flow resistance should hence be written as

$$\phi_0 = \phi_x \left(1 + \frac{1 - \varepsilon}{\varepsilon} \varepsilon_{\text{int}} \right) \quad (2.9)$$

Since internal porosity ε_{int} of real monolith ranged from ca. 0.45 to 0.54, we assumed $\varepsilon_{\text{int}}=0.5$ and rescaled the calculated theoretical flow resistance values according to eq. (2.7). Using this relation, flow resistance $\phi_{\text{TSM},x}$ was calculated into $\phi_{\text{TSM},0}$

$$\phi_{\text{TSM},0} = 55 \left(\frac{1 - \varepsilon}{\varepsilon} \right)^{1.55} \left(1 + \frac{1 - \varepsilon}{\varepsilon} \varepsilon_{\text{int}} \right) \quad (2.10)$$

and $\phi_{\text{Happel},x}$ into $\phi_{\text{Happel},0}$

$$\phi_{\text{Happel},0} = \frac{9}{2} \gamma^3 \frac{3 + 2\gamma^5}{3 - (9/2)\gamma + (9/2)\gamma^5 - 3\gamma^6} \cdot \varepsilon \cdot \left(1 + \frac{1 - \varepsilon}{\varepsilon} \varepsilon_{\text{int}} \right) \quad (2.11)$$

Figure 2.3 shows the dependency of flow resistances on porosity. The actual values of flow resistance and structural parameters are listed in Table 2.2. Relatively higher flow resistance of packed sphere, $\phi_{\text{Happel},0}$, than that of TSM

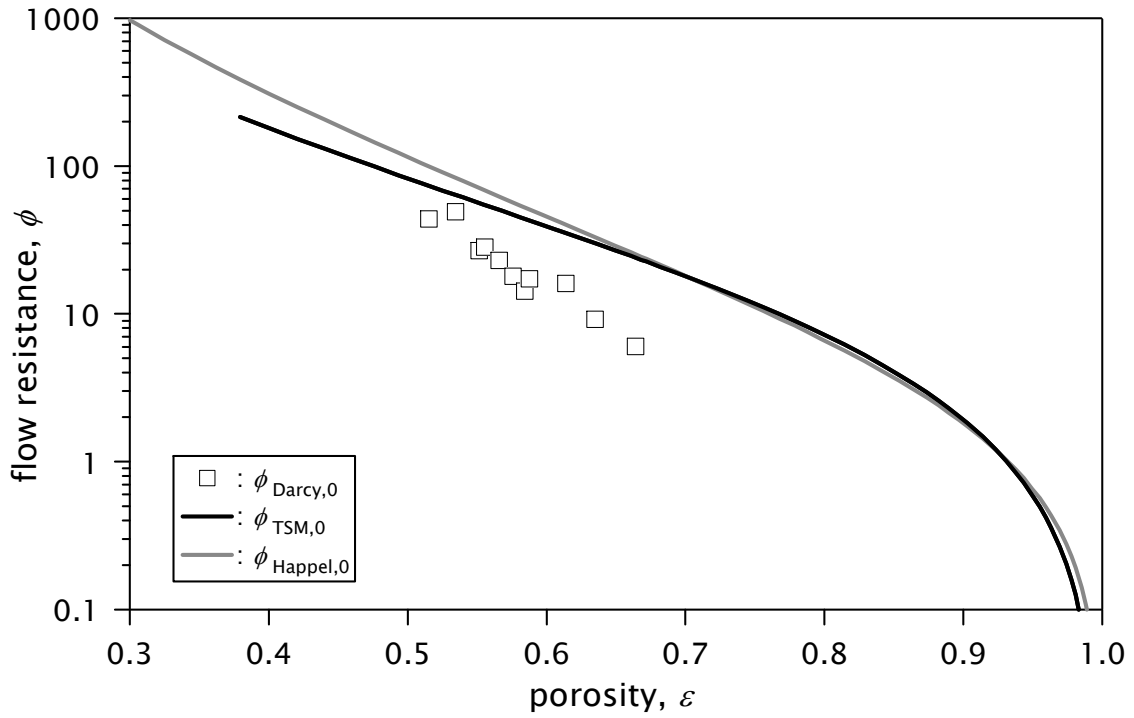


Figure 2.3

Flow resistance obtained from real monolith, TSM and Happel equation are shown. The solid line corresponds to the flow resistance obtained from TSM, the broken line corresponds to the one obtained from Happel equation and the open squares correspond to those obtained from real monolith.

Table 2.2

An overview of structural parameters and shape factors of real monoliths

	ε	$d_s / \mu\text{m}$	$d_p / \mu\text{m}$	$a / \mu\text{m}^{-1}$	k_s	k_v	K_v	$\phi_{\text{Darcy},0}$
A	0.515	2.73	3.16	0.836	0.112	0.0237	4.72	48.8
B	0.534	3.45	4.17	0.641	0.0538	0.0113	4.76	38.1
C	0.551	2.88	3.67	0.750	0.090	0.0187	4.82	29.4
D	0.555	2.55	3.20	0.841	0.128	0.0265	4.84	28.0
E	0.565	3.21	4.02	0.668	0.0645	0.0130	4.95	24.3
F	0.575	3.13	4.03	0.668	0.0679	0.0138	4.94	20.3
G	0.584	7.41	9.37	0.280	0.00510	0.00102	4.99	17.5
H	0.587	3.36	4.40	0.618	0.0548	0.0109	5.03	16.5
I	0.613	4.70	6.17	0.423	0.0192	0.00372	5.14	12.4
J	0.634	2.39	3.26	0.794	0.138	0.0266	5.20	9.0
K	0.664	2.91	4.36	0.617	0.0730	0.0137	5.34	5.9

model, $\phi_{TSM,0}$, reasonably reflects the tortuosity difference between them [21].

Comparing $\phi_{Darcy,0}$ and $\phi_{TSM,0}$ the flow resistance of real monolith, $\phi_{Darcy,0}$ exhibited lower flow resistance and stronger decline on porosity increase compared to that of TSM model, $\phi_{TSM,0}$. There is a general tendency that flow resistance decreases with increasing porosity due to flow-through path magnification, however the difference in the decline can not be explained only by this idea. Since TSM model well represents the geometry of real monolith on the basis of averaged surface area, it is expected that there exists some other difference between them. The possibilities are structural heterogeneity, surface curvatures and branch numbers and they are discussed in the following.

3.2 The Influence of the Heterogeneity

One of the differences between real monolith and TSM model is macropore heterogeneity. When the flow-through pore has a distribution in its size, the pressure drop is a resultant of the contributions from smaller pores and larger pores, which increases and decreases flow resistance, respectively. Flow rate through pores is proportional to the biquadratic of pore diameter, and hence the influence of larger pores overwhelms that of smaller pores. This implies that the flow resistance in heterogeneous macropores will be always smaller than that in the homogeneous macropores from this discussion.

Vervoort *et.al*/ actually introduced a distribution in TSM and reasonably explained the flow resistance reduction due to macropore heterogeneity [21]. They adapted a procedure outlined by Schisla et al. [44] for the calculation of the effective pressure drop in a bundle of capillaries with a polydisperse diameter.

A dimensionless parameter, Z , was introduced

$$Z = \frac{I_s - I_{sm}}{I_{sm}} \quad (2.12)$$

where l_s is the unit skeleton length and l_{sm} is its mean value, and the relation between flow resistance and porosity was re-calculated assuming Gaussian distribution of z . The flow resistance was actually made 20% small from that of homogeneous model when the distribution with standard deviation, $\sigma_z=0.4$ is introduced in z .

In order to eliminate the influence of macropore size heterogeneity from the measured flow resistance, standard deviation of dimensionless parameter, z' , was calculated.

$$z' = \frac{d_p - d_{pm}}{d_{pm}} \quad (2.13)$$

where d_p is the macropore size and d_{pm} is its mean value. Macropore sizes in TSM are proportional to its unit skeleton length, l_s , and hence the identification of parameters z and z' is adequately reasonable for the present discussion. The macropore size was calculated by skeletonization, and the obtained parameters were plotted against porosity in Figure 2.4. It showed that the heterogeneity in the macropore size increased with porosity.

Filled squares in Figure 2.5 is calculated from $\phi_{Darcy,0}$ so that the standard deviation of macropore in real monolith, $\sigma_{z'}$, equals to zero. (Simply calculated by $\phi_{Darcy,0}^* ((\phi_{TSM,0} |_{\sigma_z=0}) / (\phi_{TSM,0} |_{\sigma_z=\sigma_z'}))$) In the intermediate porosity range ($\epsilon < 0.6$), the flow resistance in real monolith had higher value than that in TSM and with increasing porosity, $\phi_{Darcy,0}$ exhibited lower value than $\phi_{TSM,0}$. The discrepancy between real monolith and TSM was eliminated to a large extent, but there were still some differences.

3.3 The Influence of the Curvature

3.3.1 Structural Unit with Curvature

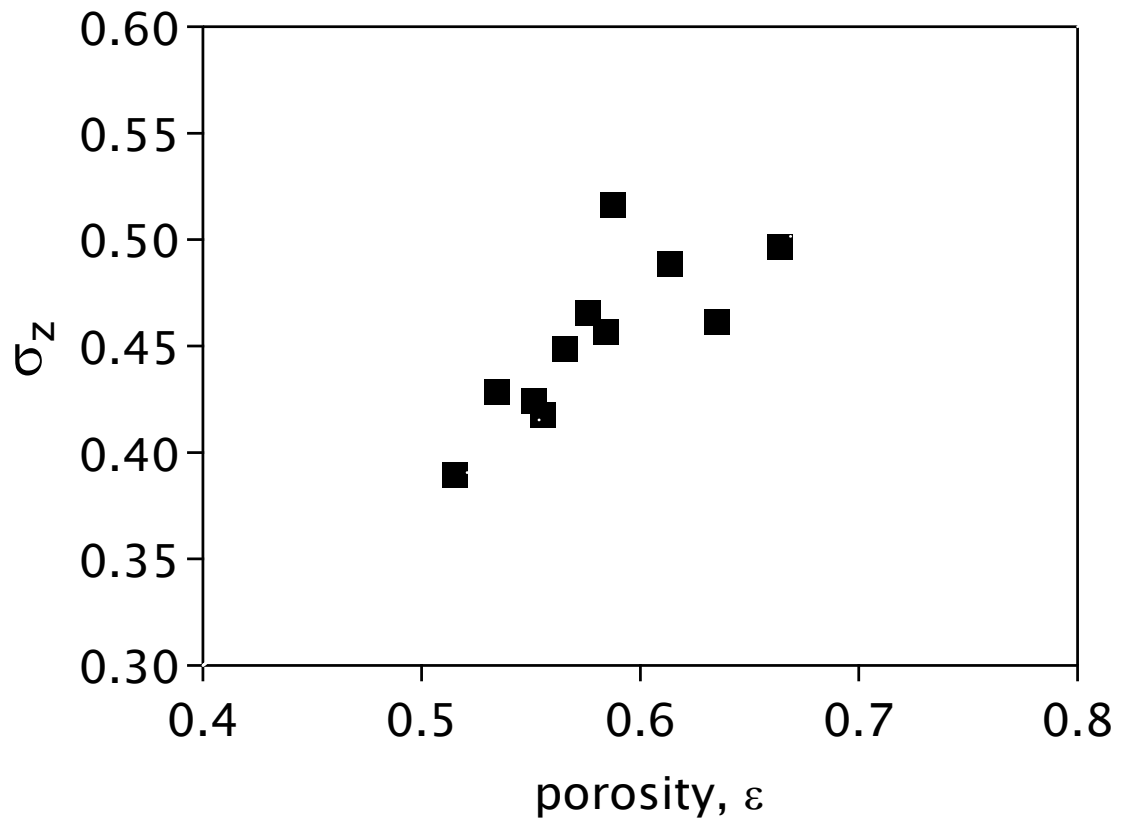


Figure 2.4

The porosity dependency of standard deviation, σ_z of macropore is depicted. The standard deviation, σ_z was calculated from the distribution of macropore obtained by skeletonization.

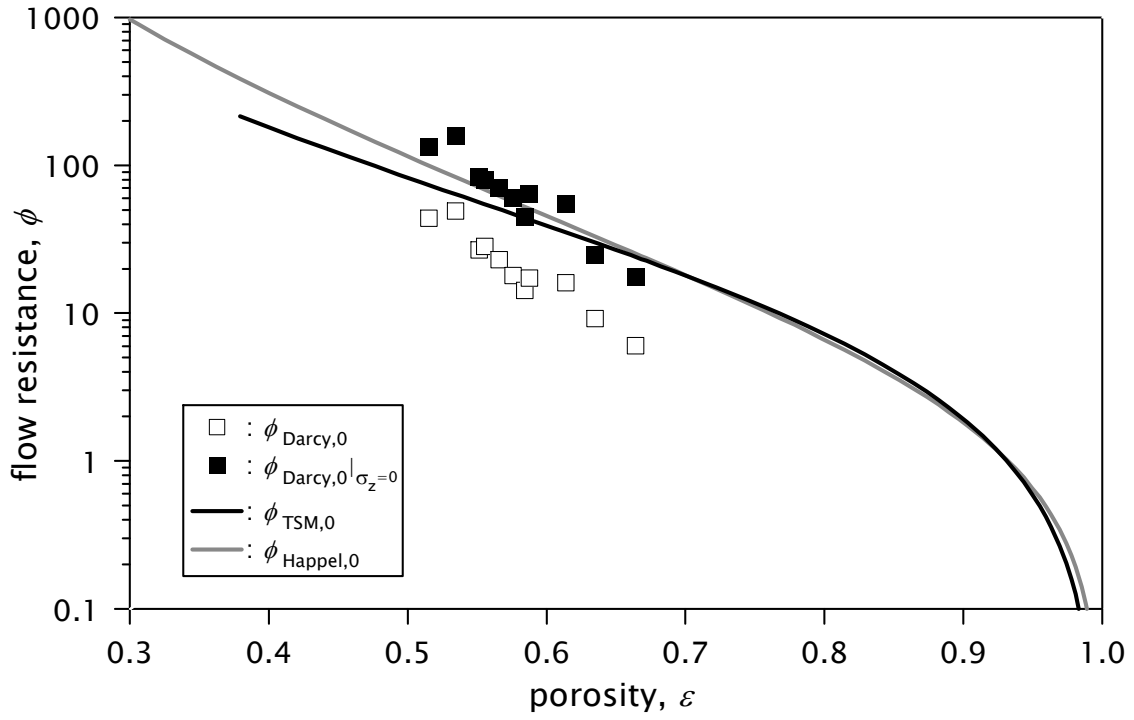


Figure 2.5

The flow resistance values (filled squares) were calculated from $\phi_{\text{Darcy},0}$ assuming the standard deviation of macropore, σ_z , equals to zero.

The mean curvatures of the macropore surface, $\langle H \rangle$, of real monolith are plotted against porosity in Figure 2.6. The mean curvatures were normalized on the basis of specific surface area so that the influence of structural dimension can be eliminated. A curvature is classified as positive if its osculating circle locates in macropore region, negative in skeleton region and equal to zero at the surface, in this work. On the basis of this definition, the surface can be assumed to be extending relative to macropore region if the mean curvature has positive value at a point of interest, since the radius of osculating circle in macropore side is smaller than that in skeleton side, and vice versa.

The mean curvature $\langle H \rangle$ decreased with increasing porosity from ca. 0.2 to ca. -0.2. In the intermediate porosity region ($\epsilon < 0.6$), mean curvatures took positive value. It suggests that macropore surface is curved inward relative to macropore side, and accordingly that the skeleton is extending outward relative to macropore side. On the assumption that real monolith can be regarded as being constructed by cylinders with curved surface as discussed in chapter 1, the structural unit can be regarded as a cylinder with its both edges extending outward. The convex skeleton can behave as an obstacle against permeating fluid, to increase the flow resistance.

When the mean curvature $\langle H \rangle$ equals to zero, the radii of the osculating circles in macropore and skeleton sides have same value and the concavity and convexity on macropore surface are offset. The surface contour of the structural unit cylinder can be assumed to have little influence on flow resistance when $\langle H \rangle$ equals to zero. The idea is easy to understand by discussing tortuosity, which is defined as (effective flow path)/(medium length). It is apprehended that higher value of tortuosity contributes to the higher flow resistance and vice versa. The flow path is lengthened at the region where skeleton convexes relative to macropore side while shortened at the region where the skeleton is concaved. On the whole, the concavity and convexity

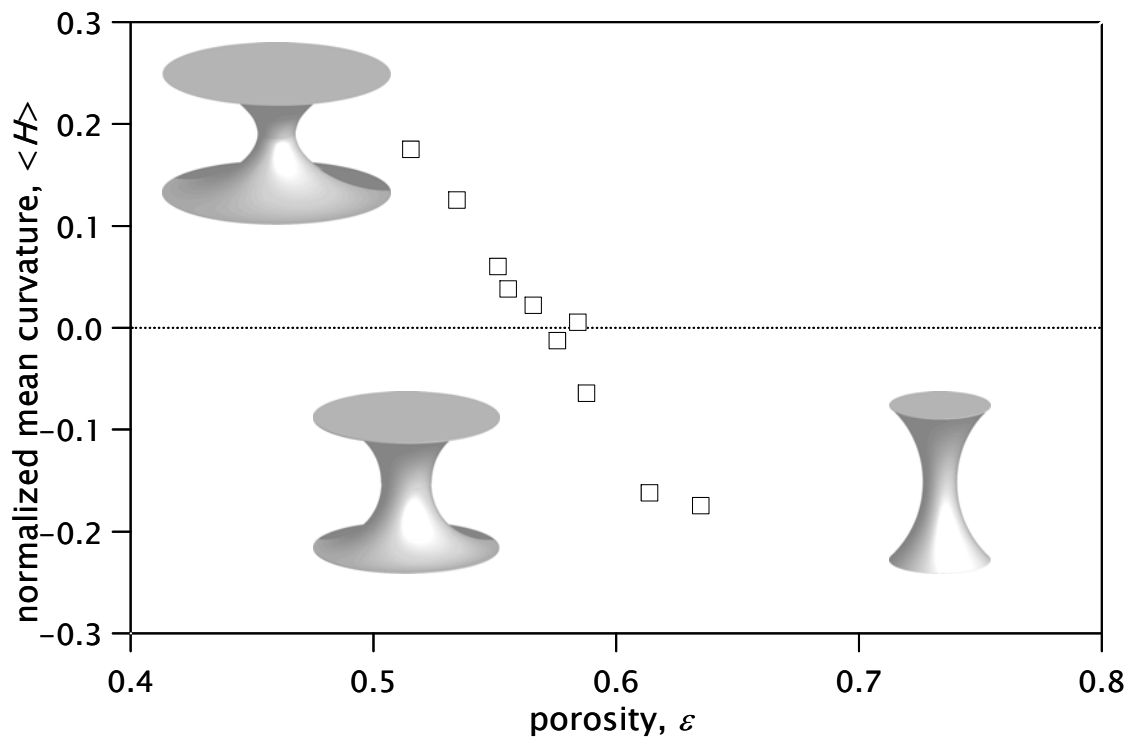


Figure 2.6

The mean curvatures of macropore surface in real monolith are plotted against porosity. The curvatures are normalized on the basis of specific surface area in order to eliminate the influence of structural dimension.

which offsets each other does not influences on the tortuosity, and so does on the flow resistance.

In the higher porosity region, the mean curvature took negative value. The macropore surface can be regarded as curved inward relative to skeleton side, and the structural unit can therefore be assumed as a cylinder with its middle concaved inward. The effective flow path decreases and the tortuosity becomes lower than that of TSM model, which has cylinder with constant radius. The flow resistance accordingly decreases in this region.

3.3.2 Validation of Curved-TSM

The structural unit with curvature thus well explains the difference between real monolith and TSM in flow resistance, and it was validated by CFD with the curved-TSM. Curved-TSM was constructed upon the relation between mean curvature and mean skeleton thickness in real monolith. The actual model is depicted in Figure 2.7.

The model construction had some difficulties since the overlapping of structural units at the joining points does not always exist especially in the lower porosity region. The CFD simulation was carried out only for two models with high porosity over 0.7 [Figure 2.8]. The values adopted to construct curved-TSM are listed in Table 2.3. The results show that the surface curvature on the structural unit certainly decreases flow resistance in high porosity region and the contribution is not significant as structural heterogeneity.

3.4 The Influence of Branch Number

3.4.1 Discussion on the Influence of Branch Number

Branch number is the coordination number of skeleton at a junction. The average branch number of macropore increased and that of gel skeleton

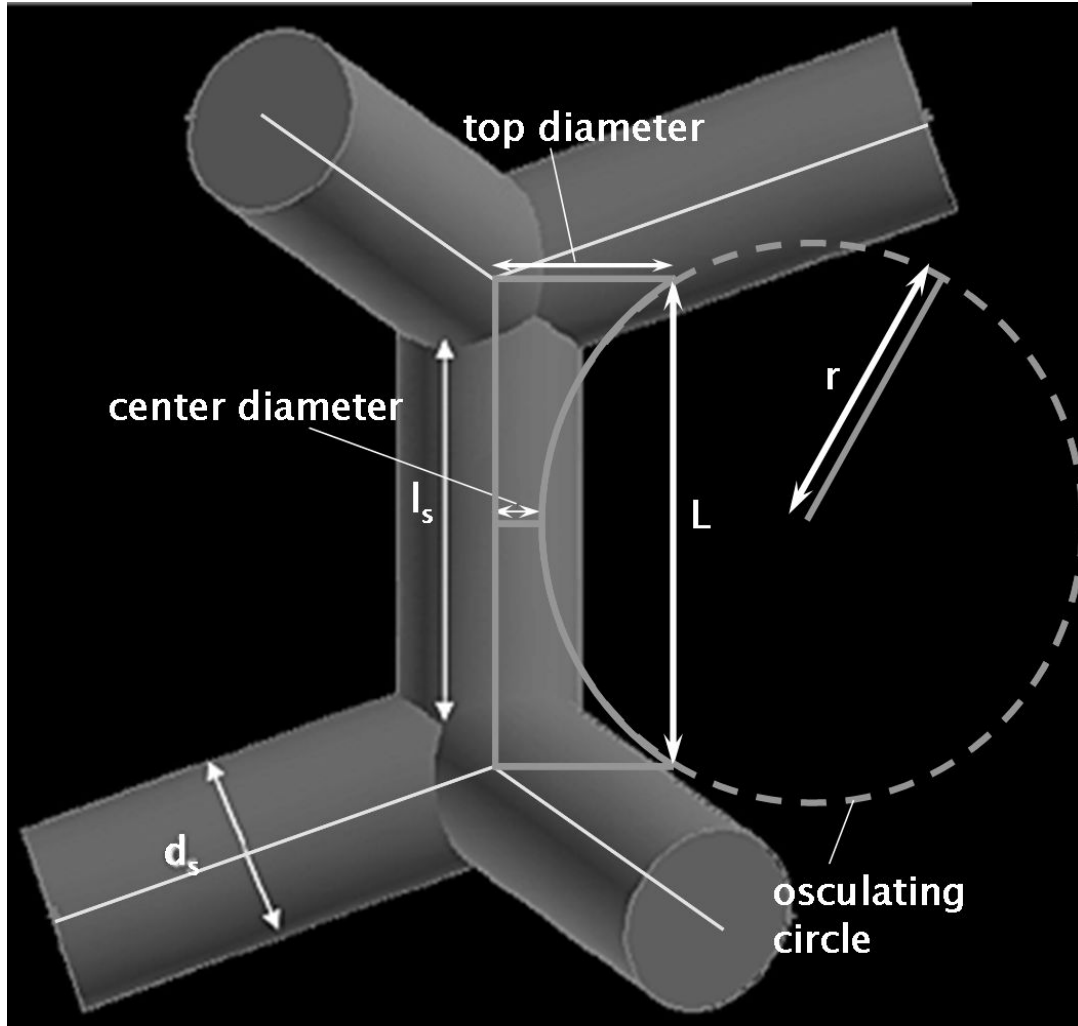


Figure 2.7

Schematic of the construction procedure of curved-TSM is depicted. Assuming the osculating circle with diameter, r , which is calculated in the following relation.

$$\frac{1}{2} \cdot \left(\frac{1}{(d_s/2)} + \frac{1}{r} \right) = \langle \tilde{H} \rangle_{\text{monolith}}$$

The mean curvature, $\langle \tilde{H} \rangle$, was calculated from the approximation between porosity and mean curvature in real monolith.

$$\langle \tilde{H} \rangle_{\text{monolith}} = -3.4324\varepsilon + 1.9762$$

Where porosity was calculated by equation 1.9, Chapter 1.

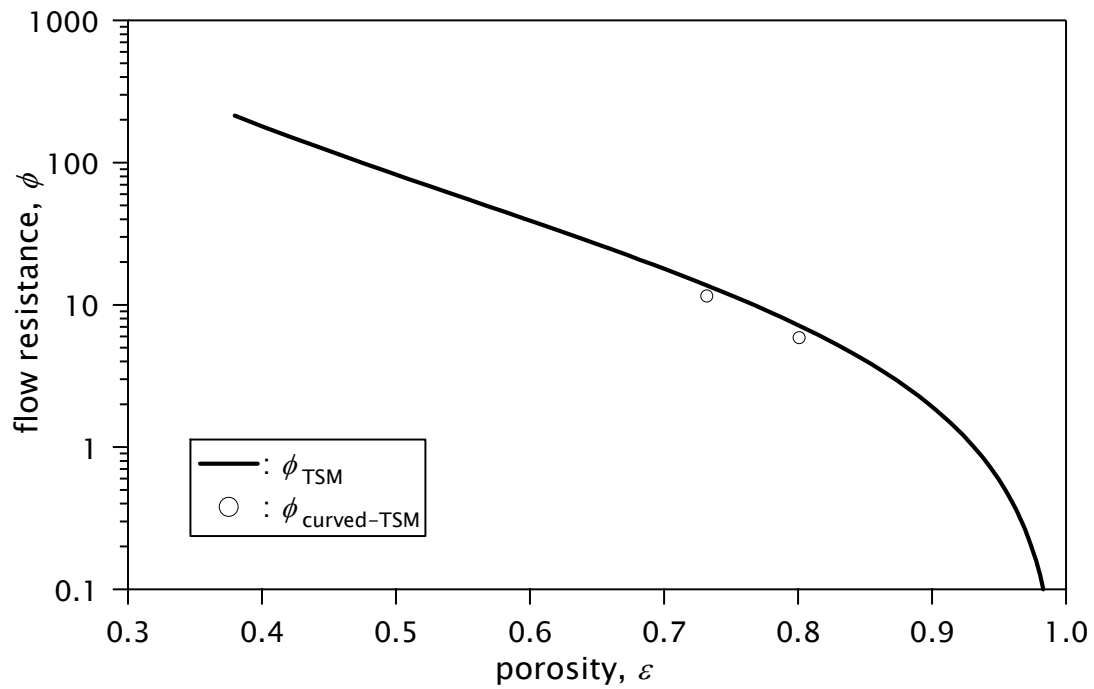


Figure 2.8

The flow resistance values obtained for two curved-TSM models are plotted against porosity. The solid line corresponds to flow resistance of TSM, and the open circles to those of curved-TSM. Curved-TSM exhibited relatively smaller flow resistance compared to TSM.

decreased with porosity. The increase in the branch number of macropore corresponds to the extension of flow-through path, and at the same time, the decrease in the branch number of gel skeleton corresponds to the decrement of the obstacles for flow-liquid. Both of the effects account for the additional decline of flow resistance, which is notable when compared with TSM.

3.4.2 Validation of the Influence of Branch Number

Both of the branch numbers of macropores and skeleton in TSM is 4, and in order to validate the influence of branch number, another model was constructed, which is called gyroid model in the present study. Gyroid model was based upon the ideal structure for spinodal decomposition, which is generated using trigonometric approximation as represented in the following

$$f(x, y, z) = \sin\left(\frac{2\pi}{L}x\right)\cos\left(\frac{2\pi}{L}y\right) + \sin\left(\frac{2\pi}{L}y\right)\cos\left(\frac{2\pi}{L}z\right) + \sin\left(\frac{2\pi}{L}z\right)\cos\left(\frac{2\pi}{L}x\right) \quad (2.14)$$

Both of the branch numbers of macropores and skeleton is 3, and the gyroid model is constructed with cylinders with the length l_s and thickness d_s in the same way as TSM [Figure 2.9]. The considered combinations of l_s , d_s , and corresponding porosity values are listed in Table 2.4.

The CFD simulations were carried out with a commercial CFD package, FLUENT (v.6). The software was installed on a PC with an Intel Pentium IV processor running at 1500MHz and equipped with 2Gb RAM. The grids were generated with GAMBIT (v.2) software run on the same hardware configuration. In order to reduce the computational load, all simulations were carried out on a unit cell, representing the minimal building block from which an infinite gyroid model can be reconstructed. For each combination of l_s and d_s , the simulation was repeated for at least five different mass flow rates, chosen such that the

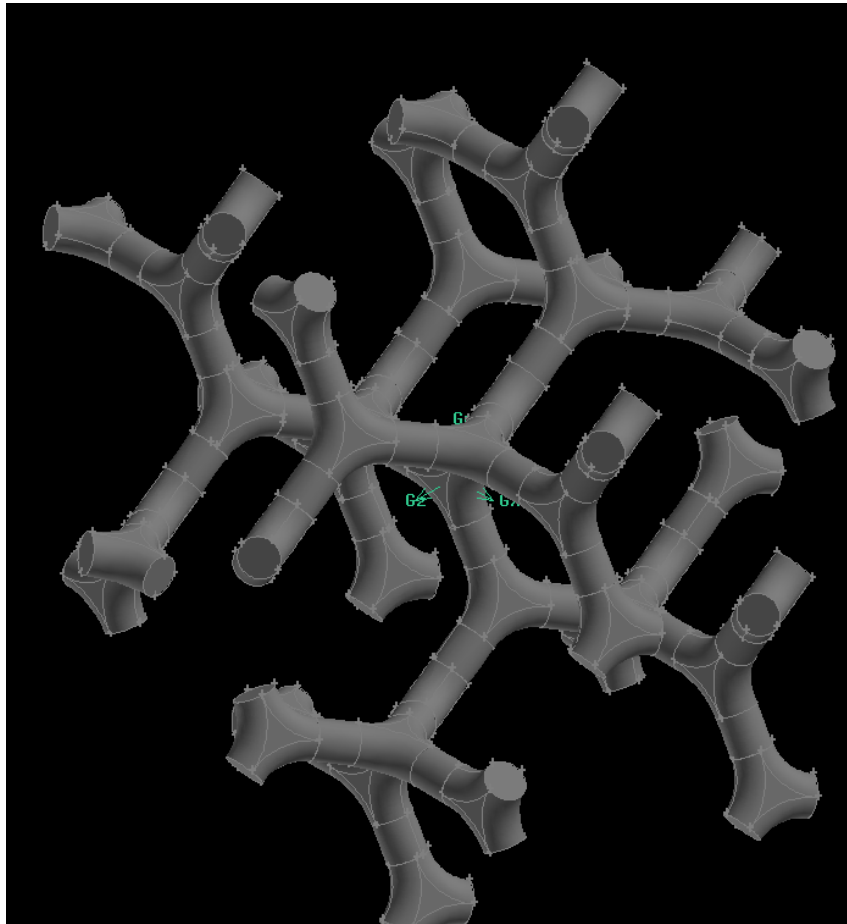


Figure 2.9

Schematic of gyroid model is shown. Each of the junction has three branches. Gyroid model also has the advantage that the simple parameters like l_s , d_s can control the porosity and effective macropore size independently.

Table 2.4

An overview of skeleton thickness, d_s , and skeleton length, l_s , adopted to construct gyroid model, porosity, ε , and the flow resistance, ϕ_{GYROID} .

$d_s / \mu\text{m}$	$l_s / \mu\text{m}$	ε	ϕ_{GYROID}
1.50	3.00	0.783	7.09
1.75	3.00	0.715	12.61
2.10	3.00	0.610	29.57
2.30	3.00	0.545	48.18
2.60	3.00	0.442	99.05
2.75	3.00	0.388	147.95

imposed average interstitial fluid velocities were in the range of 10^{-3} and $2 \cdot 10^{-2}$ m/s. The working fluid chosen was water with a density of 1000 kg/m^3 and a viscosity of $1.003 \cdot 10^{-3} \text{ kg/(ms)}$. The corresponding Reynolds numbers (based upon the skeleton diameter as the characteristic length) were on the order of $0.001 - 0.1$, and hence it can be concluded that the flow conditions were strictly laminar.

The calculated permeability was further generalized into flow resistance using skeleton thickness as characteristic length in the same way as TSM. Flow resistance values thus obtained are listed in Table 2.4, and plotted against porosity in Figure 2.10. Theoretically, the smaller branch number of skeleton should decrease the flow resistance, but there was not highly remarkable difference between gyroid model and TSM. The possible explanations are discussed in the following.

Flow resistance value is significantly influenced by obstacles in the flow path. The obstacles can be the skeletons and junctions of skeletons. At such obstacles, the flow should be split into two or more, and the position of the obstacle is more important compared to its frequency: if the obstacle locates at the same y-z coordinates (assume that the liquid flows in x-direction), the liquid flows around the sequence of obstacle points, and the flow resistance should be low. In gyroid model, the position of skeletons and junctions is periodic, and the influence of porosity is reflected only on the thickness of skeleton. This also explains the consistency between gyroid model and TSM about the flow resistance change with porosity. It can be concluded that branch number itself does not have a significant influence on flow resistance.

3.5 Mutual Consistency in Flow Resistance

In the previous discussion, the flow resistance of real monolith was compared with that of TSM obtained from CFD simulation, and the influences of structural

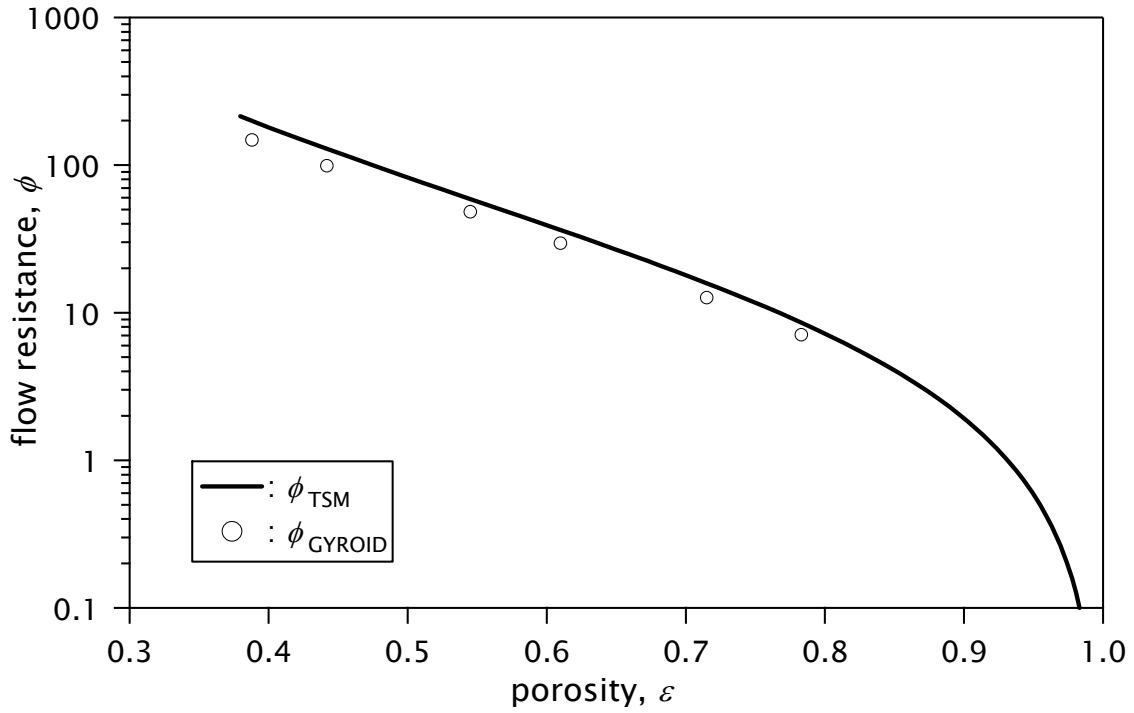


Figure 2.10

The flow resistance values calculated for gyroid model are plotted against porosity together with ϕ_{TSM} . The solid line corresponds to flow resistance of TSM, and the open circles to those of gyroid model. The flow resistance of gyroid model exhibited smaller flow resistance compared with TSM, reflecting the small branch numbers.

heterogeneity, macropore surface curvature and branch numbers were examined separately. On the whole, CFD simulation combined with TSM can be reasonably concluded that it well reconstructs the flow behavior of real monolith. The following discussion brought about the influences of structural factors, which are characteristic to silica monolith, on the basis of the reproducibility of TSM, and it pointed out that the most influential structural factor on the flow resistance is the structural heterogeneity since the heterogeneity alone can decrease the flow resistance five times smaller while the other factors decrease a few percents at most.

4. Conclusions

The structural parameters and flow resistance was calculated for real macroporous silica monolith. The obtained relation between flow resistance and structural parameters were compared with that of tetrahedral skeleton model (TSM). After eliminating the influences of the difference between real silica monolith and TSM, i.e., structural heterogeneity, surface curvature, branch numbers, the relations were in a reasonable agreement.

In the last decade of monolith study, the problems in reproducibility and repeatability of separation efficiency measurement has been often pointed out. One of the most serious problems is that the doneness of cladding often affects the measurement results. Heat-shrinkable tubes are used to tighten the obtained silica gels in the process of cladding, and the surface roughness on the gels sometimes prevents the tubes and gels from their intimate attachment, and the resultant gaps induce collateral flow. The collateral flow does not affect on the flow resistance since the minor flow contributes little to pressure drop. As for separation performance, on the other hand, collateral flow results in the different transport rate of specimen, and even the slight difference induces peak broadenings or peak-split in an extreme case. The difficulty in the estimation

has been an obstacle for drastic improvements of separation performance. Reliable and reproducible methods to estimate the separation efficiency on the basis of macropore structure have been needed for a long time.

In the discussion on flow resistance, the mutual consistency between measured and simulated systems was inspected in the previous discussion. That is, the simulated system is adequately reliable to plot strategy for efficiency improvements of silica monolith.

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Chapter 3: Three Dimensional Observation of Macroporous Silica gels and the Study on Structural Formation Mechanism

1. Introduction

Well-defined monolithic macroporous silica gels with so-called co-continuous structure have been synthesized via sol-gel method accompanied by phase separation [1–11]. The co-continuous macroporous silica gels provide an excellent liquid transport property, and have been successfully applied to the separation media in the field of high performance liquid chromatography (HPLC) for nearly a decade. The characteristic macropore morphology brings about a significant influence on the liquid transport and separation efficiencies, and therefore the detailed examination on the macropore structure is required for the further optimization as the separation media application. However, the detailed structural properties of co-continuous macropores still remain poorly understood due to its complexity.

Co-continuous pattern was often observed in a system under spinodal decomposition (SD) [12], one of the well-known phase separation mechanisms. An initially homogeneous system separates into two phases via SD when the system is quenched into the unstable region. In a sol-gel system, the polymerization reaction invokes viscosity increase and thermodynamic incompatibility among the constituents, and both of which are essential for the chemical quench [13]. The mechanism is called as polymerization-induced phase separation (PIPS) and PIPS can be partly explained by Flory-Huggins'

theory by interpreting the sol-gel system as a pseudo binary system comprised of siloxane -rich and solvent-rich phases. The compatibility among the system constituents can be represented by the free energy exchange on mixing, ΔG , and formally it can be expressed in terms of degree of polymerization, P_i , volume fraction, ϕ_i , and interaction parameter, χ , in Flory-Huggins' formula;

$$\Delta G \propto RT[(\phi_1/P_1)\ln \phi_1 + (\phi_2/P_2)\ln \phi_2 + \chi\phi_1\phi_2] \quad (3.1)$$

With the increase in P_i , the system becomes unstable, which can be figured out by the positive value of ΔG . The system can not retain single phase state anymore and finally separates into two phases.

The phase separation mechanism in a sol-gel system has been analyzed using small angle light scattering (SALS) [14]. The processes of SD can be divided into three successive stages: in the initial stage, only the evolution of concentration fluctuation at a constant wavelength occurs, in the intermediate stage, the evolutions of both amplitude and the most dominant wavelength of the concentration fluctuation were observed, and in the late stage of SD, only the evolution of wavelength was observed [12]. These time-evolution characteristics of phase domains are reflected in the wavenumber and intensity of SALS pattern, and the phase separation mechanism which generates co-continuous pattern was confirmed to be SD also in sol-gel systems [14].

Water-soluble organic polymer is often added to the starting composition to promote phase separation in many sol-gel systems [15-17]. The water-soluble polymer distributes either in solvent-rich phase or siloxane-rich phase depending on the mutual interaction with siloxane-polymer [15-17]. The water-soluble polymer can be assumed to provide viscoelastic effects on the phase separating pattern formation and the idea was predicted in the "viscoelastic phase separation" theory [18-22]. The phase separating pattern is

eventually frozen by a sol–gel transition, and the solvent removal provides macroporous silica gel. With increasing degree of polymerization, the SALS analysis becomes incapable because of the excessive scattering from the interfaces between the siloxane–rich and solvent–rich phases due to an increased contrast of those refractive indices. Therefore, the structural evolution of the phase separating pattern at the intermediate and the late stage of SD in sol–gel systems are not fully understood, and the resultant macropore structure is unpredictable in terms of viscoelastic phase separation theory.

Conventional methods to characterize macropore structure are scanning electron microscopy (SEM) and mercury intrusion method. One of the characteristics of SEM is the thick focal depth. It provides an excellent sight of macropore morphology, however, quantitative analysis of macropore interface on the SEM image is not easy since geometrical information from the thick focal depth is projected onto a single 2–dimensional image. On the other hand, the mercury intrusion method provides quantitative analysis of macropore, but the accuracy in geometrical information remains still ambiguous, since the cylindrical macropore shape and the specific contact angle has to be assumed in the conversion of intrusion pressure into macropore diameter.

In this chapter, the co–continuous macropore structures synthesized from different mechanisms of structural evolution were observed using LSCM [23–28] and studied the influence of phase–separation dynamics on the obtained macropore structure.

2. Experiment

2.1 Sample Preparation

Either Poly(ethylene glycol) (M.W. 10,000) (PEG) or Poly(acrylic acid) (HPAA)

was homogeneously dissolved in 1M aqueous nitric acid. Tetraethoxysilane (TEOS) was added to the solution under vigorous stirring under an ice-cooled condition. After 30 min of stirring, the resultant homogeneous solution was transferred into a polypropylene tube (i.d. 6 mm, 20 cm length) and was allowed to gel at 40°C in a closed condition. After aged at the same temperature for 10 h, the resultant gel was immersed in water for 3 h in order to remove residual acids, and was solvent-exchanged with 1M aqueous urea for 3 h. The following hydrothermal treatment was carried out 5 h at 110°C in 1.5M aqueous urea, which is needed for preventing cracks in a resultant gel. After 2 h of solvent exchange with water, the gels obtained were dried and heat-treated at 600°C for 5 h in order to remove residual organics. The obtained macroporous silica gels were further subjected to the structural observation by LSCM and the mercury intrusion method.

2.2 Structural Observation

As a preparation for the LSCM observation, the obtained macroporous silica gels were sliced into 2.5 mm pieces, and immersed in a mixture of formamide, benzyl alcohol and fluorescein solution (1:3:0.05 wt) which has the same refractive index as that of the gel skeleton. This process is needed to allow the laser light to transmit the sample and to obtain a better contrast.

A laser with 488 nm wavelength was used to excite fluorescein. A long-pass filter (LP505) was installed in front of a photomultiplier in order to detect only the fluorescent light (approximately 519 nm) and an oil-immersed 100 $\times$ /NA=1.40 (Plan-Apochromat, Carl Zeiss) objective was employed. The increment along the optical axis of the microscope perpendicular to the focal plane, Δz , used for observation was 0.15 μm . The laser was scanned in the lateral plane, measuring the fluorescent intensity in a 2D optically sliced image composed of N^2 ($N=512$) pixels², where N is the number of pixels along the edge

of the 2D image. The obtained LSCM images were further subjected to image processing, reconstructed into three dimensional image [Figure 3.1] and provided for image processing in the same way as described in chapter 1.

3. Results and Discussion

3.1 Fundamental Parameters

The fundamental parameters which have been used to characterize the macropore structures were calculated on the three dimensional images reconstructed with LSCM images. The fundamental parameters include porosity, surface area, skeleton thickness and macropore size [Table 3.1].

The porosity, macropore size and standard deviation of macropore size distributions were calculated by mercury porosimetry data [Table 3.2]. The porosities of the PEO- and HPAA- derived gels exhibited comparable values between LSCM and mercury intrusion methods, while the macropore size obtained by mercury intrusion method exhibited relatively smaller value. The difference was caused by the measurement principle of mercury intrusion method, and was discussed in detail in Chapter 1.

The porosities of gels prepared with PEO and HPAA had comparable values. The spinodal interface is known to be influenced with the change in the volume fractions of co-existing phases, and the comparable porosity of both gels ensures that it is unnecessary to consider on this problem.

The volumetric specific surface areas were also comparable values. Since the size of mesopores is below the resolution of LSCM, only the macropore surfaces were examined in this case. The macroporous specific surface area can be a measure for comparing the dimensions of macropores if the porosities are similar, and the comparable values for gels prepared with PEO and HPAA

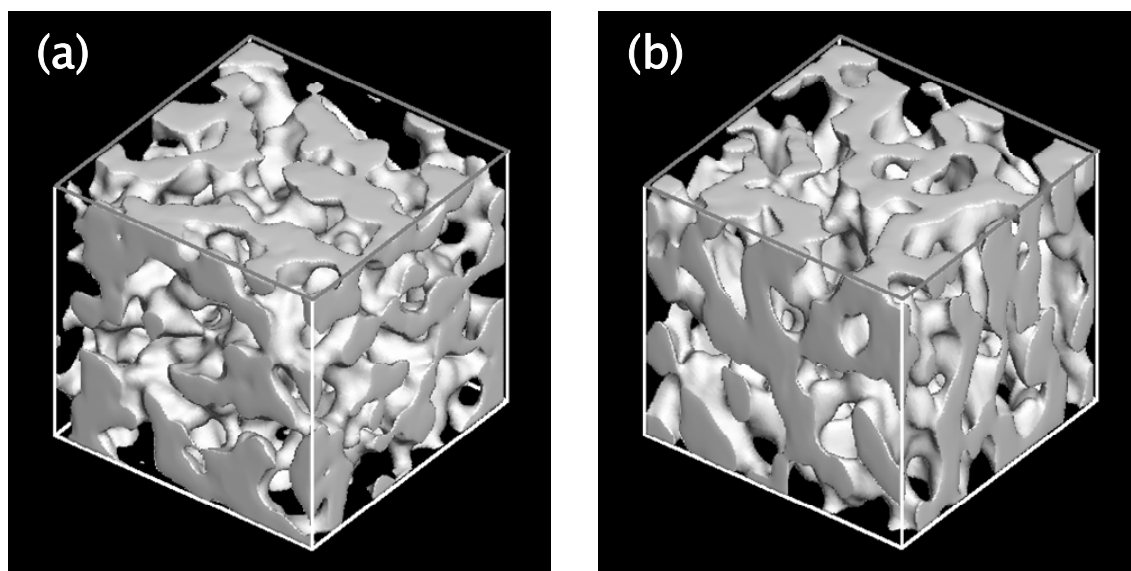


Figure 3.1

Overview of three dimensional structures reconstructed by image processing: (a)HPAA-containing system, (b) PEO-containing system.

Table 3.1

Fundamental parameters of surface structure in HPAA and PEO

systems	VF (LSCM)	S/V	skel/ μm	pore/ μm (LSCM)	$\sigma(\text{skel})$ (LSCM)	$\sigma(\text{pore})$ (LSCM)
HPAA	0.563	0.0950	1.11	1.31	0.37	0.28
PEO	0.549	0.0932	1.16	1.34	0.34	0.25

	$\langle H \rangle$	$\langle K \rangle$	branch number (skel)	branch number (pore)
HPAA	-0.0457	-1.4241	3.15	3.21
PEO	-0.0540	-1.3168	3.15	3.20

Table 3.2

Fundamental parameters of macropore in HPAA and PEO systems obtained by mercury intrusion method.

	VF (Hg)	pore/ μm (Hg)	$\sigma(\text{pore})$ (Hg)
HPAA	0.557	1.19	0.21
PEO	0.553	1.21	0.17

indicate that the macropores of the gels are similar in size. The skeleton thickness and macropore size had also comparable values, being consistent with the comparable specific surface area values. The calculations based on the skeletonization are discussed in detail in the following.

3.2 Probability Density Distributions of Curvatures

The Gaussian and mean curvatures exhibit the principal shape of surfaces as discussed previously, and hence the overall characteristic of the macropore surfaces can be examined by plotting the probability density distribution of the combination of the mean and Gaussian curvatures, $P(H,K)$.

Concerning the interface structure in the late stage of SD, the local compositions of the co-existing phases have already reached equilibrium values, and the excess free energy is localized at the interface between the two phases. The phase-separating pattern evolves so as to decrease the overall interface free energy, i.e., the interface area in this case.

The mean curvatures on the spinodal interface typically show symmetrical distribution around $H=0$, indicating that the spinodal interface curves equally inward and outward to one of the phase-separating domains and the Gaussian curvature mostly distributes in the $K<0$ region. The interface area of a hyperbolic surface goes through minimum when the mean curvature equals to zero and there are several known so-called minimum surfaces such as G-surface, P-surface and D-surface, etc [29–30]. The spinodal interface ideally has the nature of the minimum surface, and the probability densities of the mean and Gaussian curvatures are mainly localized around $H=0$ line in $K<0$ region.

Figure 3.2 shows probability density distributions of the curvatures on the macropore surfaces of the gels prepared with PEO and HPAA. Concerning PEO system, the probability density of the mean curvature, $P_{\text{PEO}}(H)$, shows

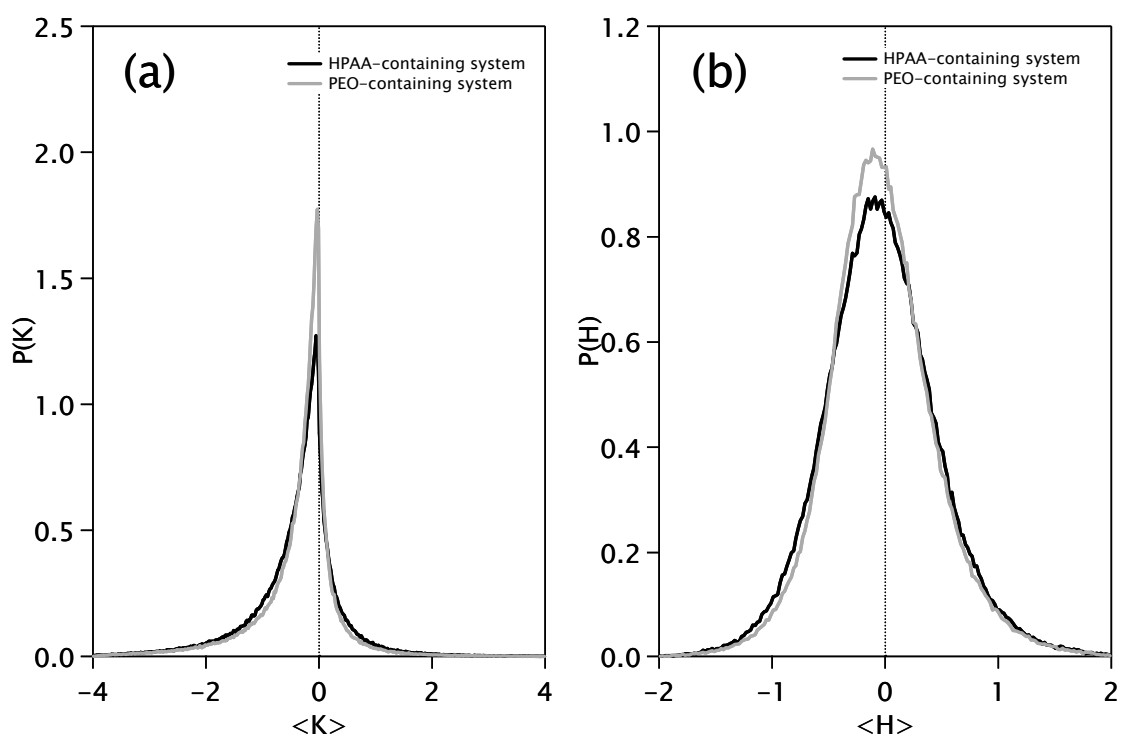


Figure 3.2

Probability density distributions of (a) Gaussian curvature and (b) mean curvature on the macropore surface of HPAA- and PEO-containing system.

distribution slightly misaligned from $H=0$ to $H<0$ side, which indicates that the macropore surface curves relatively outward to the macropore region. The probability density of the Gaussian curvature, $P_{PEO}(K)$, distributes mainly in the $K<0$ region, and most of the macropore surface in PEO system is classified as being hyperbolic. The probability density of the combination of mean and Gaussian curvatures on the macropore surface in PEO system [Figure 3.3] shows distinct aspect from typical spinodal interface; in $K<0$ region, the curvatures are distributed in a radial pattern from the origin and in $K>0$ region, they are distributed along the $K=H^2$ curve.

The probability density of the mean and Gaussian curvatures for HPAA system, $P_{HPAA}(H)$ and $P_{HPAA}(K)$ [Figure 3.2], respectively, exhibits similar distribution to those of PEO system, $P_{HPAA}(H)$ was slightly misaligned to $H<0$ side, and $P_{HPAA}(K)$ is distributed mainly in the $K<0$ region. The probability density of the combination of mean and Gaussian curvatures for HPAA system, $P_{HPAA}(H,K)$ [Figure 3.3], exhibited the intermediate distribution between $P_{PEO}(H,K)$ and that of ordinary spinodal interface; in $K<0$ region, the curvatures did not localized around $H=0$, however the distribution extended along $H=0$ from radial pattern and in $K>0$ region, they elongated in K -positive direction along the $K=H^2$ curve further than $P_{PEO}(H,K)$. The total distribution area for HPAA system were larger than that of PEO system, suggesting more disordered macropore structure in HPAA system than in the case of PEO system.

The macropore surfaces in both systems deformed from the minimal surface, which suggests that there exists other causes which invoke structural evolution, in addition to the interfacial energy localized around spinodal interface. The difference of viscoelasticity between co-existing phases can account for the previously observed deviation of macropore surfaces from normal spinodal interface.

In PEO-containing system, PEO is known to mainly distribute in the

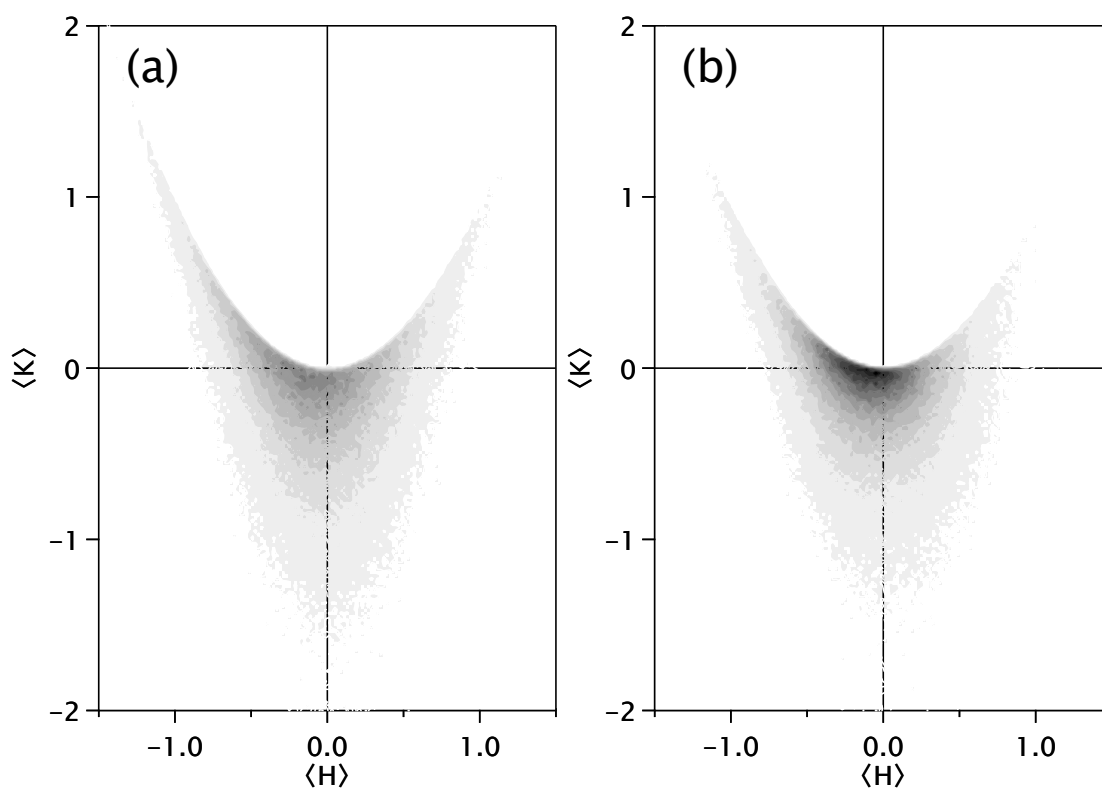


Figure 3.3

Probability density distributions of the combination of mean and Gaussian curvature for (a) HPAA-containing system and (b) PEO-containing system.

siloxane-rich phase, forming a molecular-level composite with siloxane polymer. The PEO distributed in siloxane-rich phase supports percolated network inside the siloxane-rich phase. In the process of syneresis, the condensation reaction between non-reacted silanol or alkoxy groups, the network tends to reduce its effective volume by squeezing solvents from the siloxane-rich to solvent-rich phase. The network inside the siloxane-rich phase tries to maintain its cross-linking against the non-uniform deformation due to syneresis, which generates elastic energy. This is the origin of the so-called bulk mechanical stress. The competition between the coarsening induced by interfacial energy and this bulk stress plays a key role in pattern evolution during phase separation. Since the elasticity resists against the deformation of the siloxane-rich phase, the deformation tends to localize at the interface of co-existing phases. The interface structure takes squeezed shape, and deviates from the ideal minimal surface. It is reflected in the radial pattern in the $K < 0$ region in $P_{\text{PEO}}(H, K)$. Because of the shrinkage of the siloxane-rich phase, the interface curves outward relative to the solvent-rich phase, which results in the misalignment of $P_{\text{PEO}}(H)$ from $H=0$. The local stretching caused by the syneresis leads to the stress accumulation on the stretched part, and it results in the break-ups of the siloxane-rich phase and generates elliptic surfaces. This explains the distribution of the probability densities of the mean and Gaussian curvatures along $K=H^2$ curve.

In HPAA-containing system, HPAA is known to distribute almost exclusively in the solvent-rich phase. The generation of the bulk mechanical stress inside the siloxane-rich phase is also induced, it is, however, contemplated that the elastic energy generated in HPAA-containing system is smaller than that in PEO-containing system since the polymer chains do not exist in the siloxane-rich phase to support the network. Besides the smaller stress than PEO-containing system, HPAA-polymers distributed in the solvent-rich phase

can mediate the dynamic asymmetry between the siloxane-rich and solvent-rich phases to some extent, which will reduce the resultant influence of the bulk stress in the siloxane-rich phase. This idea explains the better symmetrical property of $P_{\text{HPAA}}(H,K)$ compared to $P_{\text{PEO}}(H,K)$. At the same time, the weaker networks of the siloxane phase in HPAA-containing system tolerate inhomogeneous deformation of the interface between co-existing phases more effectively compared to PEO-containing system, and it results in the more inhomogeneous macropore surface.

3.3 Skeletonization

The distributions of skeleton thickness and macropore size were obtained from skeletonization. The most probable values were determined by the Gaussian fitting on the distribution and thus the standard deviations were calculated. The standard deviations of the distributions were calculated for comparison. The standard deviation of skeleton thickness in PEO system, $\sigma_{\text{PEO}}(\text{skel})$ is smaller than that of macropore size in PEO system, $\sigma_{\text{PEO}}(\text{pore})$, and the similar tendency is observed in the case of HPAA system. The standard deviations of skeleton thickness and macropore size in HPAA system, $\sigma_{\text{HPAA}}(\text{skel})$ and $\sigma_{\text{HPAA}}(\text{pore})$ respectively, are larger than those of PEO system. It reflects the relatively disordered macropore surface of HPAA system compared to that of PEO system.

The skeletonization also provides branch numbers. The branch number is defined as the coordination number of gel skeletons at a junction. The ideal structure for the spinodal surface with regard to the interfacial energy is considered to be G-surface. The branch number in G-surface is uniquely 3, and the branch numbers in both systems suggest that the topological properties of the initial spinodal pattern are conserved after the deformation of the interface between the siloxane-rich and solvent-rich phases.

3.4 Area-averaged Curvatures

The area-averaged mean, $\langle H \rangle$, and Gaussian, $\langle K \rangle$, curvatures obtained from parallel surface method is shown in Table 3.1. The curvatures are scaled with volumetric specific surface area to eliminate the influence of structural dimension. The absolute value of area-averaged mean curvature of PEO system, $\langle H \rangle_{\text{PEO}}$, exhibits smaller values than that of HPAA system, $\langle H \rangle_{\text{HPAA}}$. It reflects the macropore surface deformation mentioned previously. The Gaussian curvature in HPAA-containing system, $\langle K \rangle_{\text{HPAA}}$, had smaller values than that of PEO-containing system, reflecting that the interface between co-existing phases in HPAA-containing system has nature of minimal surface more than that in PEO-containing system.

3.5 Chord Length

The chord length method has been used to estimate the wavelength of periodic repetition of co-existing phases in the spinodal pattern. The chord length distributions of both systems do not exhibit clear differences [Figure 3.4]. It suggests that the overall pattern of the macropore is indistinctive on average. The standard deviations of skeleton thickness and macropore size suggest that the macropore structure in HPAA system is more disordered than that in PEO system. This inconsistency can be explained as the following. The shrinkage of the siloxane-rich phase results in thinner siloxane-rich phase and at the same time thicker solvent-rich phase. Since the volume fractions of two phases are close to each other, the increase in the thickness of the solvent-rich phase would cancel the decrease in that of the siloxane-rich phase, and it results in the resemblance in the chord length distributions.

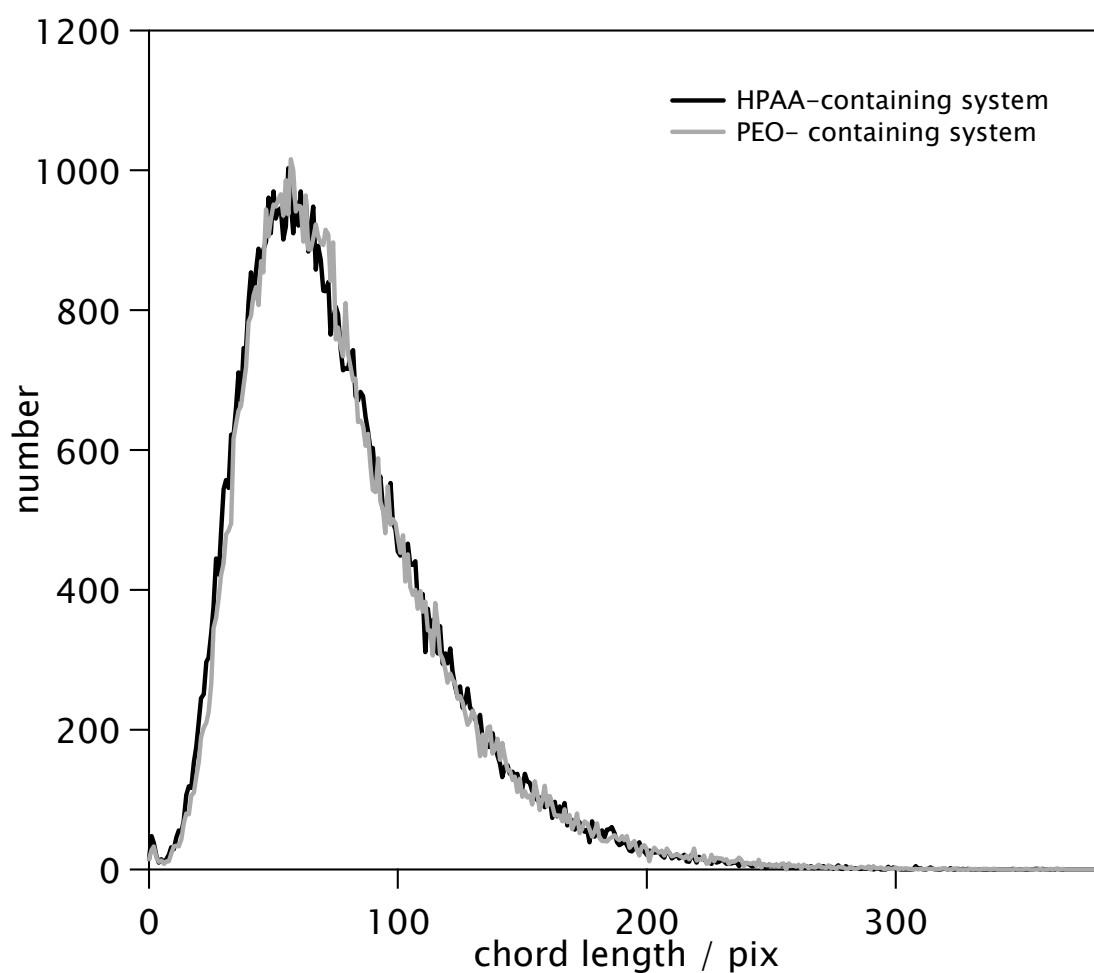


Figure 3.4

Chord length profile of HPAA- and PEO- containing system.

4. Conclusions

The three-dimensional structures of the co-continuous macroporous silica gels were observed using laser scanning confocal microscopy, and the influence of viscoelasticity on the structural formation mechanism was examined. The obtained LSCM images were binarized and reconstructed into three-dimensional representations. The analysis of the reconstructed images provided porosity, skeleton thickness and macropore size. By statistical processing, probability density distributions of curvatures of the macropore surface, and topological properties, such as branch numbers have also been obtained.

The macropore surface represented by the curvature distribution was found to be significantly influenced by viscoelasticity, and the topological properties were independent of the influence of viscoelasticity. This suggests the localization of stress around the interface between co-existing phases, though the structural formation mechanism is still not fully understood. Three-dimensional observations on the time evolution of phase-separating patterns in sol-gel systems will help to gain insight into the influence of viscoelasticity.

The representative application of co-continuous macroporous silica gels is the separation media in high performance liquid chromatography, and the 3D observations of the macropore structure can contribute to the optimization of macropore structure suitable for more efficient liquid transport behaviors.

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CHAPTER 3: THREE DIMENSIONAL OBSERVATION OF MACROPOROUS SILICA GELS
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CHAPTER 4: Real Space Observation of the Silica Monolith Formation Process

1. Introduction

Since its first appearance in the field of high performance liquid chromatography (HPLC), macroporous silica monolith has been attracting attention as a highly efficient separation media worth noting for more than a decade [1–6]. The most remarkable characteristic of silica monolith is continuous network of silica, which replaces the conventional particulate packing. This allowed the external macropore porosity to increase, and resulted in respectable performance at much higher flow rate compared to standard packed bed column [7].

The continuous networks in silica monolith derive from spinodal decomposition, one of the phase separation mechanisms [8]. Phase separating structure between polymerizing silica and solvent is frozen by sol–gel transition and the following removal and drying of solvent result in the co-continuous macropore structure. The principal factor which produces the macropore structure is the timing of phase separation and sol–gel transition: premature freeze of the phase separating structure leads to micro–mesoporous silica and too late freeze leads to particulate aggregation, or macroscopic two phases. Both rates of sol–gel transition and phase separation have to be adjusted to obtain continuous network structure.

The sol–gel transition is a transformation of a polymerizing system from “sol” to “gel”, which can be recognized by a formation of an infinitely large cluster in the length scale of the reaction vessel. The time evolution of the

polymerizing cluster size can be interpreted as a kind of percolation process [9], however the exact description of the sol-gel transition in detailed time and space domains is difficult since the time-evolution of cluster size exhibits non-linear behavior.

Phase separation has been studied for long and the structural evolution through its process is predictable on the composition, physical properties of the two phases, interaction between the phases and the reaction temperature. The combination of sol-gel reaction and phase separation, however, ingenerates further complexity: both the compositions and physical properties of the separating phases keeps changing during of the progression of sol-gel reaction,

The complexity in the formation mechanism of macroporous monolith has posed obstacle to the optimization of its macropore structure as a support, and it took nearly ten years for significant improvement of separation performance in monolith [10]. It is noted that increased phase ratio, smaller domains and increased homogeneity of the flow path always increases the separation performance [11], and thus there arises necessity for the knowledge of the formation process to make the best use of monolith.

There are several systems which produce monoliths [12–14]. The induction of phase separation in sol-gel systems provides well-defined macroporosity in as mentioned previously [11], and there are several ways to induce phase separation: addition of polar solvent and/or water-soluble polymers. The water-soluble polymers can be further categorized into those having strong attractive interaction with silanol groups and those not. The existence or nonexistence of interaction with silanol-bond lead to considerable difference in the phase separation mechanism [15–19], and the knowledge helps understanding of the structural evolution mechanism in the other monolith producing systems.

In this chapter, the macropore structure evolution process of silica

monolith was observed in two kinds of systems which contain water-soluble polymers with or without interaction between silanol-bond. Laser scanning confocal microscopy (LSCM) was adopted for observation [20–23] since it provides cross-sectional images, which can be further processed in image analysis and gives the measure of volume fraction, domain size and homogeneity. On the obtained parameters, the optimum composition to prepare monolith for chromatographic support is discussed.

2. Experimental

2.1 Sample Preparation

Poly(ethylene glycol) (M.W. 100,000) (PEO) or Polyacrylic acid (M. W. 100,000) (HPAA) was firstly homogeneously dissolved in a mixture of 0.2M aqueous nitric acid and benzyl alcohol and 0.05M ethanol solution of fluorescein-5-isothiocyanate coupled 3-aminopropyltriethoxysilane (FITC-APS) was added. The preparation of FITC-APS begins with dissolution of fluorescein-5-isothiocyanate into ethanol and was followed by the addition of 3-aminopropyltriethoxysilane and 24 hours of stirring. After 20 min of stirring, tetraethoxysilane (TEOS) was added to the mixed solution under vigorous stirring in an ice-cooled condition and after 40 min of stirring, the resultant homogeneous solution was encapsulated in an observation brass-cell and laid still at a constant temperature of 30°C. The actual starting compositions are listed in Table 4.1.

2.2 Structural Observation and Image Analysis

Laser scanning confocal microscopy (LSCM) was adopted to observe the phase separating structure. Thin focal plane generated by the confocal pinhole allows observing the cross-sectional structure, and the cross-sectional image is

Table 4.1

Starting compositions of HPAA and PEO systems.

	0.2MNA	Benzyl Alcohol	HPAA/PEO	FITC-APS	TEOS
HPAA system	2.93 g	5.4 g	0.83 g	1 ml	7 ml
PEO system	2.86 g	2.6 g	0.30 g	1 ml	7 ml

best suitable for image analysis to analyze the structural evolution mechanism. A laser with 488 nm wavelength was used to excite fluorescein. A long-pass filter (LP505) was installed in front of a photomultiplier in order to detect only the fluorescent light (approximately 519 nm) and an oil-immersed 100 $\times$ /NA=1.40 (Plan-Apochromat, Carl Zeiss) objective was employed. The laser was scanned in the lateral plane, measuring the fluorescent intensity in a 2D optically sliced image composed of N^2 ($N=512$) pixels², where N is the number of pixels along the edge of the 2D image.

The obtained LSCM images were further subjected to image analysis, to obtain volume fraction, phase thickness, and interface curvature.

3. Results and Discussion

3.1 General Observation

The phase separating structure is known to grow in size and enlarge the composition difference between two phases with the elapse of time. The common features were observed in both of HPAA- and PEO- containing systems ((hereafter denoted as HPAA system and PEO system, respectively) [7]. Figure 4.1 shows the LSCM images obtained during the phase separation. Bright colored parts are designated as siloxane-rich phase because of the dye-coupled monomer, FITC-APS, co-polymerized with TEOS. These images show that the phase separating structure grows in size and the composition difference, which can be seen from the brightness difference in LSCM images, becomes large with time.

Differences in structural evolution mechanism, however, were observed between HPAA and PEO systems. The difference originates from the different interaction between HPAA/PEO and silanol groups on the surfaces of polymerizing silica oligomers. Although hydrophilic carboxyl groups are

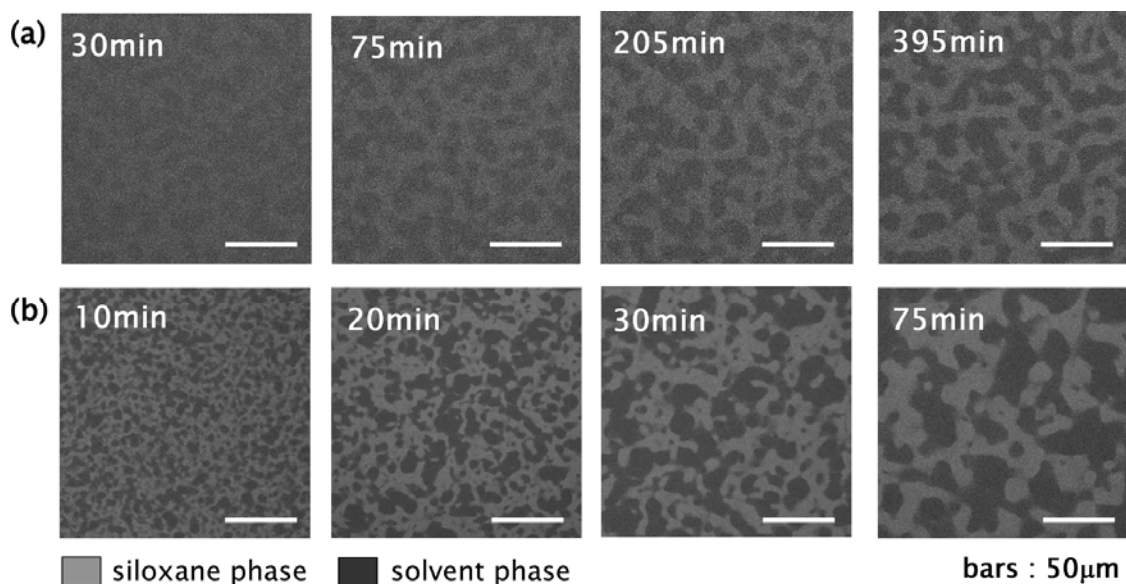


Figure 4.1

LSCM images obtained during phase separation for (a) HPA system (b) PEO system. Bright part corresponds to siloxane phase, and dark part to solvent phase. Each of the pictures were taken (a) 30, 75, 205, 395 minutes and (b) 10,20,30,75 minutes after the onset of phase separation. The length of the bars are 50mm.

attached on the side chain, HPAA does not strongly interact with silanol groups, and HPAA becomes eliminated out from the polymerizing silica phase. This incompatibility comes from the loss of mixing entropy due to the polymerization of silica. As a result, conjugate separating phases becomes one rich in silica and the other rich in HPAA. Poly(ethylene oxide), on the other hand, exhibits strong (specific) attractive interaction with silanol groups on silica oligomers, and become coexist with silica to form one phase, the other phase being rich in solvent mixture.

This difference in phase relation was proven by the differential thermal analysis (DTA). Figure 4.2 shows the DTA profiles of silica and solvent phases for HPAA and PEO systems. The exothermal peak around 230 °C corresponds to the decomposition of C–H and C–O bonds, which indicates that polymers are distributed to the solvent phase in the case of HPAA system and to silica phase in the case of PEO system.

3.2 Structural Evolution

The structural evolution process was further analyzed from three kinds of aspects: structural size, volume fraction and structural homogeneity, which have been reported that they are significantly related to the separation efficiency [10]. Figure 4.3 shows the change in the thicknesses of siloxane- and solvent-rich phases during phase separation in HPAA and PEO systems, which have been calculated by skeletonization as described previously. For HPAA system, the thickness was first around 5 μm for each of solvent and siloxane phases, grew in size for 40 minutes after the onset of phase separation, and stabilized around 10 μm for solvent phase and 8 μm for siloxane phase. For PEO system, on the other hand, the thickness at the beginning of phase separation was around 3 μm , grew in size for 100 minutes, and stabilized around 16 μm for solvent phase and

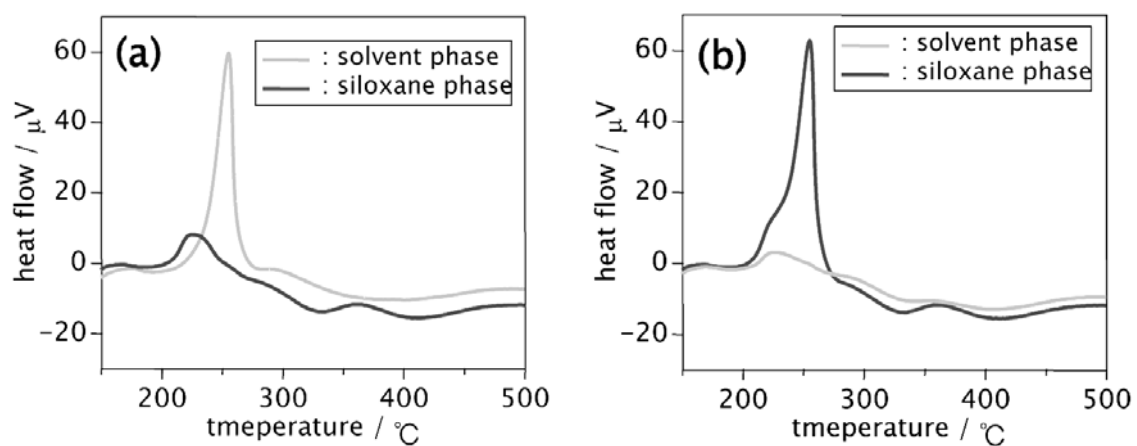


Figure 4.2

Profiles of differential thermal analysis for (a) HPAA and (b) PEO systems. Black lines corresponds to the profile of solvent phase and grey lines to siloxane phase.

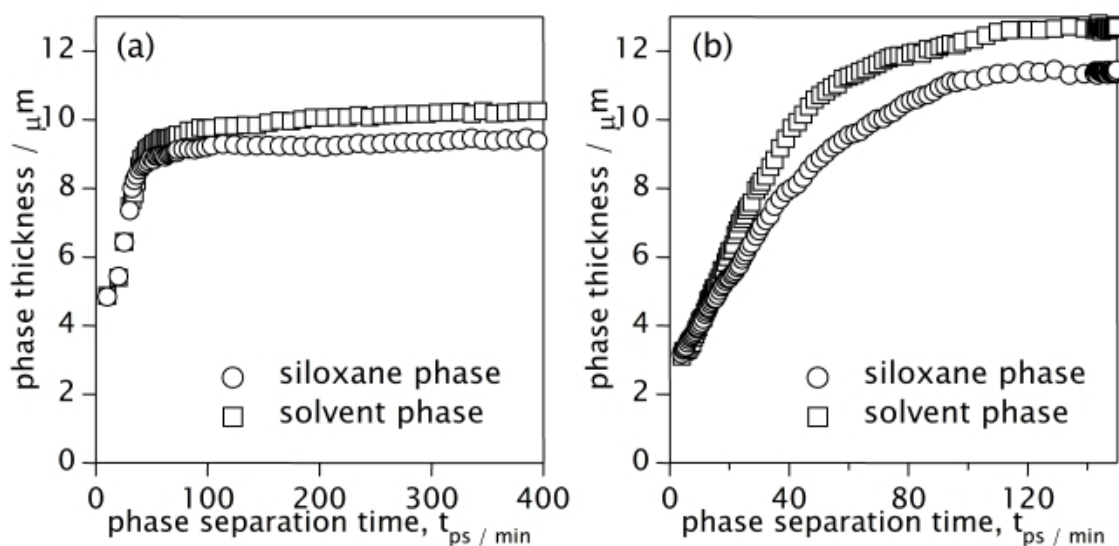


Figure 4.3

The thickness change in (a) HPA system and (b) PEO system. Open circle corresponds to siloxane phase and open square corresponds to solvent phase.

12 μm for siloxane phase.

The principal difference between HPAA and PEO systems is the growth rate of the structure. The difference in dynamic (viscoelastic) property of the silica and solvent phases is expected to be significantly affected by the presence of adsorbed polymer. In HPAA system, HPAA is mainly distributed to solvent phase as discussed previously, and the difference in viscosity of the silica and solvent phases is relatively small. The viscosities of both phases are expected to be much higher than that of a simple low-molecular-weight solvent. This leads to the slower growth rate compared with the case in PEO system. In PEO system, the polymer is preferentially distributed to the silica phase, and hence the dynamic asymmetry between silica and solvent phases becomes high. The adsorption of PEO influences the polymerization degree of the silica oligomers (Takahashi, Faraday Discussion 1995), and hence the polymerizing silica phase in PEO system increases its inherent viscosity only slowly. The relatively “mobile” silica phase in PEO system compared to that in HPAA system allows the significant coarsening and deformation of phase-separated domains until the sol-gel transition.

3.3 Volume Fraction Change

Figure 4.4 shows the change in the volume fraction of silica phase, ϕ_{sil} , in HPAA and PEO systems. In HPAA system, volume fraction of siloxane phase, ϕ_{sil} was ca. 0.51 at the beginning and decreased with time to 0.49, while in PEO system, ϕ_{sil} was first ca. 0.61 and decreased down to 0.45 with time.

The difference can be explained by considering the origin of phase separation in HPAA and PEO systems. In HPAA system, HPAA and silica oligomers are molecularly separated but fairly entangled in the solution before the onset of phase separation. With the progress of the polymerization of silica oligomers, highly polymerized and cross-linked silica begins to exclude HPAA

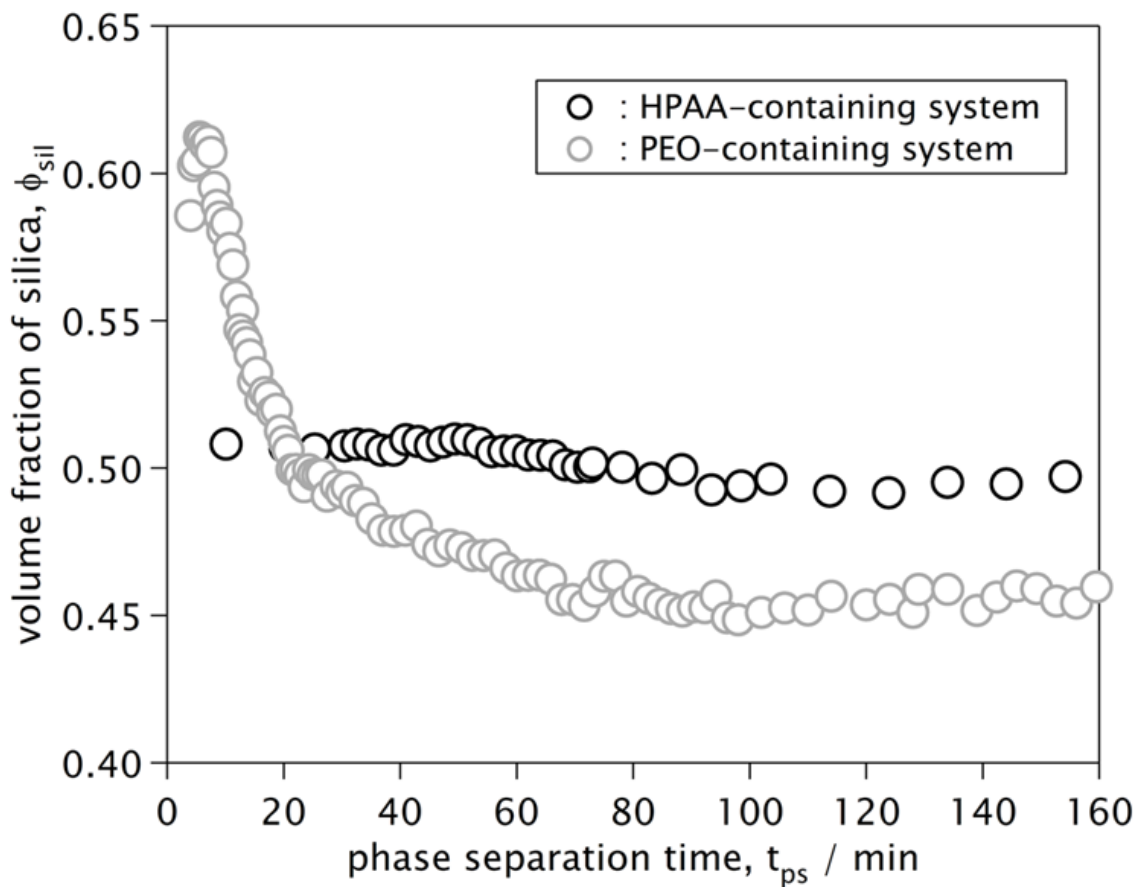
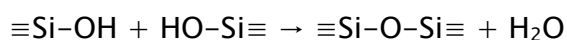


Figure 4.4

Volume fraction change after the onset of phase separation. Black open circle corresponds to HPAA system and grey open circle corresponds to PEO system.

as explained previously, and this is the microscopic starting point of phase separation in HPAA system. Phase separation in HPAA system hence begins after the considerable growth of silica oligomers.

In PEO system, on the other hand, PEO and siloxane chains are much more closely attached in the solution before the onset of phase separation than in the case of HPAA system. The difference between HPAA system comes from the strong attractive interaction with silanol groups, which results in the formation of PEO-silica complex. With the elapse of time, the hydrogen-bonded PEO-silica complex becomes less soluble to the solvent due to the consumption of hydrophilic sites, and this is the origin of phase separation in PEO system. Phase separation in PEO system occurs at the relatively early stage of polymerization with low degree of cross-linking, and the polymerization still continues well after the onset of phase separation. In the process of polymerization, the reactants exclude water:



The excluded solvents are included in the solvent phase, and it decreases the volume fraction of silica, ϕ_{sil} .

3.4 Structural Homogeneity Change

The origin of phase separation in HPAA and PEO system differs as discussed in the previous section, so does the phase separation mechanism. In HPAA system, HPAA chains migrate from silica phase to solvent phase, and silica oligomers also migrate to fit in the interspaces produced by the exclusion of HPAA. It is probable that silica oligomers grow while excluding HPAA chains, so that at the sol-gel transition the silica phase is consisted of nearly pure silica oligomers with minor inclusion of HPAA. This results in relatively steep

increase in viscosity near the sol-gel transition, and the phase-separating structure can be frozen in a short time with minimal chance of allowing domain deformation and resultant inhomogeneity.

In PEO system, the hydrogen-bonding adsorption of PEO begins as soon as a large enough silanols are formed on the surface of silica oligomers. The PEO-silica oligomer complex thus formed exhibits high viscosity and at the same time contains considerable amount of silanols loosely blocked by the PEO chains from free condensation with other silanols. Both inter- and intra-molecular condensation is slowed down, and the separated phase domains remain viscous but deformable before firmly crosslinked by prolonged condensations. As discussed previously, solvents are squeezed out from PEO-silica phase to solvent phase when the condensation between those unreacted groups occurs, and the volume fraction of siloxane phase decreases. In addition to this volume change, there arises interfacial tension (energy) gradient due to the curvature distribution along the initially hyperbolic domain surfaces. Depending on the sign and the magnitude of the local curvature, the PEO-silica phase domains have to deform to minimize such local strains. After these complex and spatially inhomogeneous coarsening processes, the PEO-silica domains are stiffly cross-linked to give continuous macroporous structures.

The difference in the structural evolution mechanism naturally influences on the obtained monolith structure. Figure 4.5 shows the three dimensional reconstructed images of the obtained monolith from HPAA and PEO systems. On these images, macropore size distribution and standard deviations were calculated using skeletonization. The obtained standard deviations were further normalized with volumetric-based specific surface area, since the value is known to be the most reliable measure for structural dimension. For both of the macropore and skeleton size, the normalized standard deviation values in

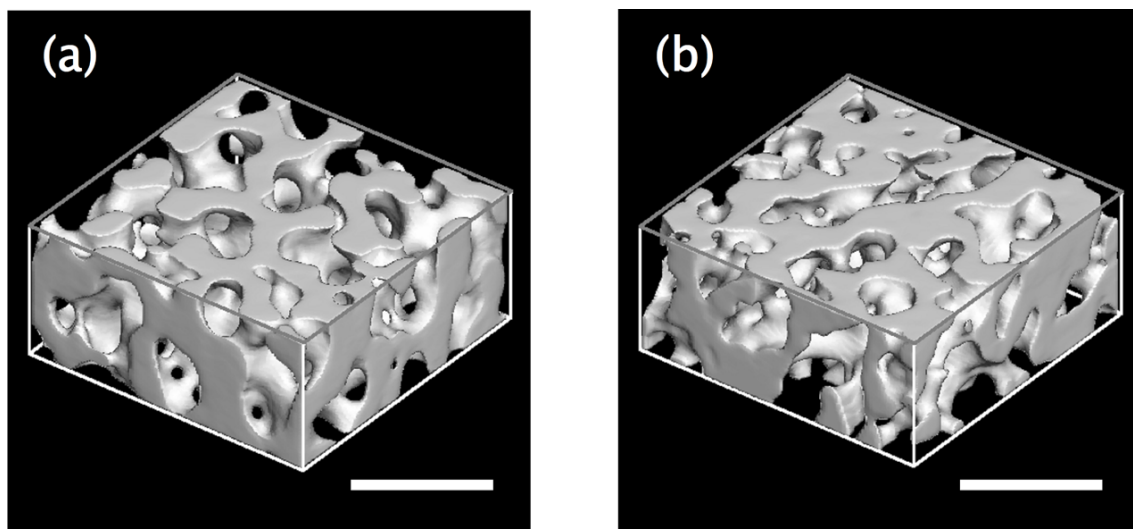


Figure 4.5

Three dimensional (3D) reconstructed images of the (a) HPAA and (b) PEO derived monoliths. The binarized images were reconstructed with marching cube algorithm into 3D images. Each of the reconstructed images has $512 \times 512 \times 162$ voxels, which have black or white in color, and their size is $0.45 \times 0.45 \times 0.35 \mu\text{m}^3$. The length of the bars are $25 \mu\text{m}$.

the HPAA-derived monolith showed smaller values than those in the PEO-derived monolith [Table 4.2].

3.5 Relation between Starting composition and Separation Efficiency

The suggestion from the computational fluid dynamics [11] is that the increased phase ratio, smaller domains and increased homogeneity in the flow path improves the separation efficiency. The phase ratio and domain size can be adjusted by simply changing the component ratio in the starting composition. In order to find the optimal composition to prepare macroporous monoliths with higher performance, it is important to gain insight into the systems in which monoliths with higher homogeneity are obtained.

In PEO system, the originally contained heterogeneity is enhanced during structural evolution process, while in HPAA system, there is few, if ever exists, process which adds excess heterogeneity. From these observations, the HPAA-derived monolith is expected to provide the better performance than PEO-derived monolith, which so far has been a main stream in the area of silica monolith preparation.

4. Conclusions

The formation process of monolith was observed by laser scanning confocal microscopy (LSCM), and compared two kinds of systems. One of the systems contains HPAA, which does not have strong attractive interaction with silanol groups, and the other system contains PEO, which has strong attractive interaction with silanol groups. The phase separating structure evolved in different mechanisms, and the HPAA-derived monolith showed higher

Table 4.2

Standard deviations of macropore and skeleton for HPAA and PEO derived monoliths. Each of the Standard deviations is normalized with volumetric-based specific surface area.

	macropore size (μm)	skeleton size (μm)	$\sigma_{\text{macropore}}$	σ_{skeleton}
HPAA system	10.11	8.80	0.43	0.29
PEO system	12.70	11.29	0.52	0.34

homogeneity compared to PEO-derived monolith. Based on the suggestion from computational fluid dynamics, it is expected that the HPAA-derived monolith will give higher performance.

Monolith has been studied for more than a decade. The performance of monolith, however, is not optimized yet, and the study to obtain monolith with improved performance should also be proceeded. The computational fluid dynamics is highly useful to predict the performance and to develop a workable strategy. The strategy by itself can not stand alone, and the knowledge of the structural evolution mechanism is also essential. Systematic study on structural characterization, simulated separation behavior and real chromatographic performance has just begun. The same kind of real space observation in the other systems, for example, systems with different components or systems in capillary will provide valuable proposition for monolith preparation technology.

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Summary

The present thesis deals with the formation mechanism of macropores, relation between macropore structure and liquid flow and ideal structure for separation media.

Chapter 1 was devoted to the structural observation and the analysis methods. There are several methods to observe and analyze macropore structure and the comparison between those methods drew a conclusion that laser scanning confocal microscopy (LSCM) and the related image analysis is a promising technique for macropore structure evaluation. Structural parameters calculated by image analysis quantified the so-called co-continuous structure, and provided the measure for appropriate modeling of the structure together. The technique introduced in chapter 1 are sufficiently complete and well established, and the author hopes it will be employed to help the application of materials with complex structure.

In chapter 2, relation between liquid flow and macropore structure was discussed. Macropore structures were observed laser scanning confocal microscopy (LSCM) and the obtained LSCM images were subjected to image analysis, to provide structural parameters. Liquid flow was estimated using dimensionless flow resistance, which represents difficulty to flow through a structure. The flow resistance decreases with porosity, and the results were compared with the results from computational fluid dynamics simulation (CFD) carried out on tetrahedral skeleton model (TSM), which was constructed upon SEM images of co-continuous structure. The comparison exhibited discrepancy which derives from the major difference between co-continuous structure and TSM, curvature.

In chapter 3, the time evolutions of phase separating structures in sol-gel systems were discussed. The observation was prosecuted using laser scanning

confocal microscopy (LSCM). Two kinds of systems were compared: one of the systems contains poly acrylic acid (HPAA) and the other system contains polyethylene oxide (PEO). These polymers exhibit different interaction with silanol groups and the phase separating structure evolved in different mechanisms between the two systems containing HPAA and PEO, respectively. HPAA-derived monolith showed higher homogeneity compared to PEO-derived monolith.

In chapter 4, the influence of starting composition on the separation efficiency is discussed. The macropore structures synthesized from HPAA and PEO containing systems were observed using laser scanning confocal microscope (LSCM) and further subjected to image analysis. The macropore surface curvature distribution represented the significant influence of viscoelasticity on the obtained structure, while the topological properties were independent of the influence of viscoelasticity. This suggests the localization of stress around the interface between co-existing phases. The suggestion from computational fluid dynamics simulation (CFD) accounts for the higher efficiency of HPAA-derived monolith compared to PEO-derived monolith, which has been commercialized for more than a decade. Systematic study on structural characterization, simulated separation behavior and real chromatographic performance has just begun. The author hopes that this study helps the further developments of monolith as a separation media.

List of Publications

CHAPTER 1

“Three Dimensional Structure and Liquid Transport Behavior of Siloxane Gels with Co-continuous Macropores”

Haruko Saito, Kazuki Nakanishi, Kazuyuki Hirao, Hiroshi Jinnai, Kei Morisato, Hiroyoshi Minakuchi

MRS Proceedings, **847.EE9.2**, 2004.

“Three Dimensional Analysis of Macroporous silica”

Haruko Saito, Kazuyoshi Kanamori, Kazuki Nakanishi, Kazuyuki Hirao, Hiroshi Jinnai

To be submitted to Colloids and Surfaces A.

CHAPTER 2

“Mutual Consistency between Simulated and Measured Pressure drops in Silica Monoliths Based on Geometrical Parameters Obtained by Three-dimensional Laser Scanning Confocal Microscope Observations”

Haruko Saito, Kazuki Nakanishi, Kazuyuki Hirao, Hiroshi Jinnai

Journal of Chromatography A, **1119**, 95–104, 2006.

“Experimental Validation of the Tetrahedral Skeleton Model Pressure Drop Correlation for Silica Monoliths and the Influence of Column Heterogeneity”

Nico Vervoort, Haruko Saito, Kazuki Nakanishi, Gert Desmet

Analytical Chemistry, **77**, 3986–3992, 2005.

CHAPTER 3

“Three-Dimensional Observation of Macroporous Silica Gels and the Study on Structural Formation Mechanism”

Haruko Saito, Kazuyoshi Kanamori, Kazuki Nakanishi, Kazuyuki Hirao, Yukihiro Nishikawa, Hiroshi Jinnai

Colloids and Surfaces A, **300**, 245–252, 2007.

CHAPTER 4

“Real Space Observation of Silica Monolith in the Formation Process”

Haruko Saito, Kazuyoshi Kanamori, Kazuki Nakanishi, Kazuyuki Hirao

Journal of Separation Science, **17**, 2881–2887, 2007.

“Real Space Observation of Phase Separating Structure in Sol–gel Systems”

Haruko Saito, Kazuyoshi Kanamori, Kazuki Nakanishi, Kazuyuki Hirao

To be submitted to Physical Review Letters.

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Kyoto winter 2008

Haruko Saito