



ELSEVIER

Journal of Non-Crystalline Solids 243 (1999) 61–69

JOURNAL OF  
NON-CRYSTALLINE SOLIDS

# Structural analysis of poly(dimethylsiloxane) modified silica xerogels

Ling Guo, Jingyu Hyeon-Lee, Gregory Beaucage \*

*Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA*

Received 28 May 1998; received in revised form 8 September 1998

## Abstract

A new type of inorganic-organic hybrid material incorporating poly(dimethylsiloxane) (PDMS) in tetraethoxysilane (TEOS) based glassy gels has been produced by a sol–gel process. SAXS and SEM studies indicate that these PDMS modified silica xerogels possess multiple size-scale morphologies, ranging from Ångstroms to micrometers. The multiple-level hybrid materials show improved structural integrity relative to pure sol–gel glasses (xerogels). The effect of reaction time, water content, as well as content and molecular weight of PDMS on the structure of such materials were studied. These processing variables affect the relative rates of hydrolysis and condensation reactions, and consequently change the microstructure of the final product. © 1999 Published by Elsevier Science B.V. All rights reserved.

## 1. Introduction

Materials used for high-efficiency thermal insulation require nano-porous and monolithic structures. It is believed that the nano-porous morphologies determine the thermal conductivity by a Knudsen diffusion mechanism [1–3], while large scale structures in the micrometer to sub-micrometer range control structural integrity in these materials [3]. Silica xerogels produced by sol–gel processes and dried by normal drying are generally brittle, dense glass bodies which are not suitable for thermal insulation. This is because during normal drying, capillary pressure collapses the nano-porous structure to a dense structure and also causes cracking in the resulting xerogels, which makes the production of porous monolithic

bodies difficult. Several efforts aimed at organic modification of sol–gel systems have been presented in the literature [4–7]. These include organic modification leading to ‘springy’ gels [6], which result from surface modification. Springy gels are not observed in PDMS modified xerogels. The mechanism here involves elastomer reinforcement. This research has been designed to organically modify silicates using a simple organic polymer, polydimethyl siloxane (PDMS) oligomer as an additive, modifying the high stiffness and brittleness of silica xerogels, and giving toughness and flexibility to the product.

PDMS modified silica xerogels show monolithic structure and low thermal conductivities [8]. We believe this is partially due to their multiple size-scale morphologies, ranging from Ångstroms to micrometers. According to toughening mechanisms, larger-scale features, on a micrometer-scale, can relieve drying stresses and produce monolithic gels [3]. From Knudsen thermal conduction mechanisms in nano-porous

\* Corresponding author. Tel.: +1-513 556 3096; fax: +1-513 556 3773; e-mail: gbeaucag@uceng.uc.edu.

materials, smaller structures, on a nanometer-scale, will decrease the gaseous conduction and consequently reduce the overall thermal conductivity [1–3,8–11]. The presence of PDMS leads to a micrometer-scale morphology which contributes to the monolithic structure. This PDMS induced micrometer-scale morphology apparently protects the nanometer-scale porous structures from collapse during drying, which in turn contributes to the low thermal conductivity.

There are a great number of factors which control the morphology of such hybrid materials and hence their properties. Processing variables, such as catalyst type, the amount and molecular weight of the organic component added, the amount of solvent and water as well as the reaction temperature and time have proven to play an important role in the structure of the final product [7,9–11]. To investigate the dependence of the micro-structure of inorganic-organic hybrid materials on some of the reaction parameters, synthesis of PDMS modified silica xerogels with varied processing variables have been carried out. The structural features of the xerogels resulting from different reaction parameters have been examined with SAXS and SEM.

## 2. Experimental

### 2.1. Sample preparation

Tetraethoxysilane (TEOS) (Aldrich) was used as the silica source for preparing the TEOS/PDMS xerogels. Silanol terminated poly(dimethyl-

siloxane) (PDMS) with molecular weight of 4200 and 1700 (United Chemical Technologies) were used as the polymer component. HCl was used as the catalyst for hydrolysis. Isopropanol and THF were used as mutual solvents. Preparation of xerogels involved mixing of two solutions, A and B. Solution A contained PDMS/TEOS/ $(\text{CH}_3)_2\text{CHOH}$ /THF with molar ratio 0.02/1/6.27/1.67. Solution B was composed of  $\text{H}_2\text{O}$ /HCl with molar ratio 9/0.63. The reaction has been done at  $80^\circ\text{C}$  with stirring usually for 90 min [3,8]. After reaction, the solution was cast into petri dishes to gel at room temperature. The wet gel was aged at room temperature for about one week, then dried at room temperature for one week followed by further drying at  $60^\circ\text{C}$  in a vacuum oven for at least 48 h. The characteristics of all samples are listed in Table 1.

Four sets of experiments were run as variants on this base gel composition:

*Set 1:* The first set involved reduction of the time of reaction using fixed compositions of solutions A and B as described above.

*Set 2:* The second set involved reduction of the water content in the reaction mixture for reactions run to the gel point. The water content was varied by decreasing the amount of  $\text{H}_2\text{O}$  in solution B keeping the amounts of all other reactants constant. This is reported as the molar ratio of  $\text{H}_2\text{O}$  to TEOS in Table 1 which is nine in the original mixture.

*Set 3:* The third set of experiments involved variation of the molecular weight of the PDMS keeping all of the molar ratios at that of the original reaction mixture.

Table 1  
The characteristics of samples

(TEOS)/(PDMS) weight percent ratio	MW of PDMS (g/mol)	( $\text{H}_2\text{O}$ )/(TEOS) molar ratio	Reaction time (min)	<sup>a</sup> State of the xerogels
70/30	4200	9	90	M, OP
70/30	4200	9	60	P, TL
70/30	4200	9	30	P, TP
70/30	4200	6	60	M, OP
70/30	4200	3	60	M, OP
70/30	1700	9	60	M, OP
60/40	4200	9	60	M, OP

<sup>a</sup> M: monolithic; OP: opaque; P: pulverized; TL: translucent; TP: transparent.

*Set 4:* The fourth set of experiments involved increase of the PDMS amount keeping all other fractions constant.

## 2.2. Characterization methods

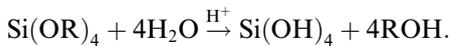
The SAXS data were collected using pinhole collimation and a  $1024 \times 1024$  Siemens, two-dimensional, wire detector. The source was a 12 kW rotating anode generator with a copper target in a point source configuration. Power was set at 40 kV and 40 mA and a nickel filter was used. Data were collected for 15 min and the resulting two-dimensional data sets were circularly integrated and corrected for background, sensitivity, transmission and dark current. The statistical error in the data was propagated through these corrections. The primary particle size, mass-fractal size and fractal dimension, discussed below, were obtained by fits to the unified equation [3,12–16].

A scanning electron microscope (S-2700, Hitachi) was also employed for the observation of morphology of the xerogels.

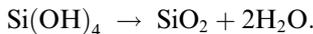
## 2.3. Reaction scheme

The typical sol–gel reaction involves both the hydrolysis and condensation of metal alkoxides, such as TEOS:

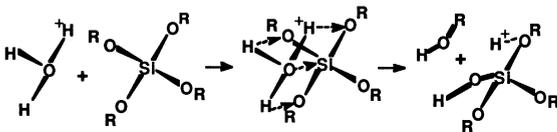
Hydrolysis



Condensation



Under the acid catalysis, the hydrolysis reaction proceeds by an electrophilic reaction mechanism [17]:

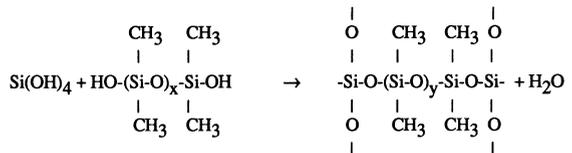


This pattern of hydrolysis leads to less highly crosslinked polymers with ramified structures [17].

However, under conditions of high acid and high water content, the condensation rate is slow, and hydrolysis may well go to completion before any significant condensation occurs, so the resulting products would be more highly crosslinked with compact structures.

When PDMS is introduced to the pure TEOS system, the hydrolysis of TEOS remains the same, but the polycondensation reaction becomes complicated. Besides self-condensation of TEOS, co-condensation between TEOS and PDMS will occur, as proposed by Wilkes et al. [7,18]:

Co-condensation with PDMS →



The bulky PDMS chains participate in gelation with TEOS resulting in a micrometer-scale morphology.

In a previous study [3], micrometer-scale phase separation at the earliest stages of this reaction were observed, apparently controlled by the presence of water. In these earlier studies it was proposed that the system separates into a predominantly PDMS phase and a phase containing the silica precursor. The two reaction schemes, described above, have the potential to occur independently in these two phases and the morphological ramifications of this are a focus of this paper.

## 3. Results

### 3.1. Effect of reaction time

Three samples of the first set, time variation set, with the same acidity and water content were synthesized at 80°C for three different time durations: 90, 60 and 30 min. A reaction time of 90 min gave a uniform, opaque monolithic xerogel, but a reaction time of 60 and 30 min gave xerogels that

showed two distinguishable phases. One phase was a transparent silica solid gel and the other a transparent PDMS rubber, which was still liquid-like even after drying. This suggested that there exists a certain critical stoichiometry and time for PDMS-involved gelation to occur. This critical stoichiometry is probably determined by the rate and extent of the co-condensation reaction of TEOS and PDMS.

Fig. 1 and Table 2 show the pinhole SAXS data for the three xerogel samples. The data indicate a broad crossover through nanometer-scales from compact structures (slope =  $-4$ ) to mass-fractals (slope =  $\sim -2.5$ ). The size of the compact structures, i.e. the primary particles, seems to be around 3 nm in all the three samples, regardless of the length of reaction time, while the mass-fractal structures increase size from 5 to 10 nm, and finally to the size beyond the detectable range of pinhole SAXS as reaction time increased from 30

to 60 and finally 90 min. The measured SAXS parameters are summarized in Table 2.

The SEM observations of these xerogels on a micrometer-scale (Fig. 2) indicate that, with longer reaction times the 90 min sample has a porous and micrometer-sized ( $\sim 1.5$  micrometer) particulate structure, contrasting to the 60 min sample which shows only compact nano-scale structures and lacks micrometer-scale structures.

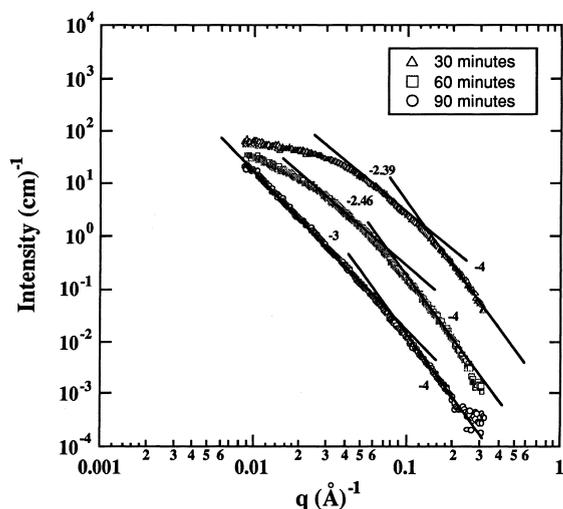


Fig. 1. Pinhole SAXS plots for xerogels: time series, set 1. (The data are offset so the intensity values are not comparable.)

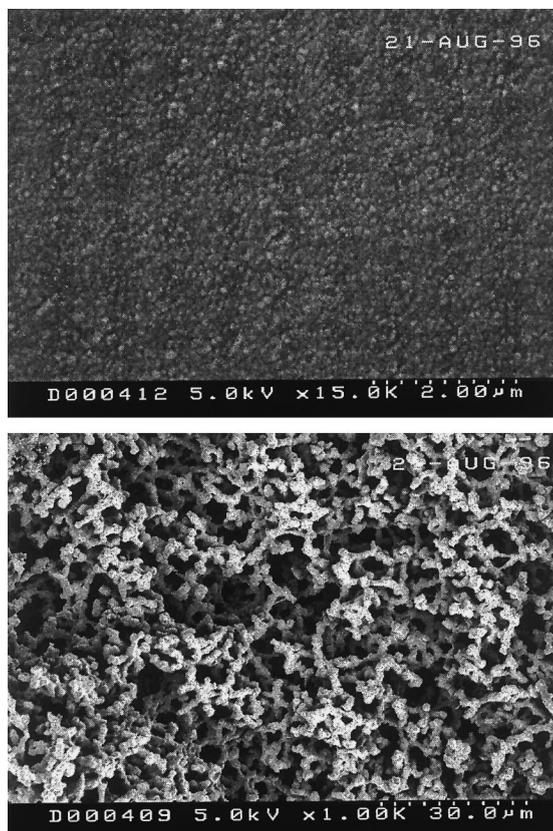


Fig. 2. Effect of reaction time on gel micro-structure, set 1. 60.; 90 min.

Table 2

Pinhole SAXS results for xerogels: time series, set 1. (Structural sizes and mass-fractal dimension were obtained by fit to the unified equation as described in Refs. [3], [12–16].)

Reaction time (min)	Slope 1 ( $\pm 0.1$ )	Primary particle $R_{g1}$ ( $\text{\AA}$ ) ( $\pm 5$ )	Slope 2 ( $\pm 0.1$ )	Mass-fractal $R_{g2}$ ( $\text{\AA}$ ) ( $\pm 5$ )
90	$-4$	37	$-3$	–
60	$-4$	40	$-2.46$	103
30	$-4$	22	$-2.39$	53

### 3.2. Effect of water content

The second set of samples have the same reaction time of 60 min, same PDMS molecular weight (4200 g/mol) and content (30 wt%) but different H<sub>2</sub>O/TEOS molar ratios of 9, 6 and 3. As water content decreased, the gelation time for TEOS increased. However, opaque and monolithic xerogels (for example the 6 and 3 molar ratio samples) were produced with shorter reaction times (60 min), indicating the incorporation of PDMS into the network. This suggested that the PDMS-involved gelation is governed by a different mechanism than that for TEOS-only gelation. A H<sub>2</sub>O/TEOS molar ratio of 3 is insufficient for complete hydrolysis. The hydrolysis rate is retarded and the rate of co-condensation of TEOS

with PDMS is drastically increased, which suppresses the nanometer-scale growth from TEOS species. This causes dominance of larger, micrometer-scale growth and no observed nanometer-scale growth in the 3 molar ratio sample, which is shown in Fig. 3.

The SAXS profile is shown in Fig. 4. As the molar ratio of H<sub>2</sub>O/TEOS is decreased from 9 to 6, nanometer-scale mass-fractal dimension is decreased from 2.46 to 2.34. When the molar ratio is 3, no nanometer-scale mass-fractals is observed. When the ratio is 9, the radius of gyration of primary particle ( $R_{g1}$ ), 4 nm, is larger than that, 2 nm, at ratio of 6. The radius of gyration of aggregates ( $R_{g2}$ ) increases from around 10–20 nm as water content is decreased. All the SAXS data are summarized in Table 3.

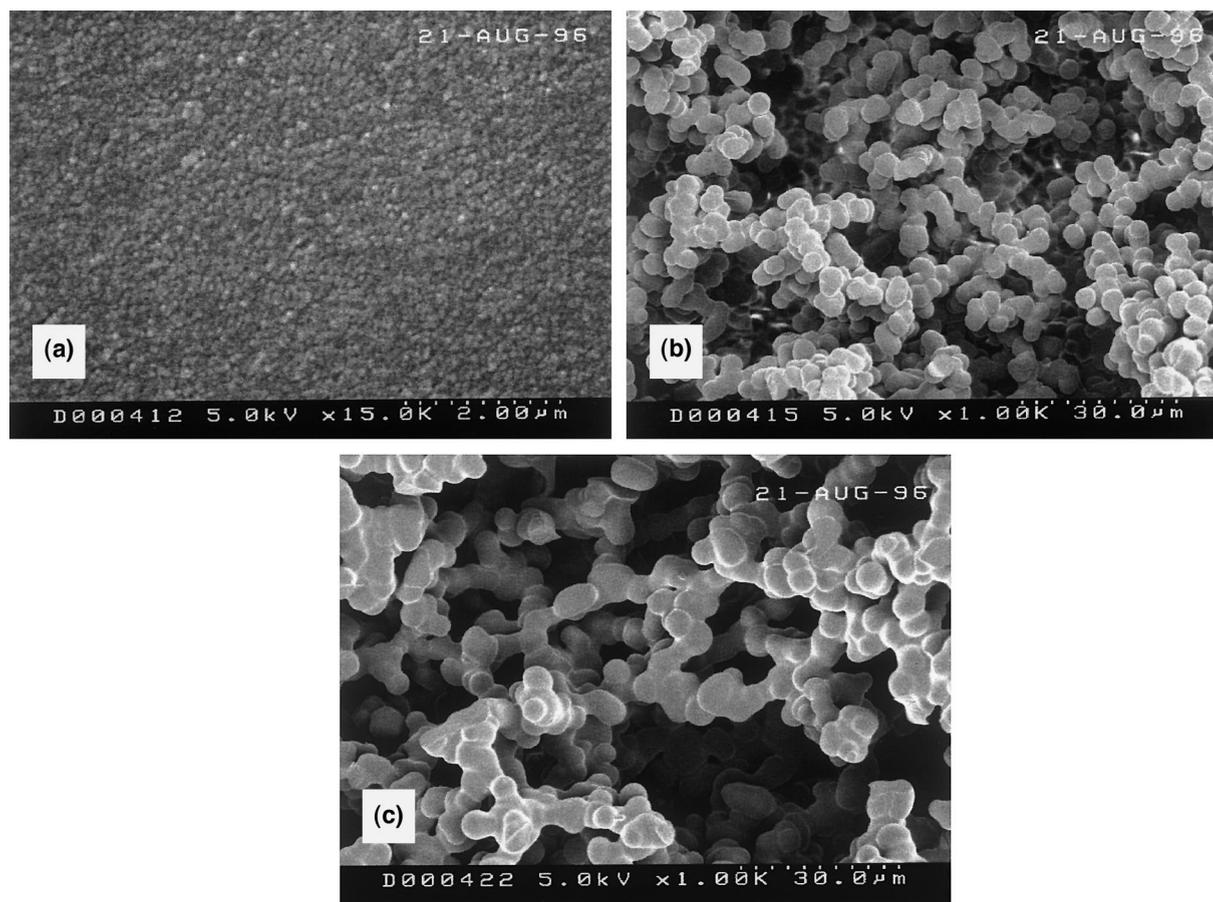


Fig. 3. Effect of water content on gel micro-structure, set 2. [H<sub>2</sub>O] / [TEOS]=9; [H<sub>2</sub>O] / [TEOS]=6; [H<sub>2</sub>O] / [TEOS]=3.

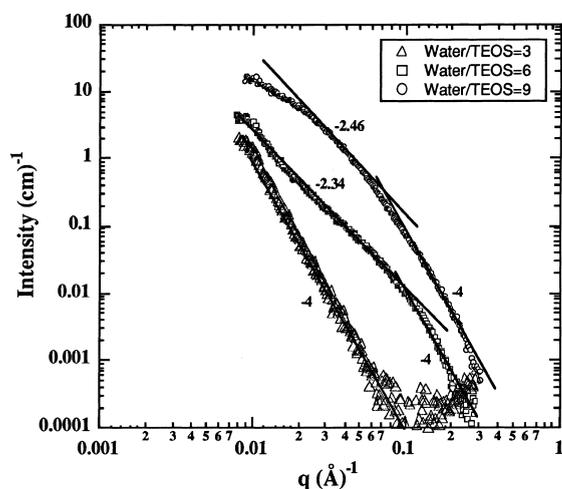


Fig. 4. Pinhole SAXS plots for xerogels: water content series, set 2. (The data are offset so the intensity values are not comparable.)

### 3.3. Effect of molecular weight and content of PDMS

For Set 3 and 4 samples with same water content and weight fraction of PDMS, the samples with lower PDMS molecular weight tended to gel faster. For samples with the same water content and PDMS molecular weight, the sample with the higher PDMS content tended to gel faster.

Fig. 5 indicates pinhole SAXS results for xerogels with varied molecular weight and content of PDMS and SAXS data are summarized in Table 4. The sample with lower PDMS molecular weight showed reduced radius of gyration ( $R_{g1}$ ) of primary particles from 4 to 2 nm and reduced radius of gyration ( $R_{g2}$ ) of mass-fractal aggregates from 10 to 5 nm. As the molecular weight of PDMS decreased, nanometer-scale

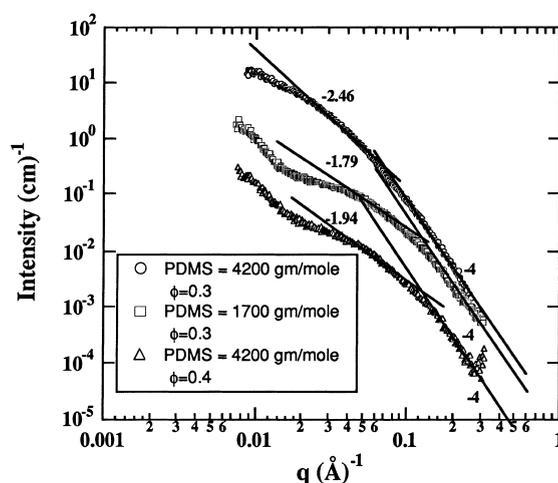


Fig. 5. Pinhole SAXS plots for xerogels: PDMS MW and content series, set 3 and 4. (The data are offset so the intensity values are not comparable.)

mass-fractal dimension was decreased from 2.46 to 1.79. When the weight fraction of PDMS increased, mass fractal dimension was decreased from 2.46 to 1.94. Fig. 6 shows the effect of molecular weight of PDMS on micrometer-scale structures, revealing increases in size. The same effect was observed when the weight fraction of PDMS was increased. There is no change in primary particle size and mass-fractal aggregate sizes.

## 4. Discussion

### 4.1. The effect of reaction time on growth mechanisms and micro-structures

Nanometer-scale primary particle growth (SAXS) is governed by the relative rate of

Table 3

Pinhole SAXS results for xerogels: water content series, set 2. (Structural sizes and mass-fractal dimension were obtained by fit to the unified equation as described in Refs. [3], [12–16].)

Reaction time (min)	(H <sub>2</sub> O)/(TEOS) molar ratio	Slope 1 ( $\pm 0.1$ )	Primary particle $R_{g1}$ ( $\text{\AA}$ ) ( $\pm 5$ )	Slope 2 ( $\pm 0.1$ )	Mass-fractal $R_{g2}$ ( $\text{\AA}$ ) ( $\pm 5$ )
60	9	-4	40	-2.46	103
60	6	-4	19	-2.34	222
60	3	-4	–	–	–

Table 4

Pinhole SAXS results for xerogels: PDMS MW and content series, set 3 and 4. (Structural sizes and mass-fractal dimension were obtained by fit to the unified equation as described in Refs. [3], [12–16].)

MW of PDMS (g/mol)	PDMS (weight percent)	Slope 1 ( $\pm 0.1$ )	Primary particle $R_{g1}$ ( $\text{\AA}$ ) ( $\pm 5$ )	Slope 2 ( $\pm 0.1$ )	Mass-fractal $R_{g2}$ ( $\text{\AA}$ ) ( $\pm 5$ )
4200	30	-4	40	-2.46	103
1700	30	-4	21	-1.79	51
4200	40	-4	22	-1.94	51

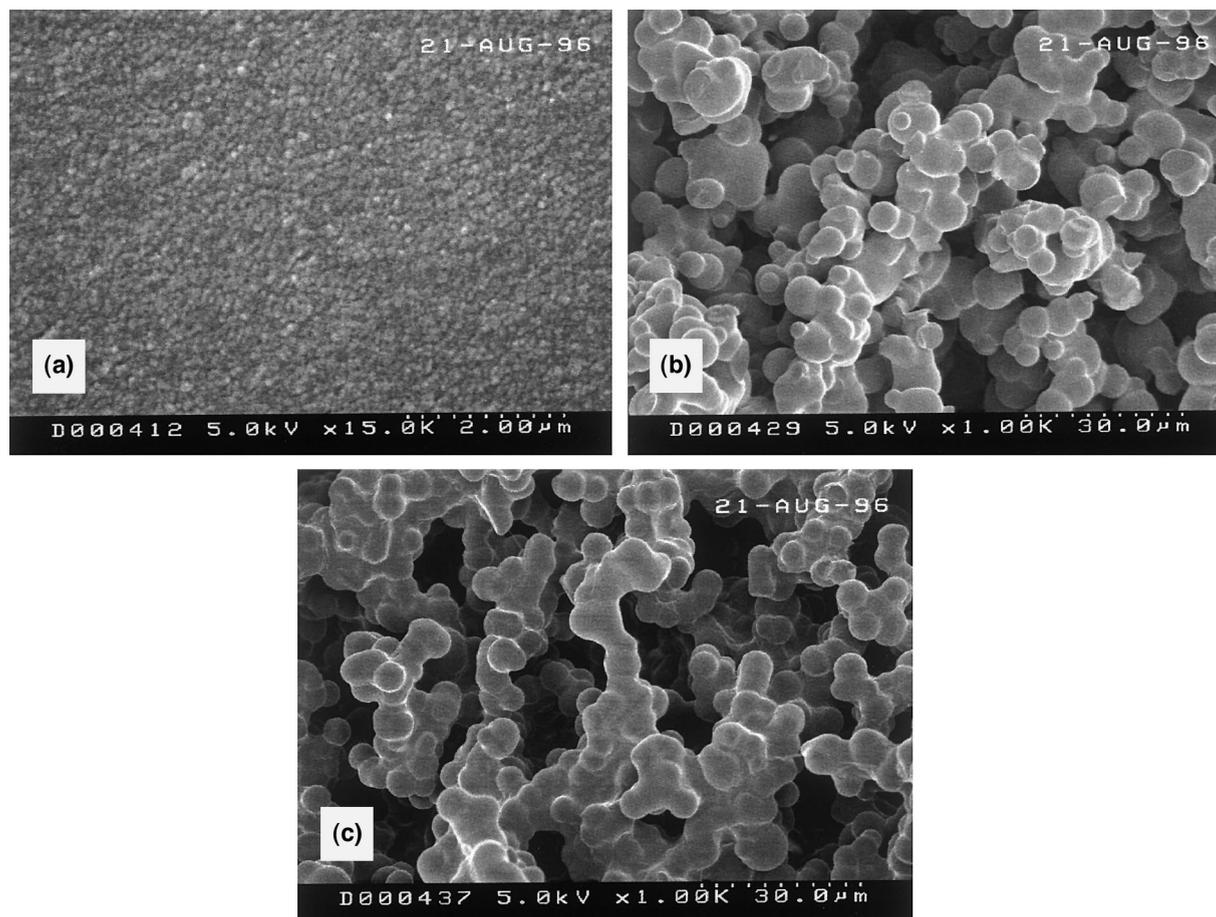


Fig. 6. Effect of molecular weight and content of PDMS on gel micro-structure, set 3 and 4. PDMS: 4200 g/mol,  $\phi = 0.3$ ; PDMS: 1700 g/mol,  $\phi = 0.3$ ; PDMS: 4200 g/mol,  $\phi = 0.4$ .

hydrolysis and condensation reactions. With high acidity and high water content, hydrolysis of TEOS is relatively fast and most TEOS monomers are likely to be fully hydrolyzed. Primary particles formed by growth from TEOS monomers are well formed during the early stage. After TEOS monomers are depleted, however, a

crossover from monomer growth to cluster-cluster aggregation leading to weakly branched structures must occur. The growth of aggregate mass-fractals composed of the nanometer-scale primary particles is by relatively slow self-condensation of TEOS and thus is reaction-time dependent.

Micrometer-scale domain growth (SEM) is controlled by the rate of co-condensation of PDMS with hydrolyzed TEOS monomers or clusters. As water with acid catalyst was added to the homogeneous mixture of PDMS, TEOS and solvents, the solution became cloudy; as water content was reduced, the solution became less cloudy. It is believed that the immiscibility between water and PDMS caused the cloudiness [3]. Due to the immiscibility between water and PDMS, water-rich and PDMS-rich phases occur. The TEOS molecules inside the PDMS-rich domains are isolated from water and stay unhydrolyzed. The co-condensation of PDMS with TEOS proceeds only at the interfaces of PDMS-rich domains and water-rich phases which contain hydrolyzed TEOS species. The rate of co-condensation is greatly limited. Thus the length of reaction time will mostly affect micrometer-scale domain growth and nanometer-scale mass-fractal aggregates growth. Shorter reaction time means stopping the reaction, at elevated temperature, earlier and further reducing the amount of condensation. Under these conditions, the nanometer-scale, mass-fractal aggregates from TEOS are not well developed, and the co-condensation of PDMS and TEOS has not proceeded to the extent for PDMS to be involved in gelation. Therefore, the resultant gels are glass-like and full of densely packed small TEOS species without incorporation of PDMS oligomers and lack monolithic structures. In contrast, given extended reaction times for self-condensation of TEOS to proceed to a more complete extent, and for co-condensation of PDMS with TEOS to proceed to the critical extent for gelation, larger TEOS clusters and more PDMS oligomers will be incorporated into the gel network which results in highly porous and strongly interconnected monolithic structures.

#### 4.2. Effect of water content

Variation in water content changes the sol–gel chemistry of the pure TEOS and affects co-condensation of PDMS with TEOS, and thus has different effects on the nanometer-scale growth and

the micrometer-scale growth. In the nanometer-scale TEOS phase, the reaction is governed by pure sol–gel chemistry. Lower water content is considered to speed up condensation but slow down hydrolysis which favors the growth of more extended mass-fractal structures and inhibits the growth of the compact TEOS primary particles. In the micrometer-scale PDMS phase, reduced water content gives better contact of PDMS with hydrolyzed TEOS. Co-condensation of PDMS with TEOS commences at an earlier stage and proceeds at a faster rate, and therefore causes significant micrometer-scale growth.

#### 4.3. Effect of molecular weight and content of PDMS

In the same PDMS fraction, the sample with lower molecular weight of PDMS should have more PDMS silanol functional groups, i.e. more reacting sites on PDMS, and in the case of same molecular weight, the sample with the higher content of PDMS. Though PDMS and water are still immiscible, the increased reacting sites on PDMS cause faster co-condensation of TEOS with PDMS, which dominates over the hydrolysis rate and self-condensation rate of TEOS. Once TEOS is hydrolyzed, it is more likely to experience co-condensation with PDMS than to experience self-condensation or further hydrolysis. The system will gel at a shorter time and lead to enhanced micrometer-scale growth and limited nanometer-scale growth.

### 5. Conclusions

(1) Multiple size-scaled monolithic gels were produced by sol–gel reaction of PDMS and TEOS with an acid catalyst.

(2) Morphology of the porous gels could be controlled by changing reaction time, solvent content, molecular weight and content of PDMS.

(3) It is suggested that nanometer-scale primary particle growth is governed by hydrolysis and condensation of TEOS. However, micrometer-

scale domain growth is due to PDMS involved condensation/polymerization reactions.

## References

- [1] W. A. Kauzman, Kinetic Theory of Gases, Benjamin, New York, 1966.
- [2] E.L. Cussler, Diffusion: Mass Transfer in Fluid Systems, Cambridge University, London, 1984.
- [3] J. Hyeon-Lee, L. Guo, G. Beaucage, M.A. Macip-Boulis, A.J.M. Yang, J. Polym. Sci., Polym. Phys. 34 (1996) 3073.
- [4] J.D. Mackenzie, Y. Hu, J. Mater. Sci. 27 (1992) 4415.
- [5] J.D. Mackenzie, Y.J. Chung, Y. Hu, J. Non-Cryst. Solids 147 and 148 (1992) 271.
- [6] S.S. Prakash, C.J. Brinker, A.J. Hurd, S.M. Rao, Nature 375 (6530) (1995) 431.
- [7] H.H. Huang, B. Orlor, G.L. Wilkes, Macromolecules 20 (1987) 1322.
- [8] M.A. Macip-Boulis, A.G. Boulis, US Patent Number 5, 525, 643 (1995).
- [9] L.W. Hrubesh, R.W. Pekala, J. Mat. Res. 9 (3) (1994) 731.
- [10] J. Fricke, Aerogels, Springer, Heidelberg, Germany, 1986.
- [11] J. Fricke, A. Emmerling, in: Chemistry, Spectroscopy and Applications of Sol–Gel Glasses, Springer, Heidelberg, 1991.
- [12] G. Beaucage, D.W. Schaefer, J. Non-Cryst. Solids 172–174 (1994) 797.
- [13] G. Beaucage, J. Appl. Cryst. 28 (1995) 717.
- [14] G. Beaucage, J. Appl. Cryst. 29 (1996) 134.
- [15] G. Beaucage, T.A. Ulibarri, E. Black, D.W. Schaefer, in: Organic hybrid materials, Am. Chem. Soc. Symp. Ser. No. 585, American Chemical Society, Washington, DC 1995 p. 97.
- [16] D.W. Hua, J. Anderson, S. Hareid, D.M. Smith, G. Beaucage, in: Better Ceramics Through Chemistry VI, Mater. Res. Soc. Proc., vol. 346, Materials Research Society, Pittsburgh, PA, 1994, p. 985.
- [17] K.D. Keefer, in: Better Ceramics Through Chemistry, Mater. Res. Soc. Symp. Proc. 32, North Holland, New York, 1984, p. 15.
- [18] G.L. Wilkes, B. Orlor, H. Huang, Polym. Prep. 26 (1985) 300.