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Transition from transparent aerogels to hierarchically porous monoliths in polymethylsilsesquioxane sol–gel system

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ABSTRACT

A transition from hierarchical pore structures (macro- and meso-pores) to uniform mesopores in monolithic polymethylsilsesquioxane (PMSQ, $CH_3SiO_{1.5}$) gels has been investigated using a sol–gel system containing surfactant Pluronic F127. The precursor methyltrimethoxysilane (MTMS) undergoes an acid/base two-step reaction, in which hydrolysis and polycondensation proceed in acidic and basic aqueous media, respectively, as a one-pot reaction. Porous morphology is controlled by changing the concentration of F127. Sufficient concentrations of F127 inhibit the occurrence of micrometer-scale phase separation (spinodal decomposition) of hydrophobic PMSQ condensates and lead to well-defined mesoporous transparent aerogels with high specific pore volume as a result of the colloidal network formation in a large amount of solvent. Phase separation regulates well-defined macropores in the micrometer range on decreasing concentrations of F127. In the PMSQ-rich gelling domain formed by phase separation, the PMSQ colloidal network formation forms mesopores, leading to monolithic PMSQ gels with hierarchical macro- and meso-pore structures. Mesopores in these gels do not collapse on evaporative drying owing to the flexible networks and repulsive interactions of methyl groups in PMSQ.

1. Introduction

Porous materials with various chemical compositions are widely used as adsorbents, gas storage, catalyst supports, filters, membranes, and separation media [1–6]. The representative protocols to tailor porous materials rely on foaming, soft- and hard-templating, and phase separation, all of which take place during solidification of the material from a precursor solution. The sol–gel technique, for example, is often employed to synthesize porous materials in liquid media with various pore characteristics. After multiphase structures are formed during hydrolysis and polycondensation reactions of precursor, removing the adequate phase(s) while leaving at least one solidified phase results in porous materials. In addition to the well-known ordered and disordered mesoporous materials [7], which are typically synthesized using the soft templates formed by surfactant micelles (structure-directing agents (SDA)), various porous materials with hierarchical structures are becoming more important [8–13]. Fast mass transport as well as high surface area is highly expected because hierarchically porous materials possess two or more discrete size levels of pores. For the applications that require enhanced contact of external fluid with the solid surface such as in separation media and catalyst supports, in particular, materials or devices designed to have hierarchical pore structures are highly demanded.

We have designed a number of hierarchically porous materials by the sol–gel technique accompanied by phase separation to enhance the separation efficiency in high performance liquid chromatography (HPLC) [14–17]. Spinodal decomposition-type phase separation in a macroscopic scale regulates macropores typically in micrometers, through which liquid flows with a low pressure drop. Mesopores typically in nanometers are developed by Ostwald ripening [18] and soft-templating by SDA [19,20].

Of various sol–gel materials, polymethylsilsesquioxane (PMSQ, $CH_3SiO_{1.5}$) typically derived from methyltrialkoxysilanes possesses unique surface characters due to the presence of hydrophobic methyl groups as well as hydrophilic silanol groups. We, for instance, have reported that separation media composed of PMSQ can separate both polar and nonpolar molecules in normal and reversed phase modes, respectively [21,22]. Rao et al. also showed that porous PMSQ can supply a superhydrophobic surface with the aid of surface roughness and surface modification [23,24]. The PMSQ materials also exhibit unique mechanical properties arising from the lower cross-linking density compared to silica and less-polar methyl groups that repel each other when compressed. Aerogels with PMSQ composition are reported to show "spring-back" and bendable features without being broken [25–30]. Methylsilsesquioxane-based films (and other organotrialkoxysilane-derived films) for low-*k* applications also exhibit unique mechanical properties such as decreased elastic modulus,

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Table 1
Stating compositions and obtained mesopore properties.[a]

Notation	F127 (g)	Shrinkage during aging (%)	Bulk density (g cm^{-3})	Mesopore size (nm)	BJH specific pore volume[b] (cm^3 g^{-1})	BET specific surface area (m^2 g^{-1})
M6-0	0	3	0.33	–	0.029	14
M6-32	0.32	25	0.42	7	0.22	414
M6-34	0.34	18	0.42	10	0.37	446
M6-36	0.36	12	0.35	15	0.52	444
M6-38	0.38	11	0.32	30	0.52	428
M6-40	0.40	10	0.30	37	0.61	437
M6-60	0.60	4	0.28	60	2.65	513
M6-80	0.80	4	0.28	35	3.08	576
M6-100	1.00	3	0.22	30	3.30	623

[a] Other components; MTMS 5 mL, 5 mM HOAc 6 mL, and urea 0.50 g.

[b] Pores between 2 and 100 nm in size are considered for evaluation of BJH pore volume.

hardness, brittleness and the emergence of viscoelastic properties [31–37].

In the course of spinodal decomposition induced during the sol–gel transition of PMSQ in a polar medium such as water and alcohol, we [15,21,22] and Dong et al. [38–40] found that well-defined macropores are formed. However, formation of monolithic gel [41] as well as the phase separation behavior is severely influenced by many factors including pH, amount and polarity of the solvent, water content, and temperature because of the hydrophobicity of the resultant networks and cyclization reactions. The cyclization reactions do not contribute to the random network formations, which are a requisite for gelation in monolith, but instead contribute to the formation of low-molecular-weight products such as polyhedral oligomeric silsesquioxanes (POSS) [42]. Only a few reports on macroporous monolithic PMSQ materials with random networks hence can be found in literatures except for those by us [15,21,22] and Dong et al. [38–40]. In addition, PMSQ with hierarchical pore structures is hardly found. Although Dong et al. [38] reported that mesopores are present in the macroporous skeletons of PMSQ monolith prepared by a two-step acid/base process, no detailed and systematic research on the formation of mesopores has been done. It is also known that PMSQ condensates cannot be structured with SDA because of the absence of specific surfactant-condensates interactions, which is fundamental for mesopore formations. For these reasons, PMSQ materials with hierarchical pore structures are difficult to be prepared, regardless of their unique properties such as hydrophobicity and mechanical flexibility.

In this research, transitions of pore structures from mesoporous to hierarchical meso/macroporous in PMSQ monolith have been

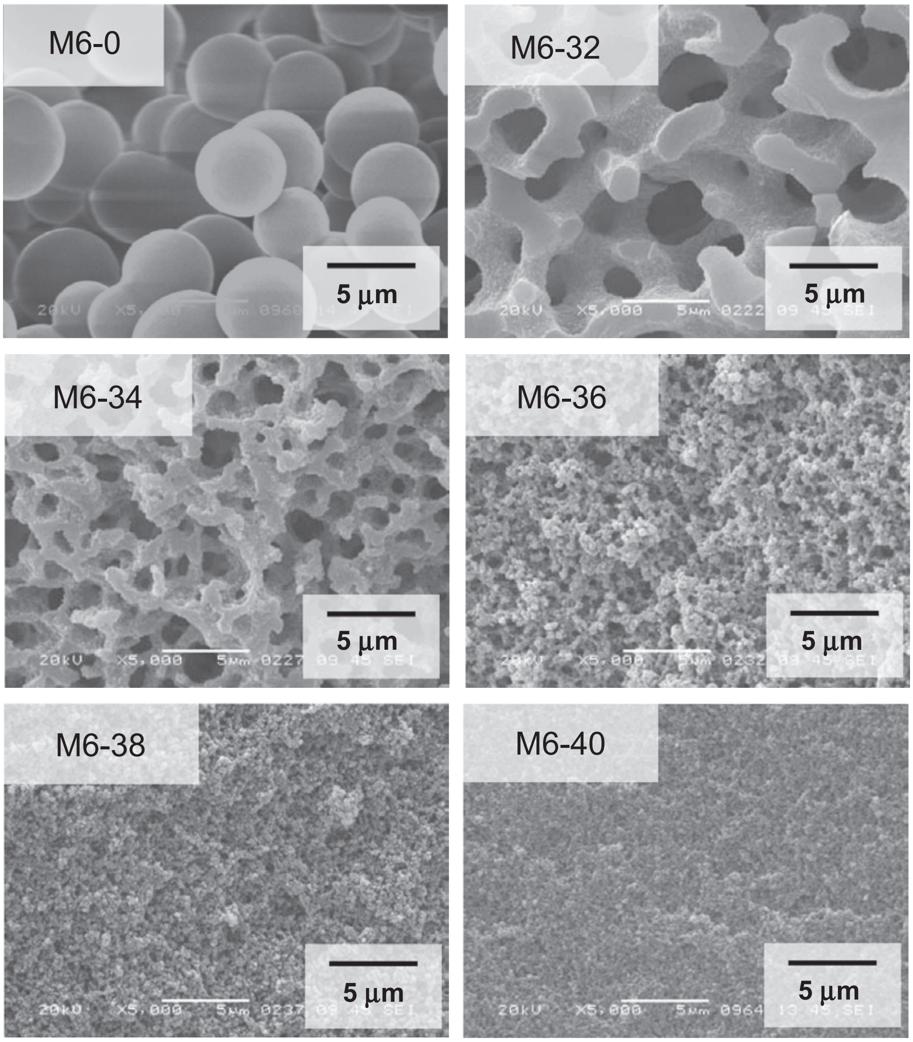

Fig. 1. Micrometer-scale macroporous structures observed with SEM. It is confirmed that macropores become smaller with increasing amount of F127 (from M6-0 (0 g) to M6-40 (0.40 g)). All images are in the identical magnification.