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Fractal Study of Mesoporous Structure in Water Molecular Condensed System

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Bis-(4-stearoylamino)phenyl ether (BSADE) can aggregate and self-assemble in water. Transmission electron microscopy (TEM) indicated that the morphology of BSADE aggregates in water was entanglement and thin fiber-like, and that a three dimensional network structure was formed. Water molecules were entrapped in this three dimensional network structure and formed a new type of condensed system (so-called water molecular gel). Water molecular gel is a typical mesoporous material which can be characterized by the fractal dimension D . Using gas adsorption method along with measurement of porosity and specific surface area, the fractal dimension D of the complicated pores was 2.1-2.2 for this water molecular gel. Using viscosity method and the Cayley fractal tree, the fractal dimension D of the fiber-like three dimensional network was determined to be 1.98. The formation process of water molecular gel can be described as nucleation followed by a repeated growing and branching cycle.

Key words: Fractal, Mesoporous structure, Water molecular condensed system

I. INTRODUCTION

In the recent years, much attention has been paid to the gelator, which is an organic compound with small molecular weight. In the proper media, such as water and organic solvents, gelators can aggregate and self-assemble into supramolecular structures [1,2]. Generally, there are some active sites for non-covalent interactions in the molecular structure of the gelators, typically hydrogen bonds or π - π stacks. The morphology of gelator aggregates is usually fibril which further assembles into three dimensional network structures. The molecules of solvents are entrapped in the network structure by capillary force. In this case, the system becomes a semi-solid gel, a so-called molecular gel, e.g. water molecular gel or other molecular gel depending on what solvent used. Water molecular gel is a physically condensed system formed by the aggregation of gelators in water [3]. In the past decade, the investigations related to the influence of media variety (such as water, aromatic or aliphatic organic solvents and their polarity) on the self-assembly of gelators have been published [1-4]. The main results of these investigations were what solvents could be gelatinized by gelators, and their micro-morphology observed by transmission electron microscope (TEM), scanning electron microscope (SEM) or atomic force microscope (AFM).

As described in our previous reports, typical mesoporosity was found by TEM, SEM and AFM in three dimensional network structures of water molecular gels

[4]. The basic feature of mesoporous material is that there are very complicated surface structures with pores. The final mesoporous structure depends on the process of pore formation. Due to the random nature of mesoporous structure, the pore shape is usually a polydispersity which is hardly describable by traditional Euclidian geometry. Fractal theory provides a useful tool to quantitatively describe tanglesome phenomena without specific length, but with self-comparability in nature [5,6]. Fractal geometry was first introduced by Avnir and co-workers [7]. For the characterization of mesoporous material, fractal theory is very convenient because the detailed shape of pores can be ignored. In practice, traditional methods for characterization of surface structures can be used for the fractal surface, such as pore filling [7] and gas adsorption [8]. The data obtained from these traditional methods are used in the fractal model and then a quantitative parameter, fractal dimension D , can be obtained. For instance, Gu and co-workers reported that the surface structures of coal and active carbon exhibit a fractal feature under non-constant pressure [9,10]. The fractal dimension D for these nonuniform porous materials was calculated by the porosity method. The influence of pressure on the fractal dimension D and pore structures was also discussed. Shen and co-workers investigated fractal properties of aerogel and xerogel of SiO_2 by small angle X-ray scattering (SAXS) [11]. The results indicated that a fractal feature was found for aerogel, but not for xerogel.

As is well known, the mass transfer in mesoporous materials, such as water molecular gel, is greatly related to their pore structures. The investigation for mesoporous structure of water molecular gels could be significant for their potential applications in the fields of drug delivery systems, catalysis, sensors, gel electrolytes

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and so on. In the present work, fractal structures of water molecular gel with mesoporosity was characterized by using gas adsorption (porosity and specific surface area), viscosity and a Cayley fractal tree.

II. EXPERIMENTS

A. Preparation of water molecular gels

Synthesis of bis-(4-stearoyl-aminophenyl) ether (BSADE) has been described previously [12]. BSADE (3wt%) was placed in water in a test tube. The mixture was heated until the solid completely dissolved. The solution was then slowly cooled at room temperature until semi-solid gel formed.

B. Measurements of specific surface area

The specific surface area of gases was measured by ST-08 specific surface area meter (Beijing Beifen Analysis Instruments Ltd. Co.). The samples were dried under ambient pressure at 373 K for 10 min and then placed in the machine. He and N₂ were used as a carrier and adsorbate, respectively. Adsorbed amount under varied pressure can be simulated by measuring amounts of adsorbed N₂ under the same pressure. Subsequently, the filling ratio and adsorption potential can be calculated. The specific surface area of adsorbates can also be calculated by using different adsorbate, such as nitrogen, methane, ethane, propane and butane.

C. TEM measurements for water molecular gel

A piece of water molecular gel formed by 3wt% of BSADE was placed on a carbon coated copper grid (0.07 mm) and then removed after 1 min, leaving some small patches of the gel on the grid. After specimens had been dried under vacuum, the samples were shadowed with OsO₄ (10 mg, 2% aqueous solution) and dried for 1 h under vacuum. The micro-morphology of the gels was examined by transmission electron microscope (JEM-100CXII) with an acceleration voltage of 80 kV.

D. Viscosity measurements of water molecular gel

The viscosity of the water molecular gel was measured by an NDJ-I rotation viscometer with homocentric dual-canisters at room temperature. The water molecular gel (before gelation) was placed in the viscometer. The external canister rotated in an instant angle speed ω and the internal canister would passively move an angle θ by the shear force of the gel until equilibrium status was reached. Compared with the known

viscosity (η_w) of water, the unknown viscosities (η_g) of water molecular gel can be calculated by following equation:

$$\eta_g = \frac{\eta_w \theta_g \omega_{we}}{\theta_w \omega_{ge}} \quad (1)$$

where, η_g and η_w are the viscosities of the gel samples and water, respectively. θ_g and θ_w are the moved angles of the internal canister for the gel samples and water, respectively. ω_{we} and ω_{ge} are the moved angles of the external canister for the water and gel samples, respectively.

III. RESULTS AND DISCUSSION

A. Porosity method for the fractal dimension D

The porosity method for calculation of surface fractal dimension D is based on the theory of pore filling. The fractal dimension D can be obtained according to the effect of relative pressure or adsorption potential (A) on the filling ratio (r). For the nonuniform porous materials, the capability of adsorption is different for the pores with varied microstructures. The theory of pore filling considering microstructure and properties of adsorption leads to a general isothermal equation (Dubinin-Astakhov equation) [10]

$$q = q_m \exp \left[- \left(\frac{A}{E} \right)^n \right] \quad (2)$$

$$A = RT \ln \frac{p_0}{p} \quad (3)$$

where q_m is the saturated adsorbed amount (it is equivalent to the volume of pore per gram, cm³/g), p_0 is saturated vapor pressure, E is specific energy of adsorption (J/mol) and n is a structural parameter related to the pore size and size distribution.

After mathematical derivation of the Dubinin-Astakhov equation (the detailed derivation process can be found in reference [13]), the relationship of filling ratio (r) and fractal dimension D is seen to be:

$$\ln r = (D - 3) \ln A + \ln K \quad (4)$$

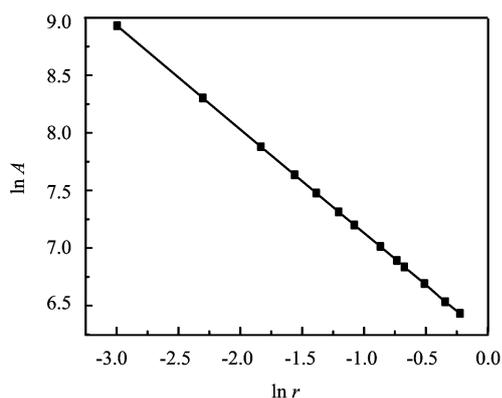
where K is a coefficient related to the adsorbates. Therefore, adsorption potential (A) can be directly calculated from Eq.(3). Generally, the term r is defined as $r=a/a_0$, where a is the adsorption amount (cm³/g) under certain pressure and a_0 is the saturated adsorption amount. In the present work, $a_0=0.1$. The values of a and A obtained from experiments are listed in Table I.

Figure 1 is the plot of logarithm of filling ratio ($\ln r$) vs. logarithm of adsorption potential ($\ln A$). The plot shows a good linear relationship. The fractal dimension D can be calculated from the slope of the curve. The regressing equation based on the data in Fig.1 is $y=-0.9013x+6.2286$, where the slope is -0.9013 . Thus, the

TABLE I Values of adsorption amount a and adsorption potential A under certain pressures

a	A	a	A
0.005	7555	0.042	1111
0.010	4033	0.048	984.5
0.016	2642	0.051	929.6
0.021	2069	0.060	805.2
0.025	1768	0.071	686.7
0.030	1501	0.080	620.9
0.034	1340		

fractal dimension D is about 2.1. This value is available because the fractal dimension D should be in the range of 2-3. As Eq.(4) indicated, the value of r would be 1 if the value of D was 3. Herein, it implies a saturated adsorption.

FIG. 1 Plot of filling ratio r vs. adsorption potential A .

B. Effective section area of molecule for D

Gas adsorption is initially used for the fractal characterization of complicated surfaces [14]. When porous materials adsorb gases with similar geometric shape, the adsorption generally follows a relationship shown below [13]

$$n \propto \sigma^{-D/2} \quad (5)$$

where n is the molar heat of adsorption for a single molecular layer. σ is effective section area of adsorbate molecule which should be in the following range:

$$\sigma_0 < \sigma < \frac{R_{\max}}{R_{\min}} \sigma_0 \quad (6)$$

where σ_0 is section area of adsorbate molecule and R is the radius of the particle. Thus, the following equation can be derived from Eq.(5):

$$S = n\sigma \propto \sigma^{(2-D)/2} \quad (7)$$

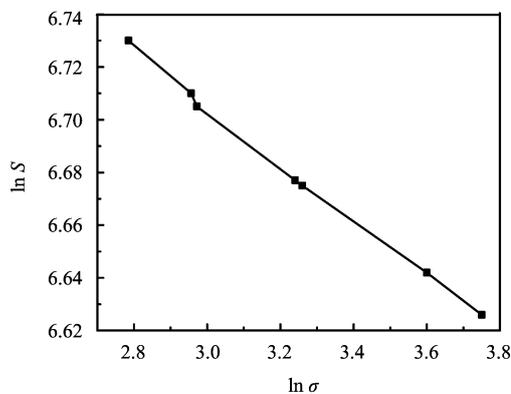
$$\ln S = \frac{2-D}{2} \ln \sigma + \text{const} \quad (8)$$

As is known from Eq.(7), D , i.e. slope for the curve of $\ln S$ vs. $\ln \sigma$, can be obtained by measuring specific surface area (S) of porous mass adsorbed adsorbates with varied effective section area of molecule. Table II lists the data of section area of adsorbate molecule (σ_0), such as nitrogen, methane, ethane, propane, butane and carbon dioxide (at 195 and 298 K), and the data of S of gel pores at 77 K.

TABLE II Surface area of adsorbate molecule cross section and specific surface area of pores in water molecular gel

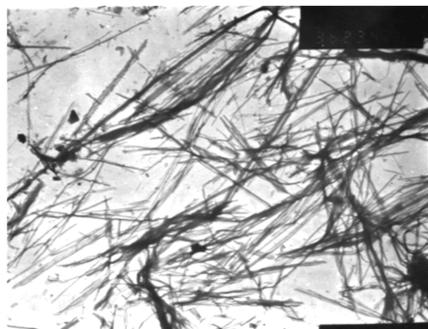
Adsorbates	σ_0	$S/(\text{dm}^3/\text{g})$
N ₂	16.2	837.147
CH ₄	19.4	820.571
C ₂ H ₆	25.9	816.478
C ₃ H ₈	36	793.934
C ₄ H ₁₀	42.1	792.347
CO ₂ (195 K)	19.5	766.627
CO ₂ (298 K)	25.3	754.458

Figure 2 is the plot of logarithm of section area of adsorbate molecule ($\ln \sigma_0$) vs. logarithm of specific surface area of gel pores ($\ln S$). Similarly, the regression equation based on the data in Fig.2 is $y = -0.1059x + 7.0222$, where the slope is -0.1059 . Thus, the fractal dimension D is about 2.2.

FIG. 2 Plot of specific surface area S vs. efficient section area σ for water molecular gel.

C. Viscosity method for D

The viscosity method is based on the existence of fiber-like network structures in the supramolecular system. The fractal dimension for this system can be characterized through investigating the relationship between the nucleation/growth of fiber-like aggregates and the system rheology. Figure 3 shows a TEM image of water molecular gel, in which the formation of fiber-like aggregates by gelator BSADE self-assembling is clearly exhibited. It is helpful to understand the

FIG. 3 TEM image of water molecular gel ($\times 7200$).

morphology of network structures in water molecular gel. The formation mechanism of fiber-like aggregates has been discussed previously [3,4]. The fiber-like aggregates further formed a physical gel with thixotropic sensibility. This physical gel easily dissociates under the action of shear force and then aggregates again when the shear force disappears. This is actually a nonequilibrium and non-linear process. Nevertheless, randomness is a main feature in this process. Compared with other structural parameters of gel, the fractal dimension is the only invariable parameter with change of test rules and is related only to the fractal structures and morphology of gel. As shown in Fig.3, the network is formed by branching. This type of nano-fiber network structure can be well represented by the Cayley fractal tree [15]. The end of every tree branch is a site of growth, at which a number of new branches formed [16,17]. Figure 4 illustrates schematically the repeating growth process of the Cayley fractal tree. The characterization of fractal tree structures can be described by three parameters: branch length (ξ), activity of growth sites and branching rates (z). Generally, ξ and z are constant during the period of growth process for a normal fractal tree. This implies that branching occurs simultaneously at all active ends of tree branches.

Obviously, the number of branches (n) is a function of layers of branch (g). The Cayley tree with fractal dimension D_ξ is described by the following equation

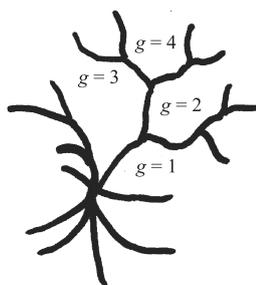


FIG. 4 Scheme of growth of Cayley fractal tree.

based on the power law [15]:

$$n(g) = zg^{D_\xi - 1} \quad (9)$$

here it is worth noting that the parameter ξ was defined as chemical distance and the related D_ξ was defined as fractal dimension in chemical space. It would be better to use D_f defined as the fractal dimension in the Euclidian geometric space instead of D_ξ .

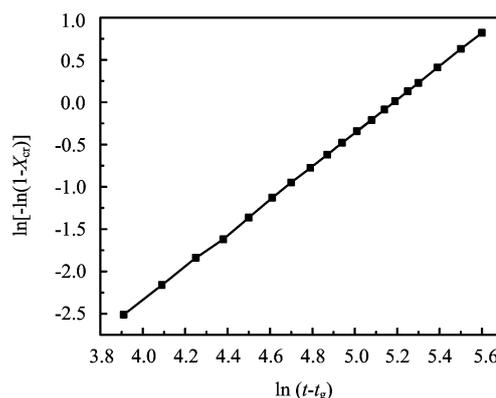
For a fractal network system grown in three dimensions, Liu and co-workers derived mathematically the relationship between D_ξ and D_f [16]. Then, the following equation was obtained based on the Avrami relation describing nucleation and growth of bulk crystals [16]:

$$\ln[1 - X_{cr}(t)] = -k(t - t_g)^{D_f} \quad (10)$$

Thus, the values of D_f can be obtained by a plot of $\ln[-\ln(1 - X_{cr})]$ vs. $\ln(t - t_g)$. Here, X_{cr} is the crystallinity of the system, which is related to the viscosity of system [16]:

$$X_{cr} = \frac{\psi(t)}{\psi(\infty)} = \frac{\eta_{sp}(t)}{\eta_{sp}(\infty)} = \frac{\eta^* - \eta_0}{\eta^*(\infty) - \eta_0} \quad (11)$$

where η^* and η_0 are the viscosities of the system and solvent, respectively. The data of viscosity were introduced to Eq.(10). Figure 5 is the plot of $\ln[-\ln(1 - X_{cr})]$ vs. $\ln(t - t_g)$. A good straight line implies the self-similarity of the fiber-like aggregates fractal patterns. The fractal dimension D_f is 1.98 calculated from slope of the plot. This is very close to our previous results obtained by using Sandbox method (1.94), Density-density correlation method (1.97) and SAXS method (1.9) [18].

FIG. 5 Plot of $\ln[-\ln(1 - X_{cr})]$ vs. $\ln(t - t_g)$ in water molecular gel.

In combination with our previous polarized fluorescence study on the polymerizable gelator in diphenyl ether [17], similarly, the BSADE aggregates in water were also entanglement and thin fiber-like, and furthermore, a three dimensional spherulite structure was formed. This spherulite structure is essentially controlled by nucleation and growth. This implies that the

growth process of BSADE aggregates occurs via crystallization. Thus, a possible mechanism for the formation of water molecular gel is proposed as a repeat process of growing and branching.

IV. CONCLUSION

Water molecular gel can be formed by the self-assembly of bis-(4-stearoylaminophenyl) ether (BSADE) in water. It is a typical mesoporous material with fractal feature. Using gas adsorption method including porosity measurement and specific surface area, the fractal dimension D of the complicated pores was 2.1-2.2 for water molecular gels. Using viscosity method and the Cayley fractal tree, the fractal dimension D of the fiber-like three-dimensional networks was 1.98.

V. ACKNOWLEDGMENT

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