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Simulation of mesophase formation of rodlike molecule, imogolite

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SUMMARY

The process of mesophase formation of rodlike molecule, imogolite, was simulated by comparing the distance distribution function computed from models with that obtained by the Fourier-transformation of small angle X-ray scattering data. In the initial state below A-point (defined as a starting point of mesophase formation), imogolite molecules assemble into loosely packed hexagonal shape with their ends aligned in a line. The columns composed of hexagonal packing are arranged side by side to form raft-like sheets near the A-point and finally form mesophase above A-point.

INTRODUCTION

Imogolite is a natural product found in clay fraction of soil or pumice bed in Japan. It consists of hydrated aluminum silicate and has been characterized as a hollowed cylinder of 25.2 Å in diameter and several thousands Å in length as schematically shown in Fig.1. Here twelve gibbsite units (one unit corresponds to $(Al_2O_3{\cdot}SiO_2{\cdot}2H_2O)_2$) form the cylinder of an imogolite unit which is 8.4 Å in length[1)].

Imogolite is dispersed molecularly in acetic acid aqueous solution by ultrasonic wave treatment and its molecule in solution is modeled approximately as a completely rigid rod from the analysis of the dilute solution properties[1)]. Imogolite forms lyotropic mesophase[2-5)] as predicted by Onsager[6)] and Flory[7)] for a rigid rod when its concentration exceeds a certain limiting point defined as an A-point.

The process of mesophase formation of imogolite is considered as the model of rod molecule assembly. The mesophase formation was observed with increasing imogolite concentration in the acidic aqueous solution by means of small angle X-ray scattering (SAXS). SAXS measurement yields information on size (from several to hundreds Å), weight and shape of particles. The distance distribution function is given by Fourier-transforming scattered intensities[8)], and describes the density correlation in real space.

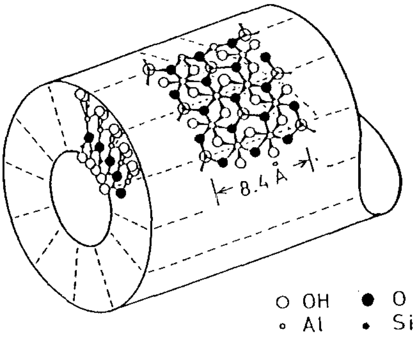

Fig.1 Schematic view of an imogolite cylinder

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In this report, we constructed the models of assembling cylindrical rods based on electron microscopic observation of imogolite mesophase[2,4,5)], and simulated the process of the mesophase formation of rod molecule, imogolite, by comparing the distance distribution function computed from the models with that obtained from SAXS profile.

EXPERIMENTAL PART

Sample and Small Angle X-ray Scattering

Imogolite solutions of various concentrations were prepared according to the procedure described previously[1)].

The molecular weight (M_w) of the imogolite sample employed in SAXS was evaluated to be 9.8×10^5 from the intrinsic viscosity, which affords 1732 Å and 69 in terms of the rod length and the axial ratio, respectively. The A-point and B-point of the mesophase (lower and upper phase boundary concentrations) were estimated as 0.0355 and 0.0577, respectively, in terms of imogolite weight fraction[9)].

The small angle X-ray scattering (SAXS) measurements were performed with a SAXES focusing optics installed at the BC-10 of the Photon Factory, Tsukuba, Ibaragi, Japan[10)]. The scattered intensity $I(q)$ was Fourier-transformed to the distance distribution function defined as:

$$P(r) = \frac{1}{2\pi} \int_0^\infty I(q) \cdot qr \cdot \sin(qr)\, dq \qquad (1)$$

Here the scattered intensity was extrapolated to both zero and larger angles according to the Guinier approximation[11)] and Porod's 4th power law[12)], in order to minimize the cut-off effect.

Model Function

In the case of computing scattered intensity or distance distribution function from a model of an arbitrary shape, Glatter has proposed "the sphere method" in which a macromolecule is replaced with an assembly of sufficiently small spheres[13)]. The advantage of this method is that the accuracy of computation is independent of the structure of the model and that the scattered intensity and the distance distribution function from an assembly of spheres can be calculated precisely by analytical equations.

The distance distribution function $P(r)$ from an assembly of n spheres is given by[13)]:

$$P(r) = \sum_{i=1}^{n} \rho_i^2\, p_o(r, R_i) + 2\sum_{i=1}^{n-1} \sum_{k=i+1}^{n} \rho_i\, \rho_k\, p_{ik}(r, d_{ik}, R_i, R_k) \qquad (2)$$

$$p_o(r, R_i) = \frac{4}{3}\pi R_i^3 r^2 - \pi R_i^2 r^3 + \frac{\pi}{12} r^5 \qquad (3)$$

Here ρ_i and ρ_k are the electron density of the i-th and k-th sphere, respectively. $p_o(r, R_i)$ is the distance distribution function of the i-th sphere with the radius R_i and the electron density equal to unity. $p_{ik}(r, d_{ik}, R_i, R_k)$ is the cross term distance distribution function between the i-th and k-th sphere (radii R_i and R_k) separated by a distance d_{ik}. When fitting a model with spheres, the sphere size should be smaller than the structure of interested details. Glatter recommends that a model is to be composed of identical spheres and the sphere radius R is approximately set to be 0.62 times of the distance *d* between the centers of the next neighbor spheres. The detail is described in the paper of Glatter[13].

We employed the Fortran-program MULTIBODY incorporating Glatter's idea to compute the distance distribution function, which was executed by Asahi Stellar GS1000 (Asahi Techno Computer Inc. Tokyo, Japan).

Model Construction

Imogolite molecule has a hollowed cylindrical shape of 25.2 Å in outer diameter and 15.5 Å in inner diameter[2]. 16 spheres with radius R=2.45 Å were arranged in circle and 10 of there rings composed of 16 spheres were piled in the form of a cylinder. The cylinder model (named STANDARD) has the size of 25.2 Å in outer diameter, 15.4 Å in inner diameter and 40.45 Å in length as shown in Fig.2. Here the radius R is approximately taken to be 0.62 times of the distance d (3.96 Å in circumference and 3.95 Å in length). 7 models composed of assembled cylinders were constructed as denoted as A to G types shown in Fig.3. The electron microscopic observation[2,4] revealed raft-like sheets and the periodic striation of an interval of 100 Å in the sheets. Hexagonal packing was also observed on the electron diffraction pattern. Thus, we constructed the D to G type models composed of hexagons of 100 Å side.

In addition, the length of the model cylinders were changed from 40.45 to 395.95 Å in A to G types.

RESULTS AND DISCUSSION

Experimental Data

Fig.4[9] shows the distance distribution function derived from Fourier-transforming observed scattered intensities of imogolite solution according to eq. (1). Below A-point, the distance distribution function is characterized by a shoulder around 30 Å, a broad peak around 70 Å, and a subsequent long tail towards $P(r)$=0. The shoulder corresponds to the cross section of a single imogolite molecule. The long tail is typical of rod molecules. Since no shift of peak was observed and the profile hardly changed in the distance distribution functions with increasing imogolite concentration, the assembling model of imogolite molecules is considered to undergo no change below the A-point.

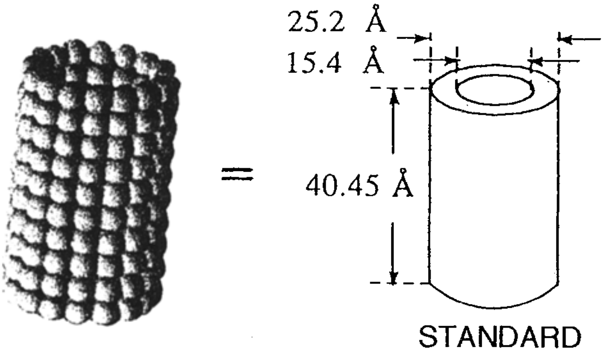

Fig.2 The illustration of the cylinder model composed of 160 spheres.

Above A-point, the distance distribution function have the peaks not only around 25 to 50 Å but also around 175 Å, which becomes more distinct with increasing imogolite concentration. The third peak appears around 270 Å when imogolite concentration approaches to nearly B-point (0.0510 weight fraction).

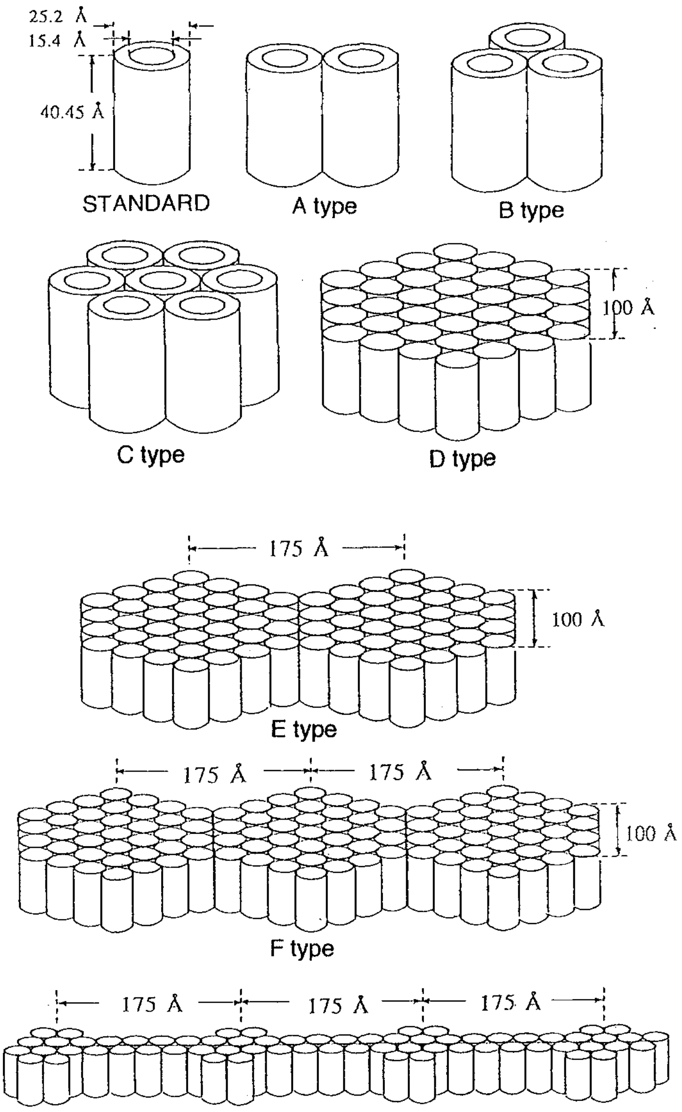

Fig.3 Schematic representation of various models. The detailed outline of the hollowed cylinders is simplified in D, E, F , and G type.

Computed Distance Distribution Function from Model

Fig.5 summarizes the distance distribution function computed from A to G type models according to eq. (2). Here the cylinder length of the models was fixed to 119.45 Å. A single peak is observed around 25 to 50 Å in A to D type models, reflecting the cross-sectional dimension of each model. The subsequent long tail gradually decreases and finally becomes zero when *r* is equal to the maximum distance (120 Å or more) of each model. The position of the peak hardly shifts and the long tail gradually decreases until *r* is equal to the maximum distance when the length of model changes from 40.45 to 395.95 Å in A to D type models. This result is qualitatively in agreement with those obtained from SAXS data below A-point shown in Fig.4 (a). Since the maximum distance in Fig.4 (a) is smaller than the length of

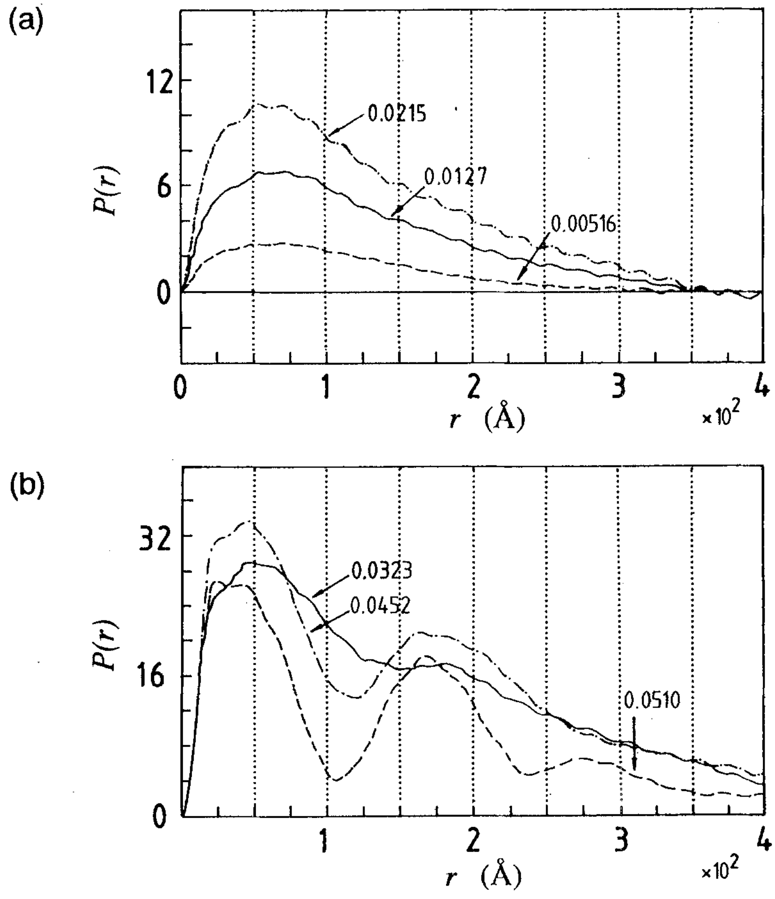

Fig.4[9] Observed distance distribution function for imogolite acetic acid aqueous solutions of various concentrations (a); below the A-point and (b); near the A-point. The values in the profiles indicates the weight fractions of imogolite.

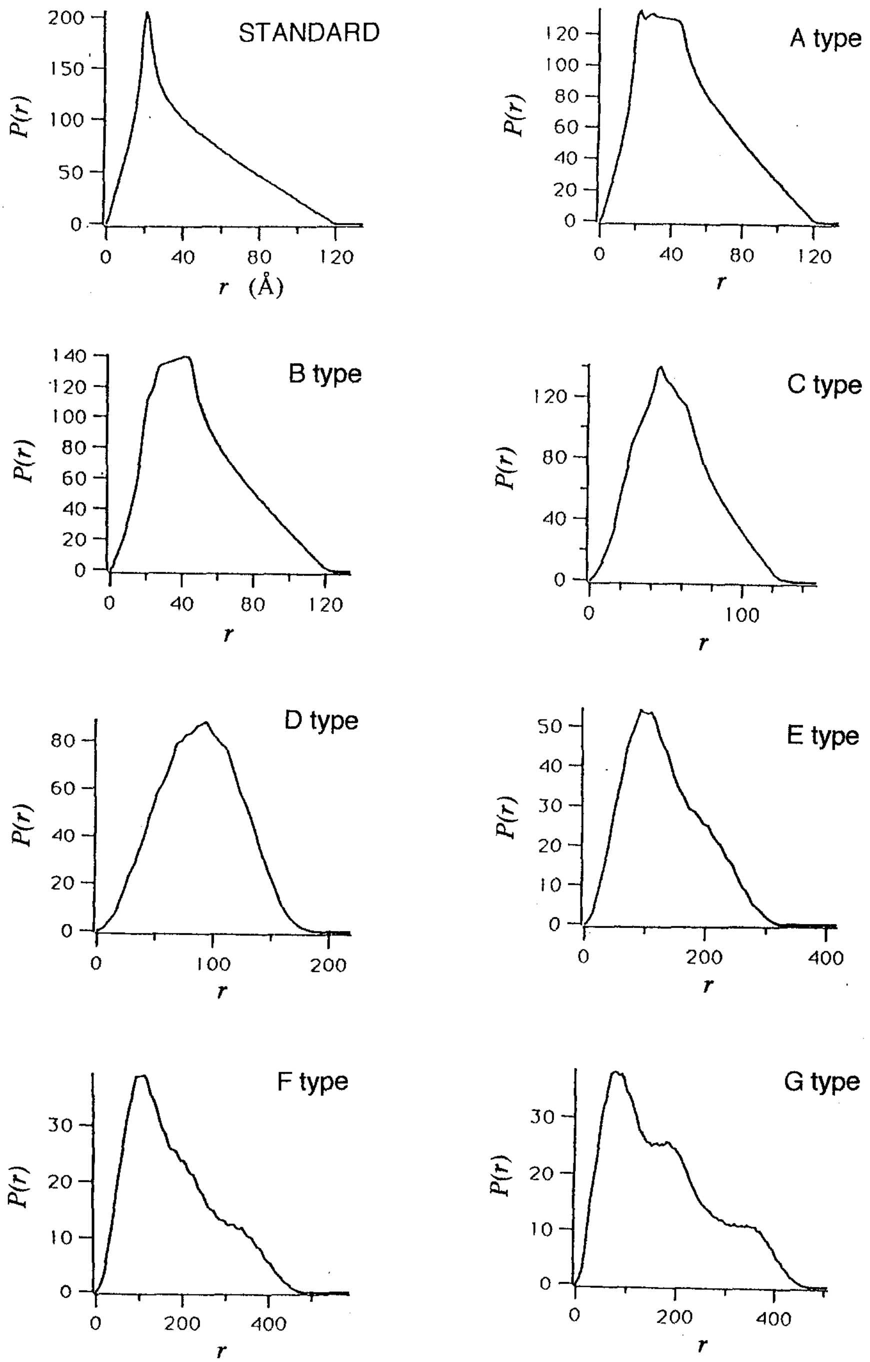

Fig.5 Computed distance distribution functions for each model in Fig.3 The length of the models is fixed to 119.45 Å.

imogolite molecule (1732 Å), the model simulation cannot be expected to fit to the observed distance distribution function in the whole *r* range. However, the peak position of the distribution function was confirmed not to be dependent on the length of the model. Thus, the imogolite molecules are assumed to assemble to form C or D type model from the result that the peak position is around 70 Å as shown in Fig.4 (a). In order to distinguish the molecular packing in further details, it is necessary to measure the absolute scale of the scattered intensity.

The distance distribution function computed from E type composed of two parallel arranged D types is marked by the double peaks around 100 Å and 175 Å (Fig.5), which correspond to a side length of hexagon and the distance between the ridges of hexagon, respectively (Fig.3). In the F type composed of three parallel arranged D types, a further peak appears around 350 Å in addition to the double peaks. The peak position is equal to twice of 175 Å, also corresponding to the distance between the ridges of hexagon. In the G type emphasizing the intervals of 175 Å, the peaks due to the ridges appear sharply round 175 Å and 350 Å.

The distance distribution function of E type yields a similar profile to that at nearly A-point (0.0323 weight fraction), which is characterized by the double peaks. The peaks of the distance distribution function become sharper with more D type of being parallel arranged side by side. That tendency is similar to those observed in the course of imogolite mesophase formation (Fig.4 (b)). The peak around the 270 Å in the 0.0510 weight fraction is considered to correspond to the distance indicated in Fig.6.

Recent computer simulation[14,15] suggests that rod molecules form a columnar mesophase by a purely repulsive hard-core interaction. For example, Stroobants etc. showed the phase diagram of a system of hard parallel spherocylinders with the length-to-width ratio *L* / *D* between zero and ∞ by Monte Carlo simulation[14]. According to the diagram, a columnar phase takes place for *L* / *D* >3. Experimentally, it is found that the systems of tobacco mosaic virus (TMV) aqueous solution[16], poly(γ-benzyl L-glutamate) (PBLG) aqueous solution[17], and DNA in NaCl-CH_3COONH_4 solution[18] form a columnar phase.

The raft-like imogolite sheet was observed by electron microscope[2,4] in imogolite mesophase, which suggests that imogolite molecules assemble side by side with their ends aligned in a line. Thus, a column is considered to be formed with rod molecules assembled together in hexagonal shape like D type, and the columns assemble in two-dimensional

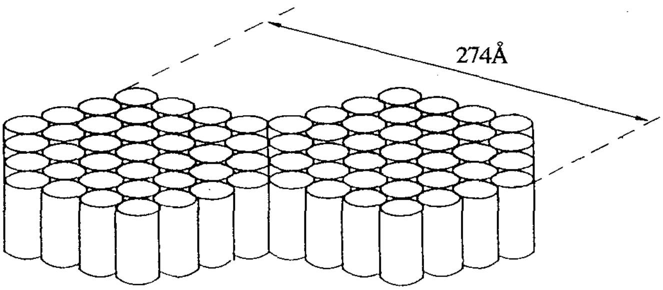

Fig.6 The dimension of diagonal for E type model composed of two parallel arranged hexagonal packing.

periodic arrangement (intervals of 175 Å) on the plane perpendicular to the columnar axis, i.e., the imogolite mesophase is considered to be characterized as a columnar structure formed by hexagonal packing.

CONCLUDING REMARKS

The distance distribution function computed from a hollowed cylinder model is consistent with that experimentally observed from imogolite mesophase. A molecular assembly represented by D type is formed in the initial state below A-point, the hexagonal units are arranged side by side near A-point, and finally form mesophase composed of raft-like sheets above A-point. Thus, the imogolite mesophase is considered to be a columnar as confirmed by computer simulation.

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