

Scaling Behavior of Gel Rigidity

T. Nashima

National Metrology Institute of Japan (NMIJ), AIST, Umezono 1-1-1, Tsukuba-shi, 305-8563

Fax:(JPN)298-50-1464, e-mail: nashima@nrlm.go.jp / t.nashima@aist.go.jp

The scaling behaviors of the gel rigidity of aqueous polymers (gelatin and agarose) and aggregated polystyrene latices were compared experimentally. The gel rigidity was measured by means of a dynamic stress method with a rheometer developed originally by the author. The gelation of latices was started in the testing tube of the rheometer by controlling the salt concentration and was developed under quiet circumstances. The rigidity of samples was scaled against their concentration. The power-law exponent of the scaling factor was related to the fractal dimension, that is, $D_s = (2 + D_f) / (3 - D_f)$, where D_s is the power-law exponent and D_f is the fractal dimension. The power-law exponents of the polymer gels were obtained in a low concentration regime, which were 4 (gelatin) and 2.8 (Agarose). The values for the latex gels were 2.9 – 3.3. It was supposed that agarose has the most extended configuration in the gel network

Keywords: scaling, fractal, aggregation, agarose, gelatin, latex

1. INTRODUCTION

The polymer gel has a three-dimensional network structure of the polymer chains in the solvent. It is thought that this three-dimensional network is permitted to have various structures. Physical properties and the function that appear in front of us do depend to this structure very much. The researches concerning this field have been very attracting, where the application of the scaling law is an important means for them [1,2]. This work reports the research concerning the scaling property of the rigidity of gels as a clue by which the relation between physical properties and the structure was understood.

If the polymer chain of the gel is stretched up, little elongation is expected for further stretching force. As a deformation inevitably includes the extension, gels that have a stretched three-dimensional network will show the high rigidity. Thus, we can expect that whether the polymer chains of the gel is stretched becomes an important measure of the gel structure. The end-to-end distance of the random coil is proportional to the 1/2th power of molecular weight when the polymer molecule is isolated in the solution. In the colloidal aggregates, the fractal structure was reported [3,4], where a similar power-law relation is approved between the size and the number of constituent particles. It is possible to interpret that the polymer chain has the fractal structure and the fractal dimension becomes 2. The node to node distances of the gel network can be expressed by the fractal dimension of the chains of monomer units by replacing the end-to-end distances when the fractal structure is maintained in the gel state. The power-law exponent of the scaling of rigidity to the concentration is related to the fractal dimension as shown in the following section. Then,

the modulus of rigidity of the gels of the water-soluble polymers and of latices was measured and the scaling property was examined.

2. THEORY

There is a report to relate the fractal dimension to the exponent of scaling where the isolated fractal bodies are packed to make a continuum gel body [5]. However, the unit of the isolated body cannot be defined when the network structure developed. In this theory, the relation between the fractal dimension and the power-law of scaling behavior is derived by applying the fractal relation to the node-to-node distances of the gel network.

The gel network can be described as a cubic lattice in a primitive model, where the chains of the network link between nodes, as shown in Fig. 1 (left). The chains wind and their length is longer than the end-to-end distance of them. In this case, end-to-end distance means node-to-node distance. This theory introduces an idea that the relation of chain length and the node-to-node distance is expressed by the fractal theory, that is,

$$n \sim a^{D_f}, \quad \dots (1)$$

where n is the number of particles or monomer units in a node-to-node chain, a is the node-to-node distance (see Fig. 1) and D_f is the fractal dimension. The chain length is proportional to n .

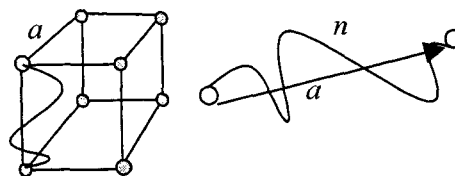


Fig. 1 A scheme of a node-to-node chain in gel network.

Modulus of rigidity, G is the reaction force against a deformation (shear strain) in unit area. We easily see that this force is in inverse proportion to the chain length. Thus, G can be obtained by multiplying the number of chains in unit area ($= 1/a^2$) to the modulus of stress to strain of the single chain, that is,

$$G \sim 1/na^2. \quad \dots (2)$$

The concentration C is proportional to the chain length, that is n , in unit volume,

$$C \sim n/a^3. \quad \dots (3)$$

This equation implies that total number of monomer units in dead branches of a chain is proportional to the length of the chain. This deems an acceptable assumption in a primitive model. Replacing n by Eq. (1) and eliminating a from these equations, the relation

$$G \sim C^{(2+D_f)/(3-D_f)} \quad \dots (4)$$

is obtained. The exponent of this equation is the value observed as the power-law of the scaling, that is,

$$D_s = (2 + D_f) / (3 - D_f). \quad \dots (5)$$

The fractal dimension is expressed as

$$D_f = (3D_s - 2)/(D_s + 1). \quad \dots (6)$$

If the scaling to the concentration is possible, the power-law exponent relates to the gel structure closely. We can see that a low power-law exponent means an extended gel structure.

3. EXPERIMENTAL

Gelatin (Wako) and Agarose-I (Dojin) were used for the polymer gel. The distilled water was the solvent for the polymer gel. Polystyrene poly-styrenesulfonic acid copolymer latices of the particle diameters 200 nm (SSS1b), 170 nm (SS170) and polystyrene latices of 350 nm (B350, B350b) were used. These latices were prepared in the laboratory of Dr. K. Furusawa, the University of Tsukuba. The polymer gels were prepared as the sample polymer solutions were warmed before the measurement to be the sol state and cooled at the beginning of measurement to be the gel state.

The aggregation of the latex dispersion was started by adding the NaCl solution to the colloidal dispersion to be the appropriate salt concentration. When the concentration of the dispersion is high, aggregated particles can be connected mutually to form a network, that is, a gel structure, which brings the measurable elastic properties (elasticity percolation). The rate of aggregation was controlled by adjusting the amount of the salt addition. Because the aggregation of colloidal

dispersion is an irreversible process, the measuring action that may gives disturbances on the aggregation behavior becomes a problem. So, a stress oscillating method was used for the least disturbances. The temperature of aggregation experiments was 20 °C.

A self-made coaxial cylinders rotational viscometer [6] was employed for the measurement of the rigidity. The dimensions are 0.9 cm in radius of the inner cylinder, 4 cm in length and 1.018 cm in radius of the outer cylinder made of the Pyrex glass.

The stress oscillating method was employed that measures the strain response to the stress of the sinusoidal vibration with high sensitivity. The cycle was 20 seconds. The data at the third cycle were used. The stress value was changed properly. As the elasticity response caused by the lead wires that are connected with the inner cylinder for the thermometry etc. is added, the modulus of rigidity becomes apparently about 4.9 Pa without the sample. So, the measured value is expressed as G'_{app} , and the true modulus G' is $G'_{app} - 4.9$.

4. RESULTS

The latex gelling showed the developing profiles of the rigidity after the addition of salt, as shown in Fig. 2, where the sample is the B350b polystyrene latex in 0.18M NaCl and the concentration 10%. The apparent rigidity grows strikingly after the certain elapsed time indicating that the mechanical percolation occurs. This implies that the gel network is formed at this time. The time for the percolation takes longer for the lower concentration samples. The developing profiles of the rigidity become gradual with the time. However, the final values of stationary states cannot be expected. For the scaling of the rigidity, the time coordinate is normalized by this percolation time, and then, the profiles of the rigidity were scaled to coincide. The values that divide the rigidity for overlapping are the factor of scaling, f_s , and are plotted against the concentration in Fig. 3. It is found that the double logarithmic plot of f_s becomes a straight line and that their slopes are about 3 for all samples.

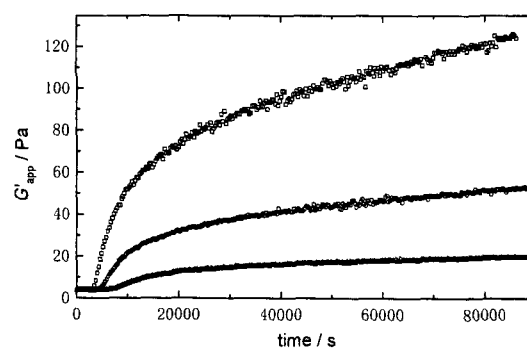


Fig. 2 Aggregation of B350b latex in 0.18 M NaCl; latex concentration: 10% (upper \square), 8% (middle \circ), 6% (lower \triangle).

As for the gelatin gel, the increase profile of the rigidity was very similar to that of the latex gel, which shows the existence of a period in which the rigidity didn't increase (see Fig. 4). The time coordinate cannot be normalized, however, as done for the latex gel. This was because the gel beginning time is difficult to decide since the gelation was started by reducing the temperature. To obtain the comparable values of the rigidity for the scaling, it was necessary to wait to reach the stationary state.

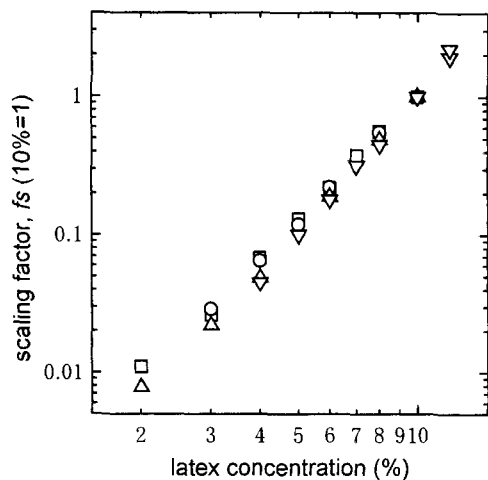


Fig. 3 Scaling factor of the rigidity of aggregates vs. latex concentration. $D_s=3.2$ (B350b Δ), 3.3 (B350 ∇), 3.0 (SSS1b \circ), 2.9 (SS170 \square).

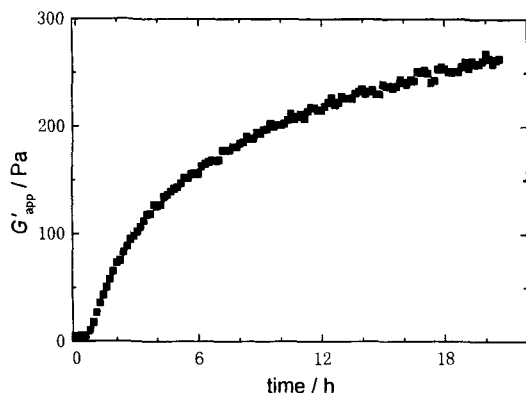


Fig. 4 A typical progress of the rigidity of gelatin gel; gelatin concentration: 2.5%, temperature set to 10 °C from 35 °C at time zero.

Figure 5 shows the change of the rigidity with time while the temperature of the gel varies upward or downward by stepwise. It is found that the upward step of temperature may obtain the steady state value in a shorter time. Then, the rigidity of the stationary state was obtained after the temperature was raised. The results are plotted against the concentration in Fig. 6.

In high concentration regime, it was shown that the slope of the plot became low. The result for the 2% sample at 15 °C is very small G' value. The cause of this seemed that the progress of the gelation slows very much

as to gelatin of a low concentration so that the gel is not formed enough or almost dissolved. The condition for Eq. (4) implies that the chain length between nodes is not so small. As the longer chain length corresponds to the lower concentration, the slope value in the low concentration regime of Fig. 6 was examined and the power-law exponent 4 was obtained.

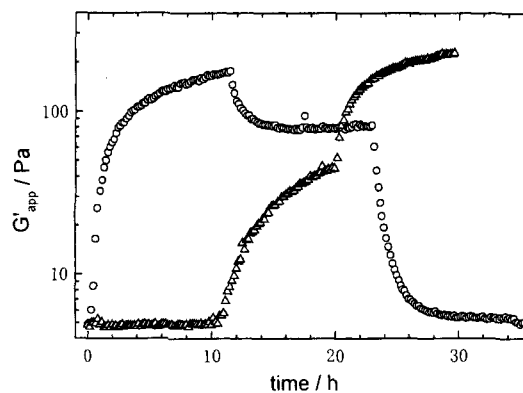


Fig.5 Experiments for the rigidity of the gelatin gel, temperature varied downward 15 – 10 – 5 °C (Δ), and upward 5 – 10 – 15 (\circ); gelatin 2%

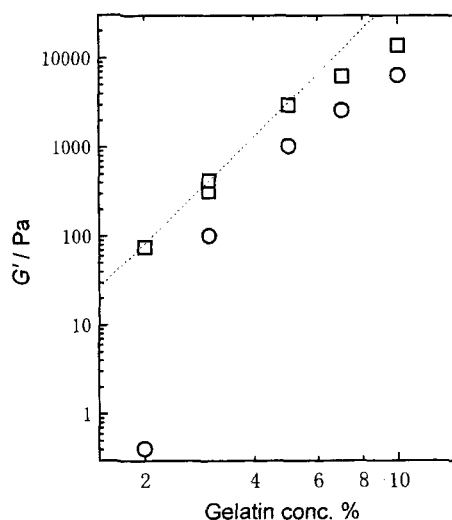


Fig. 6 Dependence of the rigidity of gelatin gel on the concentration; Temperatures \square : 10 °C, \circ : 15 °C. Dotted line: slope = 4.0 for the eye guide

It is also necessary to measure the rigidity of the stationary state for the agarose gel. The stationary states were reached quickly compared with the gelatin. Another problem was found that the rigidity of the agarose gel markedly varied when the temperature was moved up and down after the agarose gel was formed. However, the reproducibility of the rigidity for the temperature change was regained after the annealing process that the gel temperature was raised to 45 °C and maintained 2 hours. Figure 7 is a typical example of the experimental procedure about the temperature, showing that the rigidity decreased greatly but was reproducible after the annealing.

The data before and after the annealing at 20 °C were adopted to the plot of Fig. 8. It is found that the slope of the plot becomes less steep at the higher regime of concentration as well for the gelatin gel. The slope at the low concentration regime was about 2.8, which is considerably smaller than that for gelatin gel.

It is found that the annealing did not affect the slope value but the limit of concentration that the slope of the low concentration regime was maintained. Before the annealing, the slope value was maintained to the higher concentration.

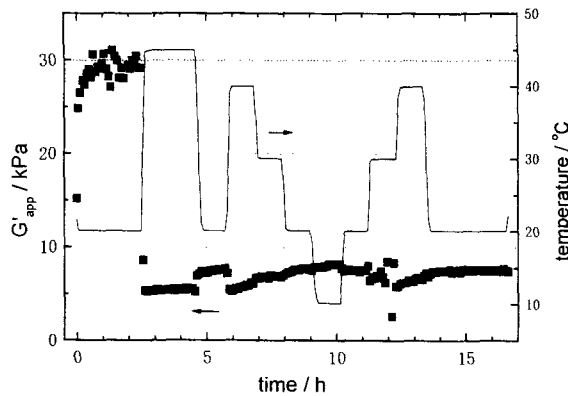


Fig. 7 Measurement for the rigidity of Agarose gel, with Temperature profile; Agarose concentration: 1.076 %.

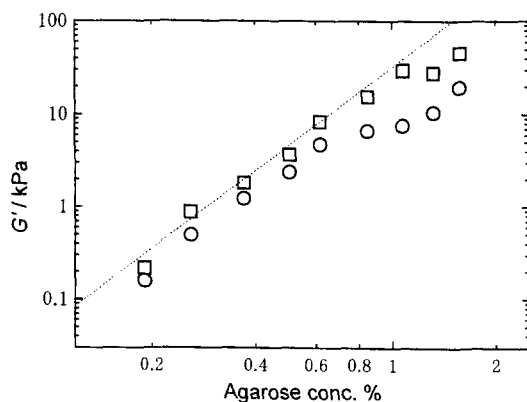


Fig. 8 Dependence of the rigidity of the Agarose gel on the concentration; \square : before, \circ : after annealing
Dotted line: slope = 2.8 for the eye guide;
Temperature 20 °C

5. DISCUSSION

It has been seen that both the latex and the gelatin gel increased continuously in the rigidity after the initial appearance of the rigidity, which means that the network structure of the gel does not complete at once but is growing gradually. The slope of the double logarithmic plot for the polymer gel is becoming small in the high concentration regime while the plot for the latex gel was a beautiful straight-line relation. This reveals that the

scaling of the polymer gel is restricted within the narrow range. One of the causes of this is speculated as the unit of the gel network constructors is so small as the average distance to the neighbor unit becomes within the reach of potential forces. As for the agarose gel, the annealing effect may suggest that the molecular structure changes with temperature, and the initial gel may freeze the polymer chain configuration at the high temperature.

The values of the slope of the straight-line relation in the double logarithmic plot are the scaling exponents (D_s) and can be converted into the fractal dimension (D_f) by the equation (6). The table I shows the result. As for the polymer gel, the D_s values were obtained using the data in the low concentration regime. The values about from 1.7 to 1.8 were reported as to the latex gels for D_f from the measurement of the isolated aggregate body[3,4,7]. It has a good coincidence with observed values for lattices. The value of 2 of the gelatins is corresponding to the fractal dimension of the random coil. On the other hand, D_f of the agarose gel is considerably small, which lead the conclusion that the agarose gel has an expanded network structure compared with the gelatin gel. The slope value at high concentration for agarose gel in Fig. 8 is near the lower limit of the scaling exponent 1.5, that is $D_f = 1$. This may suggest that the configuration of agarose chains between the nodes is entirely expanded, if the power-law can be applied.

Table I Values of scaling exponent (D_s) and fractal dimension (D_f)

	D_s	D_f
Latex B350	3.3	1.84
Latex B350b	3.2	1.81
Latex SSS1b	3.0	1.75
Latex SS170	2.9	1.72
Gelatin	4.0	2.0 (10 °C)
Agarose	2.8	1.68

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