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Rheological Properties of Hydrogels of Agar-agar. II.[*1]
Stress Relaxation of Concentrated Hydrogels[*2]

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A stress-relaxation experiment on hydrogels of agar-agar has been made over the range of concentration of about 3—11% by weight. A chainomatic balance relaxometer was used for the measurement of the relaxation Young's modulus, and the temperature was varied over the range of about 20—70°C. The obtained relaxation curves have been analyzed using a mechanical model composed of three parallel Maxwell models. The relaxation times obtained for the gels of different concentrations at the same temperature have been found to be independent of the concentration. The elastic Young's modulus, which may be attributed to the main network structure in the gels, has been found to be proportional to the 1.8 power of concentration. From the temperature dependence of the longest relaxation time, the activation energy for the relaxation process attributed to the destruction of junctions in the main network structure has been determined to be about 5 kcal/mol, irrespective of the concentration, over the whole range; this is of the order of the activation energy for the hydrogen bonds.

In previous papers[1,2] some results of measurements of the stress relaxation of hydrogels of agar-agar have been reported as a part of a series of rheological studies of polymeric thermoreversible gels. In the present study, the upper limit of the concentration of the gels examined is raised further in order to cover a wider range of the concentration than previously and the structure of the gel is discussed in detail.

Experimental

A commercially-available powder of agar-agar was used as the sample. The ask content was 1.3%. The intrinsic viscosities in the aqueous solution at 25 and 60°C, as determined by an Ostwald viscometer (flow time of water; 195.4 sec), were 14.1 and 4.2 respectively. The molecular weight of the sample, as calculated from the intrinsic viscosity, was 3.8×10^4. The viscosity equation used was:

$$[\eta]_{25^\circ\mathrm{C}} = (3.7\times10^{-4})M_v \tag{1}$$

which had been proposed by Hirai and Nishimura.[3]

The test piece of the gel was cylindrical, about 2 cm in diameter and 2 cm long. The range of concentration was 3.3—11.4% by weight.

A chainomatic balance relaxometer was used. The details of the apparatus and of the experimental procedure were reported previously.[1,4] Relaxation Young's modulus of up to 4 hr were obtained for 12 samples of the gles in different concentrations. The measurements were made at temperatures from 20 to 70°C at intervals of 5—10°C.

Results and Discussion

Viscosity of Aqueous Solutions. The concentration dependence of the viscosity of aqueous

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[*1] Part I of this series: K. Arakawa, This Bulletin, **34**, 1233 (1961).

[*2] Presented at the 15th Annual Meeting of the Society of Polymer Science, Japan, Nagoya, May, 1966.

1) K. Arakawa, This Bulletin, **34**, 1233 (1961); **35**, 309 (1962).

2) K. Arakawa and K. Atsumi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **80**, 133 (1959).

3) N. Hirai and N. Nishimura, *ibid.*, **75**, 248 (1954).

4) K. Arakawa, This Bulletin, **33**, 1568 (1960).

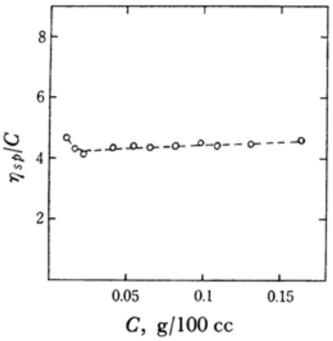

Fig. 1. Viscosity *vs.* C relation.

solutions at 60°C is shown in Fig. 1. As may be seen in the figure, the value of η_{sp}/C increases with the decrease in C in the range of extreme dilution, as in the well-known, typical behavior of the polyelectrolyte solution. The similar behavior of agar-agar solutions was reported previously by Sakamoto and Kishimoto.[5]

Stress Relaxation Curves. Relaxation Young's modulus of up to 4 hr were obtained, for twelve samples of these different concentrations: 3.3, 3.8, 5.1, 5.6, 6.2, 6.6, 7.1, 7.4, 7.8, 8.8, 9.2 and 11.4% by weight. Some results are shown in Fig. 2(a)—2(d) as illustrative examples.

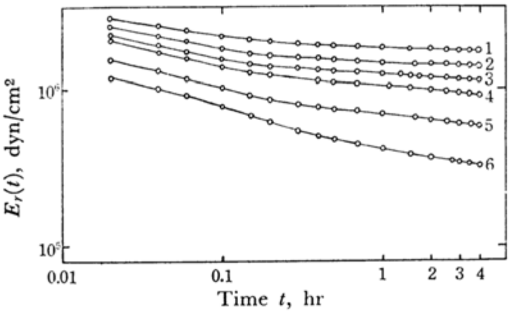

Fig. 2(a). Relaxation curves of 3.3% gel.
1. 24.9°C 2. 35.1°C 3. 42.4°C
4. 50.4°C 5. 57.5°C 6. 66.0°C

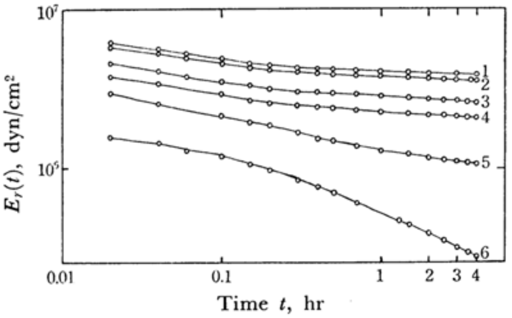

Fig. 2(b). Relaxation curves of 5.1% gel.
1. 25.0°C 2. 35.0°C 3. 44.2°C
4. 50.9°C 5. 62.5°C 6. 71.2°C

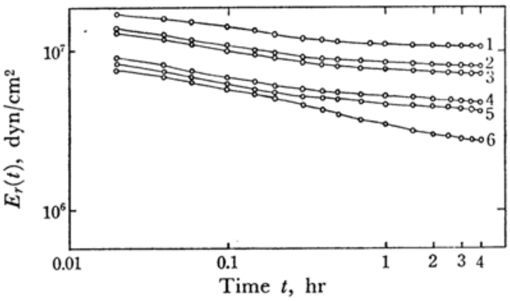

Fig. 2(c). Relaxation curves of 8.8% gel.
1. 24.5°C 2. 35.1°C 3. 43.6°C
3. 51.1°C 4. 58.0°C 6. 65.1°C

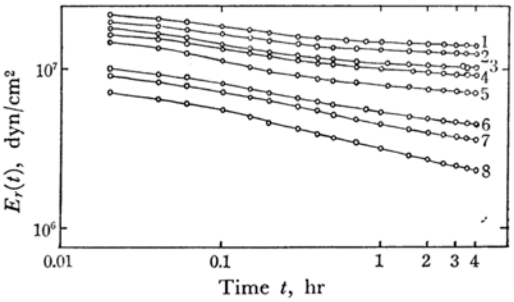

Fig. 2(d). Relaxation curves of 11.4% gel.
1. 19.6°C 2. 24.5°C 3. 35.4°C
4. 42.2°C 5. 52.0°C 6. 60.1°C
7. 62.5°C 8. 65.4°C

The mechanical behavior of these gels may be approximately represented by a six-element mechanical model consisting of three parallel Maxwell models. The model is shown in Fig. 3.

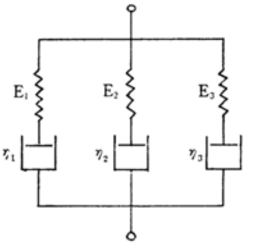

Fig. 3. Mechanical model.

$$\tau_1=\frac{\eta_1}{E_1}, \qquad \tau_2=\frac{\eta_2}{E_2}, \qquad \tau_3=\frac{\eta_3}{E_3}$$

In this model the relaxation Young's modulus, $E_r(t)$, is expressed as:

$$E_r(t) = \sum_{i=1}^{3} E_i \exp(-t/\tau_i) \tag{2}$$

The all stress relaxation curves obtained were then analyzed according to the above equation, and the values of six parameters, E_1, E_2, E_3, τ_1, τ_2, and τ_3, were determined.[2] The magnitude of τ_i was in the following order:

$$\tau_1 \gg \tau_2 \gg \tau_3 \tag{3}$$

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[5] M. Sakamoto and A. Kishimoto, *Bull. Jaanp Soc. Sci. Fisheries*, **26**, 25 (1960).

Concentration Dependence of the E_1 Modulus. The E_1 parameter, the elastic modulus of the Maxwell element with the longest relaxation time, may be attributed to the modulus of the elasticity of the main network structure linked by "secondary bonds" which break off and rejoin reversibly with the variation in temperature. The concentration dependence of E_1 is given in Fig. 4; it may be represented by the equation:

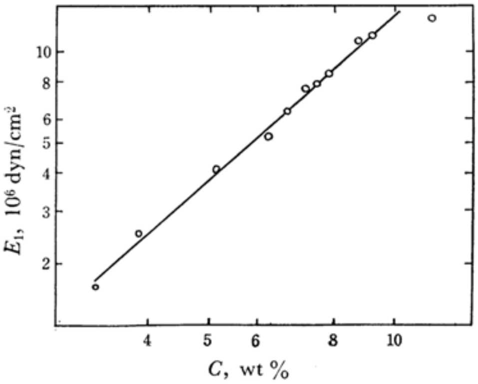

Fig. 4. E_1 *vs.* C relation.
Temperature: 24.5—25.0°C

$$E_1 = KC^{1.8} \tag{4}$$

where K is a proportionality constant.

The fact that the magnitude of E_1 is approximately proportional to the square of concentration is reasonable, for the junctions in the network structure are formed through an intermolecular process between chain molecules.*[3]

Relaxation Times. The values of six parameters, τ_1, τ_2, τ_3, E_1, E_2, and E_3, were obtained for all the relaxation curves. Of these, the values of τ_1, τ_2, τ_3, and E_1 at 24.5—25.0°C are listed in Table 1. It may be seen in Table 1 that the values of τ_1, τ_2, and τ_3 are practically independent of the concentration, though some minute deviations from the mean value are found. These deviations are not systematic and may be ascribed to the small temperature fluctuation. This approximate independence of the values of the relaxation times at the same temperature with regard to the large concentration change supports the idea that no fundamental change in the mechanism of the relaxation process occurs when the concentration is increased from about 3% to about 11%.

Table 1. Constants of mechanical model at 24.5—25.0°C

Concn. wt %	Temp. °C	τ_1 hr	τ_2 min	τ_3 min	E_1 10^6 dyn/cm
3.3	24.9	64	17	3.4	1.8
3.8	25.0	72	16	3.3	2.5
5.1	25.0	57	17	3.0	4.1
6.2	24.9	90	27	5.1	5.2
6.6	24.6	91	26	2.0	6.3
7.1	24.6	84	12	2.8	7.6
7.4	24.5	99	20	3.8	7.8
7.8	24.5	78	18	4.6	8.4
8.8	24.5	99	24	4.6	10.8
9.2	24.6	84	20	3.8	11.3
11.4	24.5	78	22	3.8	12.8
Mean value		79	20	3.7	

In the temperature range of the present experiment, the values of τ_1, τ_2 and τ_3 are found to be of the orders of ten hours, ten minutes, and a minute respectively.

Activation Energy. The values of $\log \tau_1$ are found to change linearly with respect to $1/T$ for each sample except at the highest extreme of the temperature; the activation energy, ΔH_1, is calculated from the slope.

Table 2. Activation energy ΔH_1,

Concn., wt%	ΔH_1, kcal/mol
1.0*	4.8
2.6*	5.8
2.6*	6.6
3.3	5.9
3.8	3.2
4.1*	4.5
5.1	5.9
5.6	4.6
6.2	6.6
6.6	4.4
7.1	4.9
7.4	6.3
7.8	5.3
8.8	6.0
9.2	5.0
11.4	4.7
Average	5.3

* Ref. 1

The values of ΔH_1 obtained are given in Table 2, together with the values previously obtained by one of the present authors. The mean value of ΔH_1 is found to be 5.3 kcal/mol. Some deviation from the mean value is seen for each concentration, but no consistent trend appears. The standard deviation is calculated to be 0.8 kcal/mol. This mean value of ΔH_1 is equal to the value reported in the former study,1) where the range of concentration was about 1—4% by weight, and

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*[3] The square dependence on the concentration of the elastic modulus of thermoreversible gels has been confirmed by several workers,6,7) but in their work it concerned the total elastic modulus.

6) N. Hirai, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **72**, 837 (1951).

7) A. G. Ward and P. R. Saunders, "Rheology," Vol. II, Ed. by F. R. Eirich, Academic Press Inc., New York (1958), p. 333.

nearly equal to the values of other thermoreversible gels, such as polyvinyl alcohol glycerin-water gels and hydrogels of gelatin.1),[*4] The hydrogen bonds are supposed to play an important role in the formation of thermoreversible network structure.

The values of τ_1 for samples of various concentrations fall on a line in the plot against the temperature, as may be seen in Fig. 5. The longest relaxation time, τ_1, is attributed to be relaxation process of the main network structure in the gel, in which junctions break and rejoin reversibly with the variation in temperature; the magnitude of the activation energy obtained from the temperature dependence of τ_1, 5.3 kcal/mol, may be regarded as the energy of breaking the junctions. This value is of the order of the dissociation energy of hydrogen bonds.

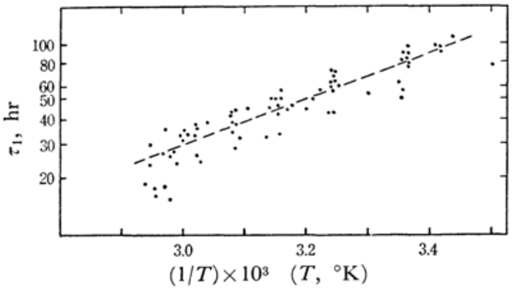

Fig. 5. Temperature dependence of τ_1.

Summary

A stress-relaxation experiment on concentrated hydrogels of agar-agar has been made by means of a chainomatic balance relaxometer, with the concentrations of the gels being varied over the range of about 3—11 wt%. The mechanical behavior of these gels may be represented by a six-element mechanical model consisting of three parallel Maxwell models. The elastic modulus, E_1, which is attributed to the main network structure forming the gels, has been found to be proportional to $C^{1.8}$ over the whole range of concentration.

From the temperature dependence of the longest relaxation time, τ_1, which may be attributed mainly to the breakage process of junctions in the structure of thermoreversible gels, the activation energy of the dissociation process of jucntions has been obtained; the magnitude of this energy has been found to about 5 kcal/mol over the whole range of the concentrations studied in the present experiment.

[*4] As for gelatin gels, the values of ΔH_1 have been found to become larger with the increase in concentration for solutions more concentrated than 20 wt%.8)

8) K. Arakawa and N. Takenaka, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 1065 (1962).