*Stress Relaxation of Thermo-reversible Gels. Molecular Weight Dependence of Relaxation Spectrum. Polyvinyl Alcohol-Congo Red-Water System**

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In the previous paper¹⁾ the author reported the results of the stress relaxation study of the gels of polyvinyl alcohol-congo red-water system, where the experiment was intended to obtain some knowledge on the concentration dependence of the relaxation spectrum of the gel which was taken as a typical example of thermo-reversible gels of polymeric nature. As a part of the series of rheological studies of thermo-reversible gels[1,2] a stress relaxation experiment has been made for the purpose of studying the molecular weight dependence of the relaxation spectrum of the gel, and the result is reported in the present paper.

Experimental

Apparatus. — A chainomatic balance relaxometer was used to measure the relaxation Young's modulus of the cylindrical gel, which was the same one as that used previously[1], and the schematic diagram of it is shown in Fig. 1. A specimen is compressed to a given strain between a plate attached to a bar and a bottom plate in a double jacket connected to a screw gauge by the rotation of it. The stress in the specimen is automatically balanced with a chain weight by means of a relay and a balancing motor, the ralaxation Young's modulus E_r is calculated form the vertical length of the suspended chain, as follows.

$$E_r = \frac{l}{\Delta l} \cdot \frac{adhg}{bs}$$

l is the height of the cylindrical specimen without strain, Δl the amount of the given compression, s the original sectional area of the specimen, a the distance from the fulcrum to the chain, b the distance from the fulcrum to the center of the pressure plate, d the linear density of the chain, h the vertical length of the suspended chain and g is the acceleration of gravity.

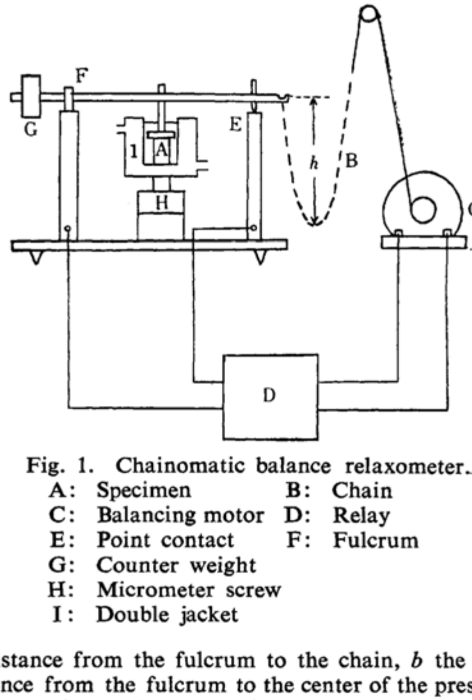

Fig. 1. Chainomatic balance relaxometer.
A: Specimen B: Chain
C: Balancing motor D: Relay
E: Point contact F: Fulcrum
G: Counter weight
H: Micrometer screw
I: Double jacket

Sample. — Commercial samples of polyvinyl alcohol were purified by precipitation from aqueous solutions with addition of acetone. The amount of residual acetyl group was smaller than 0.7% by mole for all samples used in this experiment. The values of the intrinsic viscosity $[\eta]_{30^\circ\mathrm{C}}$ determined by a capillary viscometer and the molecular weight calculated from those using the formula of Nakajima et al.[3] are given in Table I. Congo red

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[1] K. Arakawa, This Bulletin, 32, 1248 (1959).

[2] K. Arakawa, This Bulletin, 31, 842 (1958); K. Arakawa and K. Atsumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 80, 133 (1959).

* Partly presented at the Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

[3] A. Nakajima and K. Furutati, *Chem. High Polymers* (*Kobunshi Kagaku*) 6, 460 (1949).

used was Merck's analytical grade chemical. The preparation of testing specimens was made according the same procedure as described in the previous paper[1], except that in the present work an especially designed vessel with a double jacket was used in the dissolution process instead of a conical beaker and a water bath.

The composition of the prepared gel was maintained to be the same for all specimens: polyvinyl alcohol 17.5% and Congo red 1.75% by weight.

TABLE I. MOLECULAR WEIGHT OF POLYVINYL ALCOHOL

Sample	$[\eta]_{30°C}$ (100 cc./g.)	Molecular weight
I	0.54	3.5×10^4
II	0.66	4.9×10^4
III	1.03	9.8×10^4

Results and Discussion

Stress Relaxation Data. — The data of stress relaxation at various temperatures are plotted in the form $(298/T)E_r$ versus $\log t$, where t is time, in Figs. 2a, 2b and 2c. The strain

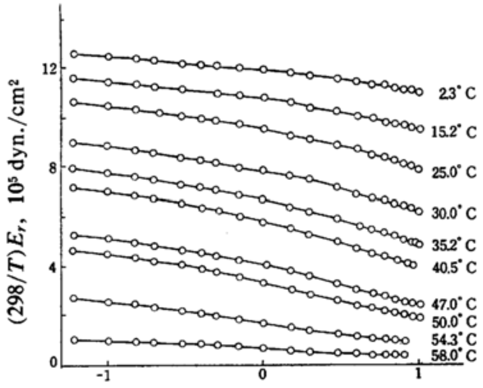

Fig. 2a. Reduced relaxation Young's modulus. Sample I (molecular weight 3.5×10^4).

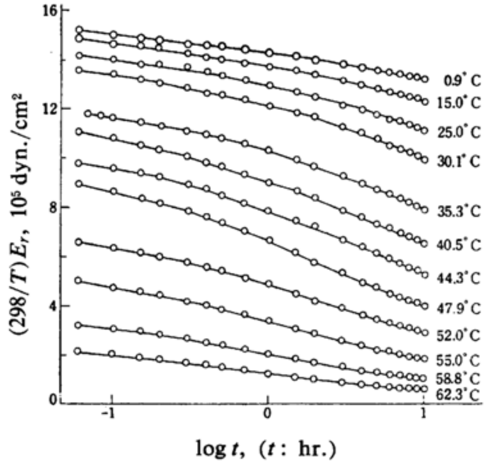

Fig. 2b. Reduced relaxation Young's modulus. Sample II (molecular weight 4.9×10^4).

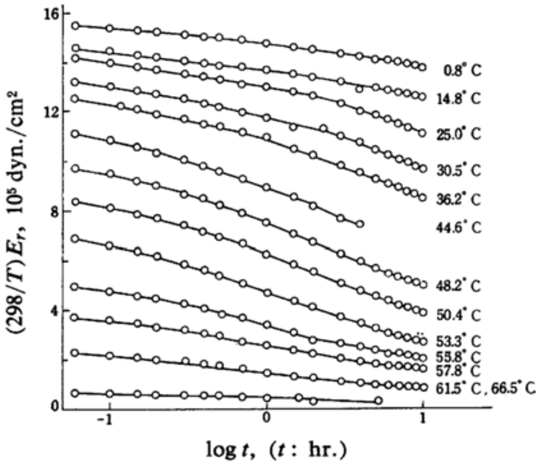

Fig. 2c. Reduced relaxation Young's modulus. Sample III (molecular weight 9.8×10^4).

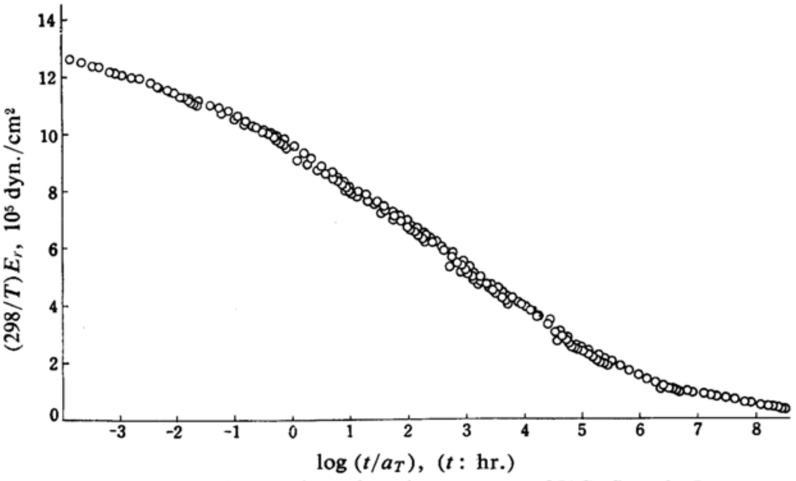

Fig. 3a. Composite relaxation curve at 25°C, Sample I.

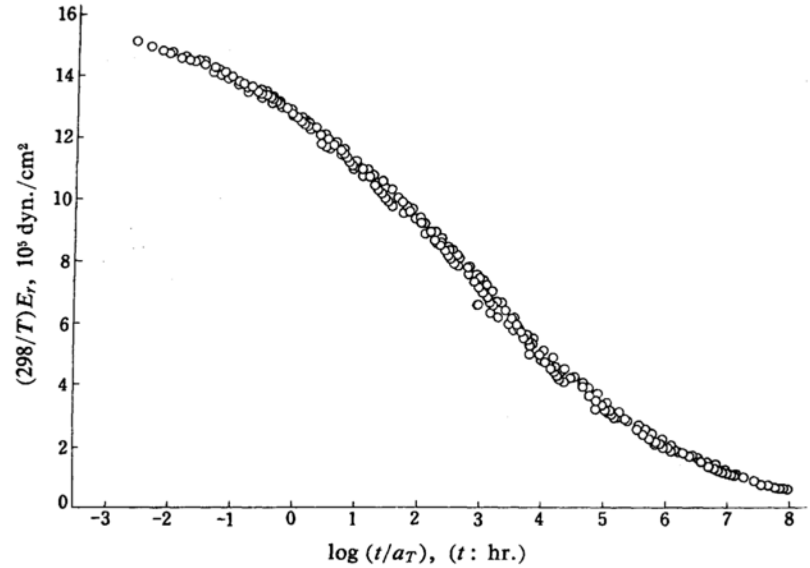

Fig. 3b. Composite relaxation curve at 25°C, Sample II.

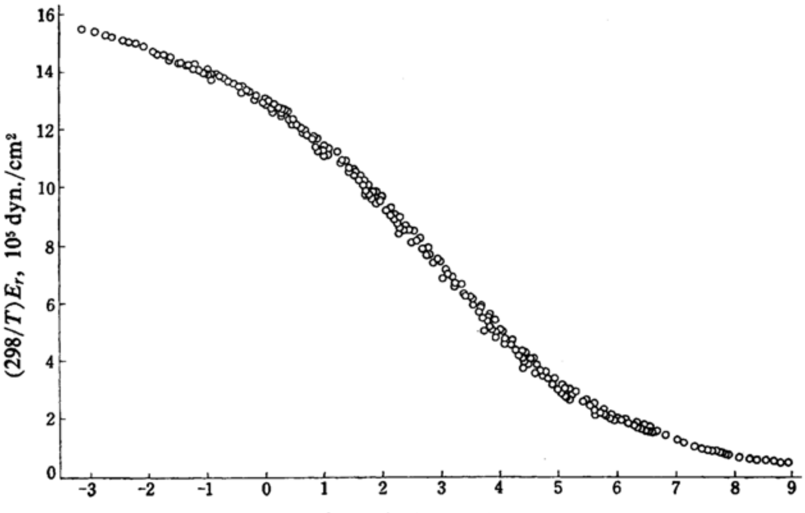

Fig. 3c. Composite relaxation curve at 25°C, Sample III.

applied in this experiment was 15% for all specimens. The data are reduced to 25°C with the multiplication by a factor $298/T$.

According to the time temperature superposition principles⁴⁾, each group of relxation curves was superposed to a composite relaxation curve by the horizontal shift of relaxation curves at different temperatures along the $\log t$ axis. The superposition of relaxation curves is good as it is seen in Figs. 3a, 3b and 3c. The density factors was ignored, because its temperature dependence was very small. The shift factors $\log a_T$ are plotted against T in Fig. 4 together with the apparent activation energy H_a, which was calculated from the mean $\log a_T$ versus T curve by the following equation.

$$H_a = \boldsymbol{R}\frac{\partial \ln a_T}{\partial(1/T)} \qquad (1)$$

From the Fig. 4 it is seen that $\log a_T$ versus T relation does not obey the W. L. F. equation⁵⁾.

Distribution Functions of Relaxation Times. —The relaxation spectra $H(\log \tau)$ defined by

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4) J. D. Ferry, *J. Am. Chem. Soc.*, 72, 3746 (1950); F. Schwarzl and A. J. Staverman, *J. Appl. Phys.*, 23, 838 (1952); C. A. Dahlquist and M. R. Hatfield, *J. Colloid Sci.*, 7, 253 (1952).

5) M. L. Williams, R. F. Landel and J. D. Ferry, *J. Am. Chem. Soc.*, 77, 3701 (1955).

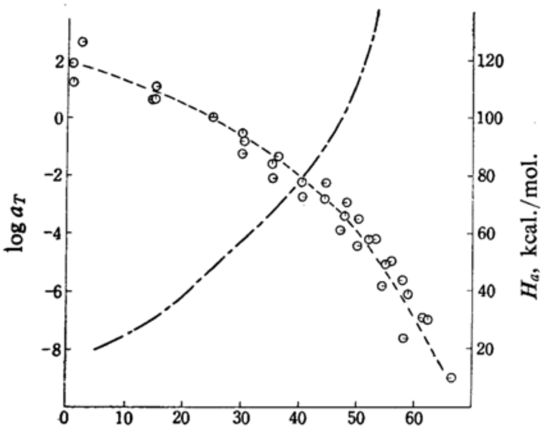


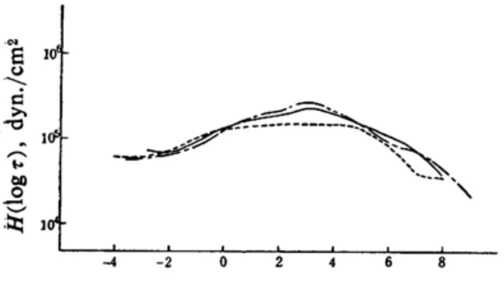
Fig. 4. Temperature dependence of shift factors.
⊖ Sample I, ⦶ Sample II, ⊖ Sample III
----- mean curve of log a_T versus T relation, --- H_a

the following Eq. 2 are calculated from the composite relaxation curves shown in Figs. 3a, 3b and 3c by the second order approximation⁶⁾.

$$E_r=\int_0^{\infty} H(\log\tau)\mathrm{e}^{-(t/\tau)}\,\mathrm{d}\log\tau \tag{2}$$

$$H\left(\log\frac{\tau}{2}\right)=\left[-\frac{\mathrm{d}\,E_r}{\mathrm{d}\log t}+\frac{1}{2.303}\frac{\mathrm{d}^2E_r}{\mathrm{d}(\log t)^2}\right]_{t=\tau} \tag{3}$$

The obtained relaxation spectra are plotted against log τ in Fig. 5. Each spectrum shows the typical box type character, except the structure in details, which is expected to follow a wedge type spectrum at the shorter time region.



log τ, (τ : hr.)

Fig. 5. Relaxation spectra.
----- Sample I
—— Sample II
--- Sample III

They nearly superpose each other at a short time region in Fig. 5. On the longer time side than one hour some difference is seen, and the spectrum goes upwards as the average molecular weight becomes larger, though in the curves of samples II and III the difference is very small and besides, when seen in details, the exchange of the mutual position is found. At the long time end the spectrum of the sample III tends to extend furthest⁷⁾.

Summary and Conclusion

A stress relaxation experiment was made for the gels of polyvinyl alcohol-Congo red-water system using the chainomatic balance relaxometer. Three samples of polyvinyl alcohol whose molecular weight were 3.5×10^4, 4.9×10^4 and 9.8×10^4 were used, and the composition of the gels was maintained to be the same for all specimens: polyvinyl alcohol 17.5% and Congo red 1.75%. The measurement was made to ten hours and the temperature was changed from about 1°C to about 66°C.

The obtained relaxation curves were superposed to a composite relaxation curves for each sample according to the time-temperature superposition principle, and the curves ranging from 10^{-4} to 10^9 hours were obtained, and from those the relaxation spectra were calculated by the second order approximation.

It is seen that the three spectra are nearly all superposed on the shorter time side than one hour and that the maximum value becomes larger as the molecular weight increases, and that the two spectra of the larger molecular weight are very close on the whole, except that at the long time end the spectrum of the largest molecular weight tends to extend further.

It is also seen that the box type spectrum of the gel nearly superposes when the molecular weight is larger than a certain value M, where $4.8\times10^4>M>3.5\times10^4$, and that the spectrum tends to extend to longer time region as the molecular weight increases.

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6) F. Schwarzl and A. J. Staverman, *Physica*, **18**, 791 (1952).

7) A. V. Tobolsky, *J. Appl. Phys.*, **27**, 673 (1956).