Viscoelastic Properties of Aqueous Solution of Methylcellulose

TAKESHI AMARI and MATAO NAKAMURA, *Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo, Japan*

Synopsis

The viscoelastic properties of aqueous solution of methylcellulose were investigated using three types of rheometers, which enabled us to cover more than 8 decades of frequency range. At first, the entanglement density X/q at various temperatures was estimated by comparing G', and G'' curves and relaxation spectra experimentally obtained with those calculated from Hayashi's theory. At lower temperatures, the concentration dependence of X/q was small as observed for polyelectrolytes, but increased at higher temperatures. The same tendency was observed in the concentration dependence of the entanglement function G_{eN}. It is supposed that water molecules adsorbed on methylcellulose and depressing the entanglement formation dissociate with increasing temperature. The relaxation mechanism was then examined from the concentration dependences of G', η', and η_0 at various temperatures and frequencies. It is concluded that the structural networks in a solution become closer with increasing temperature, and the corresponding viscoelastic mechanism varies from the intermolecular interaction such as entanglements to the intramolecular motion with increasing frequency.

INTRODUCTION

Previously, we have investigated the viscoelastic properties of aqueous solutions of carbohydrates, mainly of sodium alginate, which behave as polyelectrolytes.[1-3] In this report, the aqueous solution of methylcellulose, which is a nonelectrolytic carbohydrate, was investigated.

The behavior in water of methylcellulose containing hydrophilic OH groups and lipophilic OCH_3 groups on backbone pyranose rings is very different from other carbohydrates. The dissolving process of methylcellulose in water is exothermic, so that cooling of the solution is effective in bringing about complete solvation and aids solution stability.[4] Namely, at lower temperatures the molecular chain of methylcellulose is protected by water molecules and assumes a more extended configuration. However, as the temperature increases, water molecules which are adsorbed on methylcellulose are gradually dissociated, and the molecular chain of methylcellulose assumes a more shrunk configuration; and finally gelation occurs. Kuhn and coworkers[5] observed from the measurement of electric birefringence that strong association of methylcellulose takes place in aqueous solutions as the temperature is increased.

It is well known that aqueous solution of methylcellulose shows re-markable viscoelasticity. This property of methylcellulose is utilized in various practical fields such as paints, medicines, foods, and cosmetics. However, even though the peculiar thermal behavior of aqueous solution of methylcellulose has been examined thoroughly, the effects of temperature of the viscoelastic properties have hardly been investigated from the viewpoint of molecular theory.

In addition, for detailed investigation of the viscoelasticity of polymers in solution, it is necessary to obtain the frequency dependences of the dynamic rigidity G' and dynamic viscosity η' covering a wide range of frequency. However, the time-temperature superposition principle[6] is not applicable to methylcellulose in water whose configuration is remarkably affected by temperature. Therefore, the frequency dependences of G' and η' were obtained over more than 8 decades of frequency range at various temperatures and concentrations, using three types of rheometers, each of which covers different frequency ranges; and the relations between the viscoelastic quantities and the temperature-dependent intermolecular interactions of methylcellulose with water were mainly investigated. At first, the G' and G'' versus frequency curves and the relaxation spectra experimentally obtained were compared with those calculated from Haya-shi's theory,[7] and the entanglement density X/q was estimated at various temperatures. Second, the relaxation mechanism was examined from the concentration dependences of G', η', and η_0 at various temperatures and frequencies.

EXPERIMENTAL

Sample

A commercial product of methylcellulose (Shin-etsu Kagaku Co., Metolose SM 8000, $\bar{M}_w = 1.10 \times 10^5$, methoxyl content 29.5%) was used as the sample. Methylcellulose was uniformly dispersed in hot water at about 60°C; cold water was then added while stirring, and the dispersion was cooled gradually to dissolve completely. The solution was allowed to stand at 5°C for two days before the measurement.

Measurement

For the measurements in the low-frequency range of 10^{-2} to 10 sec^{-1}, a coaxial double-cylinder rheometer was used, in which the outer cylinder was oscillated or rotated. The measurements at frequencies ranging from 10^2 to 10^3 sec^{-1} were carried out with an audiofrequency rheometer which is of a modified magnetic transducer type and was deviced by Kuroiwa, Ogawa, and Nakamura.[8] The measurements at 4.95×10^5 sec^{-1} were carried out by the torsional crystal method.[9,10] The resonator was 50 mm in length and 5 mm in diameter. The electrodes were evaporated only on the upper half of the resonator. The level of the solution was at the lower

nodal plane of the resonator so that errors due to any variation of the level of the solution and effect of the surface tension of the solution might be minimized. The measurements were carried out in methylcellulose concentrations ranging from 0.7% to 3.0% at temperatures of 10°, 25°, and 40°C.

RESULTS AND DISCUSSION

Temperature Dependence of Viscoelastic Properties

In order to study the effects of temperature on the viscoelastic properties of methylcellulose in water, G' and η' were measured on the aqueous solutions of various concentrations at temperatures of 10°, 25°, and 40°C.

In Figure 1, the frequency dependence of G' at various temperatures is shown for an aqueous 3% solution of methylcellulose. The shape of the curve obtained at 40°C differs from those at 10° and 25°C. This indicates that the relaxation mechanism varies with temperature.
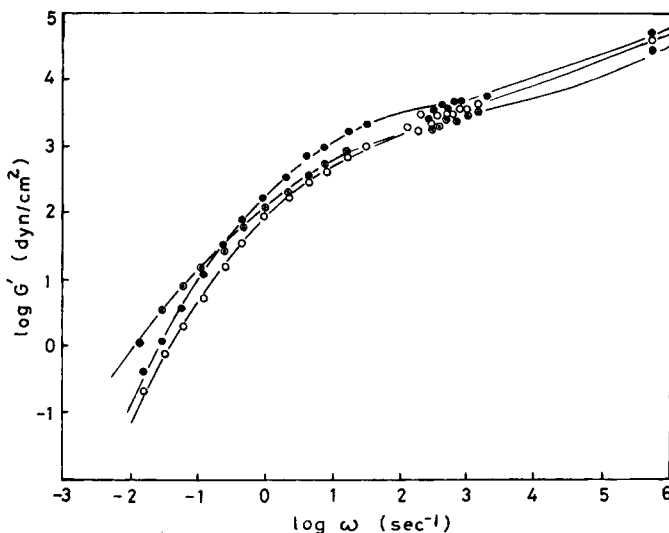

Fig. 1. Logarithmic plots of G' vs. ω for an aqueous 3% solution of methylcellulose; (●) measured at 10°C: (○) measured at 25°C: (⊙) measured at 40°C.

The frequency dependence of η' for a 3% solution is shown in Figure 2. Unexpectedly, in a low-frequency range, the measured values at 40°C are almost as large as those at 25°C. It is well known that the configuration of methylcellulose in an aqueous solution is remarkably affected by temperature. From these facts it is concluded that the time–temperature superposition principle is not applicable to this system.

Hayashi's Theory and Entanglement Coupling

A flat, so-called "box"-type region exists in the relaxation spectra of concentrated polymer solutions due to the entanglement coupling of polymer
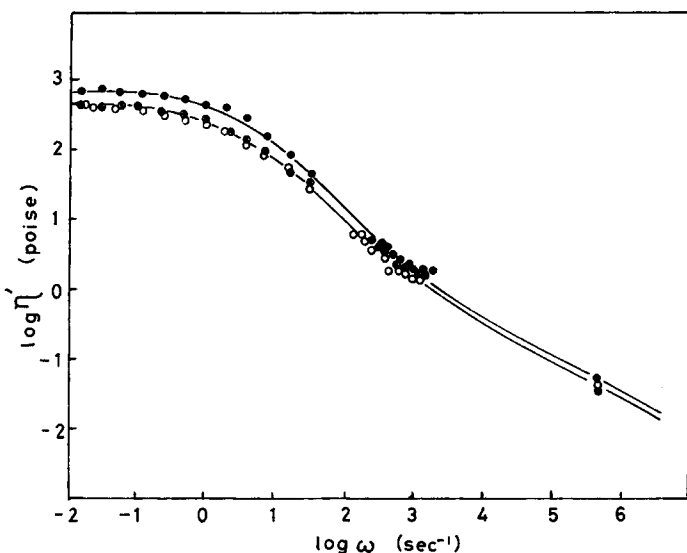
Fig. 2. Logarithmic plots of η' vs. ω for an aqueous 3% solution of methylcellulose; (●) measured at 10°C: (○) measured at 25°C; (⊙) measured at 40°C.

chains in the longer relaxation time region than the "wedge"-type region corresponding to the mechanisms described by the Rouse[10] and Zimm[11] theories. Hayashi explained these phenomena by means of weak network structure.[7]

According to Hayashi's theory, the relaxation spectrum may be written as follows:

$$
\begin{aligned}
H(\tau) &= nkTX(\kappa/2)(\tau/\tau_\alpha)^{-1/2} && (\tau_\alpha < \tau < \tau_c) \\
&= nkTX(\kappa/Fq) && (\tau_c < \tau < \tau_\beta) \\
&= 0 && (\text{otherwise})
\end{aligned}
\tag{1}
$$

The storage and loss moduli are expressed by

$$
G'(\omega) = nkTX\kappa \left\{ \int_{\tau_\alpha}^{\tau_c} \frac{\omega^2\tau^2}{2(1 + \omega^2\tau^2)} \left(\frac{\tau}{\tau_\alpha}\right)^{-1/2} \frac{d\tau}{\tau} + \frac{1}{q} \int_{\tau_c}^{\tau_\beta} \frac{\omega^2\tau^2}{F(1 + \omega^2\tau^2)} \frac{d\tau}{\tau} \right\}
$$

$$
G''(\omega) = nkTX\kappa \left\{ \int_{\tau_\alpha}^{\tau_c} \frac{\omega\tau}{2(1 + \omega^2\tau^2)} \left(\frac{\tau}{\tau_\alpha}\right)^{-1/2} \frac{d\tau}{\tau} + \frac{1}{q} \int_{\tau_c}^{\tau_\beta} \frac{\omega\tau}{F(1 + \omega^2\tau^2)} \frac{d\tau}{\tau} \right\}
$$

$$
\tag{2}
$$

where n is the number of molecules in a unit volume, k is the Boltzman constant, T is the absolute temperature, X is the number of repeating units in a molecule, q is the number of repeating units between entanglement couplings, κ and F are the parameters concerned with elastic and viscous effects, respectively, τ_c is the critical relaxation time, and τ_α and τ_β are the minimum and maximum relaxation times of the spectrum, respectively. The relaxation times are related to each other by the following relations:

$$
\begin{aligned}
\tau_\alpha &= \tau_c/q^2 \\
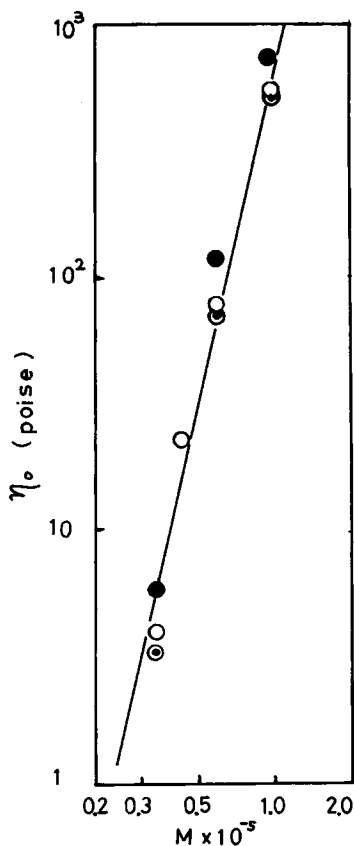\tau_\beta &= \tau_c(X/q)^F
\end{aligned}
\tag{3}
$$

Fig. 3. Molecular weight dependence of η_0 for an aqueous 3% solution of methylcellulose; (●) measured at 10°C: (○) measured at 25°C: (⊙) measured at 40°C.

In order to apply this theory to the experimental data, the parameters must be estimated. In this study, we determined empirically these parameters so that Hayashi's theory might agree with Rouse's theory[10] in the case of $X/q = 1$. Hayashi adopted a value of 3.5 as the exponent F as expressing the viscous effect on the basis of Bueche's interpretation[13] about the friction of the polymer molecule and pointed out that this value is related to the molecular weight dependence of zero shear viscosity η_0.[14] It has been concluded for many polymers that η_0 is proportional to the 3.4th power of molecular weight for sufficiently high molecular weight, while it has also been reported that this exponent varies with the constituents of polymer solutions.[15] According to Bueche's theory,[16] this phenomenon means that expansion factor and the slippage factor vary from polymer to polymer.

In the case of carbohydrate whose solution viscosity depends extremely on the molecular weight, it is more practical to determine the value of F from the molecular weight dependence of η_0. As already reported,[2,3] this procedure does not miss the validity of Hayashi's theory. The zero shear viscosities of aqueous 3% solutions were measured on methylcellulose
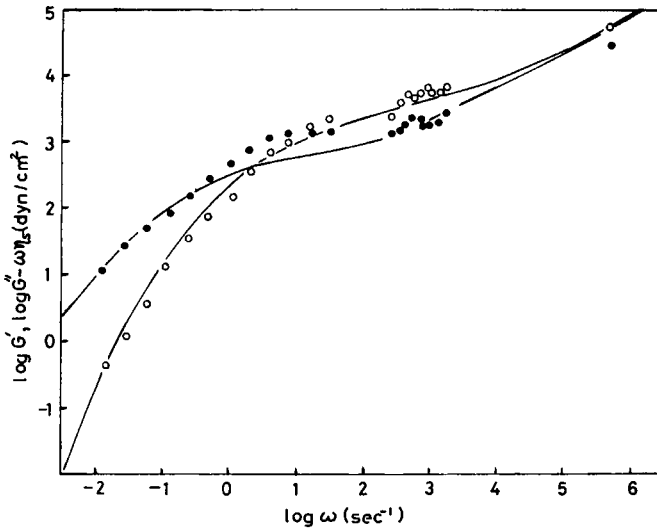
Fig. 4. Logarithmic plots of G' and $G'' - \omega\eta_s$ vs. ω for an aqueous 3% solution of methylcellulose measured at 10°C; (○) G'; (●) $G'' - \omega\eta_s$. Curves were calculated according to Hayashi's theory. The entanglement density of 3.7 was obtained from theoretical curves.
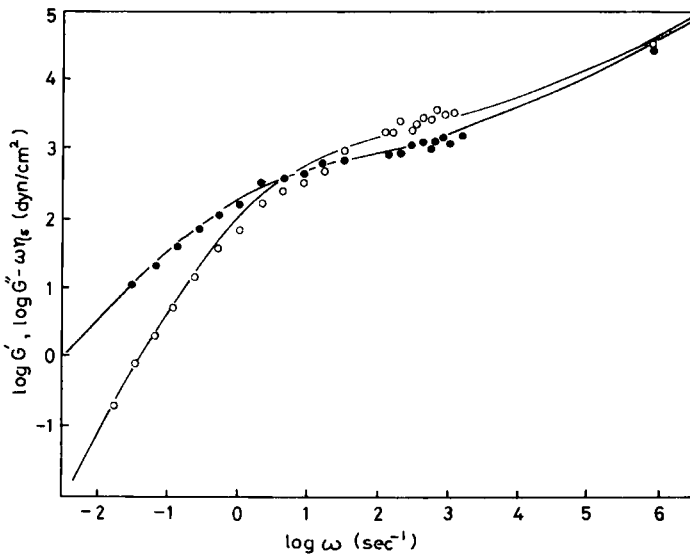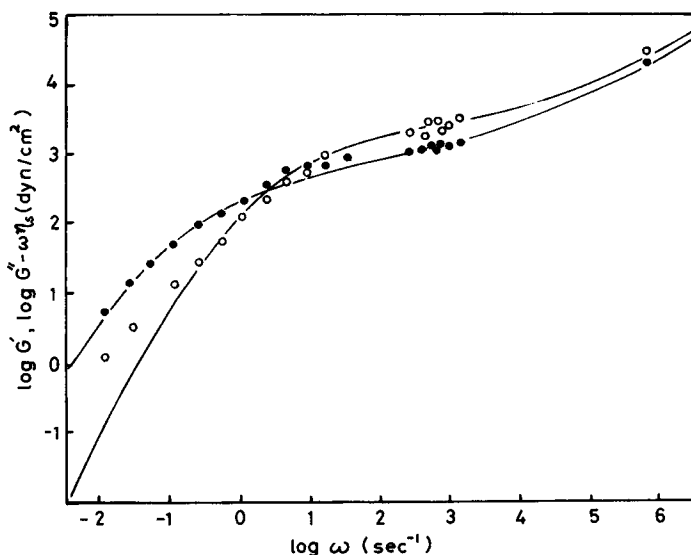

Fig. 5. Logarithmic plots of G' and $G'' - \omega\eta_s$ vs. ω for an aqueous 3% solution of methylcellulose measured at 25°C: (○) G'; (●) $G'' - \omega\eta_s$. Curves were calculated according to Hayashi's theory. The entanglement density of 3.7 was obtained from theoretical curves.

Fig. 6. Logarithmic plots of G' and $G'' - \omega\eta_s$ vs. ω for an aqueous 3% solution of methylcellulose measured at 40°C; (O) G'; (●) $G'' - \omega\eta_s$. Curves were calculated according to Hayashi's theory. The entanglement density of 4.6 was obtained from theoretical curves.

samples with various molecular weights at 10°, 25°, and 40°C. As seen in Figure 3, the molecular weight dependence of η_0 varies somewhat with temperature but as a whole η_0 is proportional to the 5th power of molecular weight; therefore, the value of F is estimated to be 5.0.

The values of G' and $G'' - \omega\eta_s$ for an aqueous 3% solution at 10°, 25°, and 40°C are shown in Figures 4, 5, and 6, where η_s is the viscosity of the solvent. In these Figures the curves theoretically calculated from Hayashi's theory[7] are also given. When the theoretical curves were calculated according to Hayashi's theory, the entanglement density X/q was selected so as to minimize the differences between experimental and theoretical curves. The entanglement density X/q thus obtained was 3.7 at 10° and 25°C and 4.6 at 40°C. The experimental values are well expressed by the theoretical curves in the whole frequency range studied.

The relaxation spectra obtained experimentally for an aqueous 3% solution are compared with those calculated theoretically at 10°, 25°, and 40°C in Figures 7, 8, and 9, respectively. The experimentally obtained relaxation spectra were determined from the measured values of G' and G'' by means of Williams-Ferry's method.[17] The theoretical relaxation spectra were calculated according to Hayashi's theory, in which viscoelastic parameters had the same values as specified above.

The values of X/q were determined by the same procedure in the concentration ranging from 0.7% to 3%, and the logarithmic X/q was plotted against the concentration in Figure 10. The concentration dependence of X/q at 10°C is similar to that at 25°C, but the data at 40°C are represented
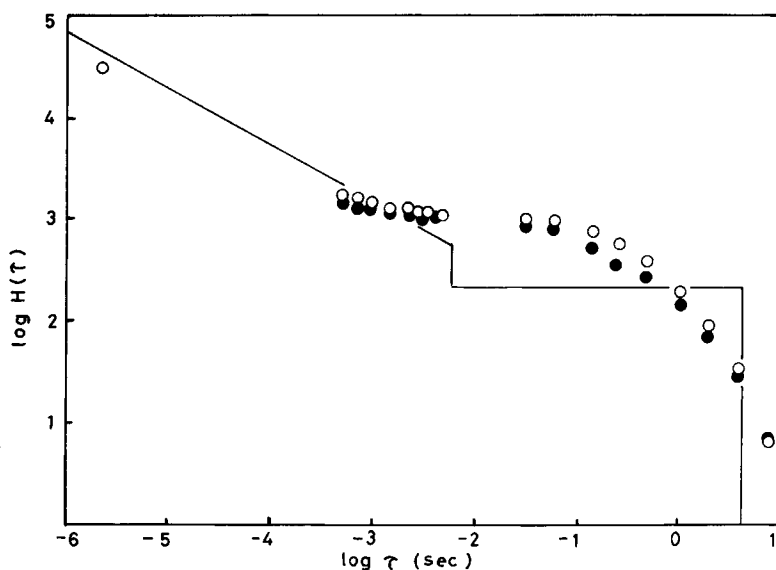
Fig. 7. Comparison between relaxation spectra experimentally obtained at 10°C and those calculated from Hayashi's theory: (○) from G'; (●) from G''.
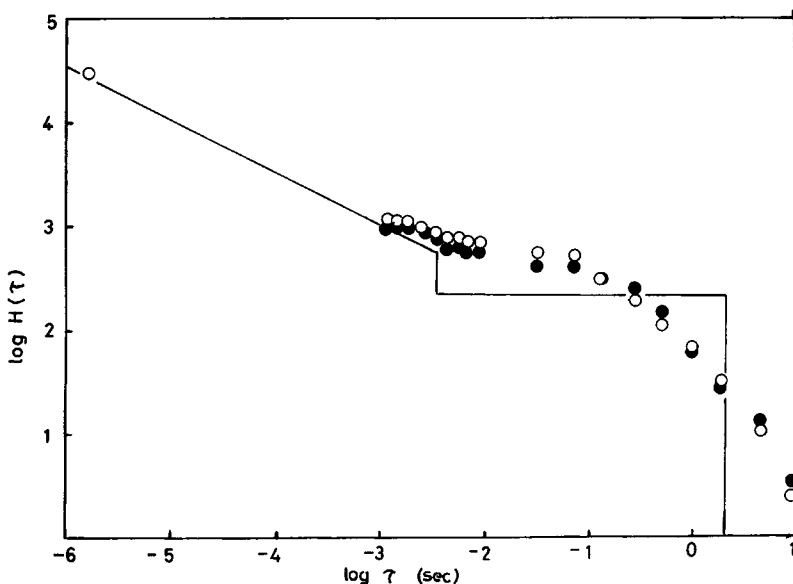

Fig. 8. Comparison between relaxation spectra experimentally obtained at 25°C and those calculated from Hayashi's theory: (○) from G'; (●) from G''.

by a straight line with a slope of 0.6. For the aqueous solution of a polyelectrolyte such as sodium alginate, we have reported that the slope is about 0.1 and increases with the addition of NaCl.[3] The smaller concentration dependence of X/q in aqueous solution of sodium alginate or methylcellulose below 25°C is attributed to the depression of the entanglement
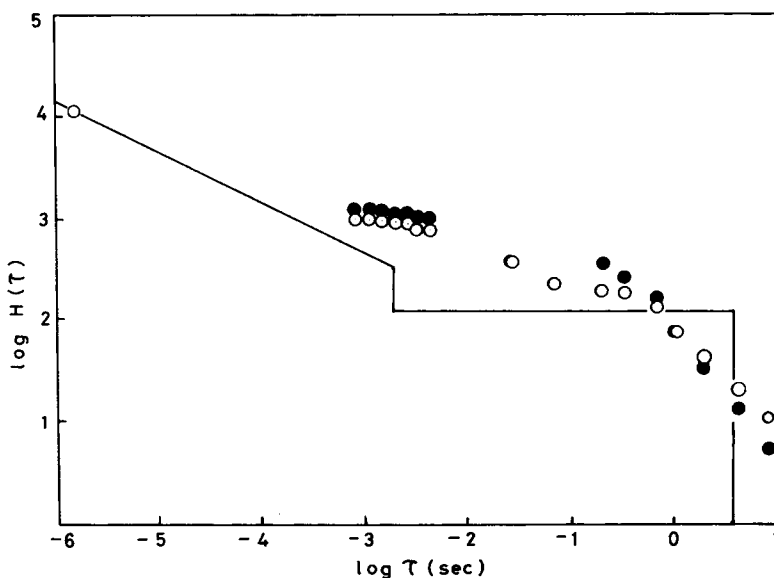
Fig. 9. Comparison between relaxation spectra experimentally obtained at 40°C and those calculated from Hayashi's theory; (○) from G'; (●) from G''.
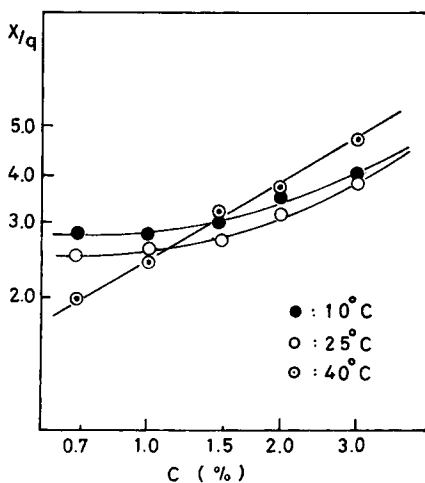

Fig. 10. Concentration dependence of entanglement density X/q at various temperatures.

formation resulted from the electrostatic repulsion or the hydration of polymer chains.

Evaluation of Entanglement Function

Recently, the modulus of the entanglement network (G_{eN}) and the entanglement compliance (J_{eN}) have been used to indicate the extent of entanglement couplings.[18,19]
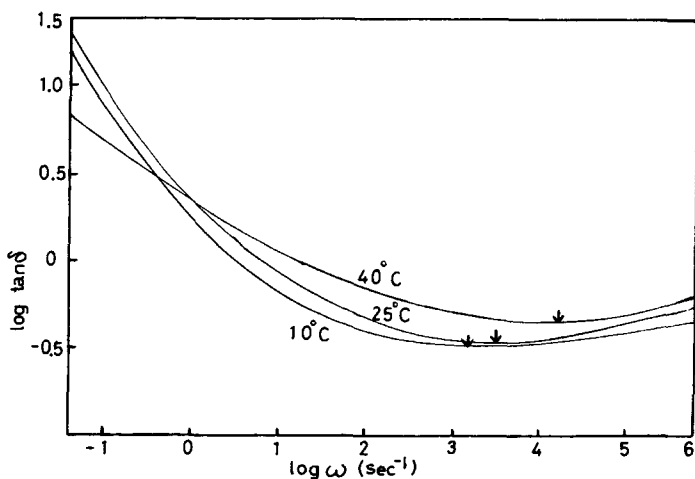
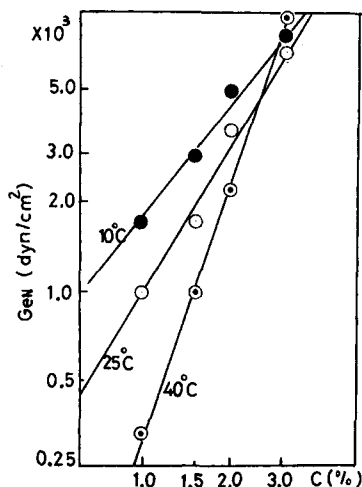Fig. 11. Frequency dependence of tan δ for an aqueous 3% solution of methylcellulose at various temperatures.

Fig. 12. Concentration dependence of G_{eN} at various temperatures.

According to Sanders et al.,[18] G_{eN} is given by

$$G_{eN} = (2/\pi) \int_{-\infty}^{a} G''(\omega) d \ln \omega \qquad (4)$$

where a is chosen to include the low-frequency maximum in G'', or lying roughly at the minimum in tan δ. In this study the parameter a was determined as the frequency in which the minimum of tan δ appeared, since the low frequency maximum in G'' was not definite.

The frequency dependences of tan δ for a 3% solution are shown for various temperatures in Figure 11. It is recognized that a minimum exists in each curve at the frequency of more than 10^3 sec^{-1}.
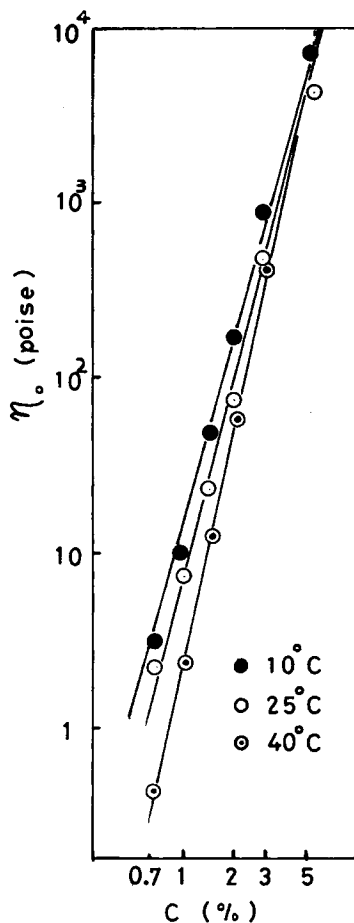
Fig. 13. Concentration dependence of η_0 at various temperatures.

Figure 12 shows the concentration C dependence of G_{eN} calculated from eq. (4). It is well known that the logarithmic plot of G_{eN} versus C can be approximated by a straight line over a wide range of concentrations. It was reported that the slope m of the logarithmic plot of G_{eN} versus C is 3.47 for poly(vinyl chloride) gels[20] and approximately 2 for gelatin gels in water.[21] For aqueous solutions of methylcellulose, log G_{eN} is proportional to log C, and the slopes are 1.2 at 10°C, 1.8 at 25°C, and 2.6 at 40°C. Namely, the slopes of G_{eN} versus concentration plots again become larger with increasing temperature.

Concentration Dependence of η_0

The relations between η_0 and the concentration of aqueous solutions of methylcellulose are shown in Figure 13. Generally, the viscosity of concentrated solutions of polymers is affected by the intermolecular interaction such as entanglements between the polymer chains. Such an effect is
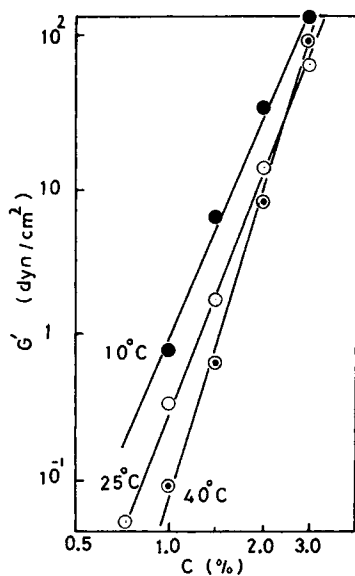
Fig. 14. Concentration dependence of G' measured at 0.625 Hz at various temperatures.
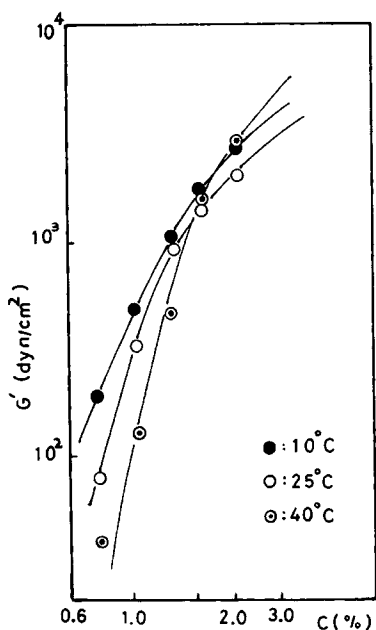

Fig. 15. Concentration dependence of G' measured at 100 Hz at various temperatures

usually observed in the concentration dependence of the zero shear viscosity η_0. It was reported that η_0 of poly(vinyl alcohol)[22] and collagen solution,[23] which show remarkable structural viscosity, is proportional to the fifth to sixth power of concentration.
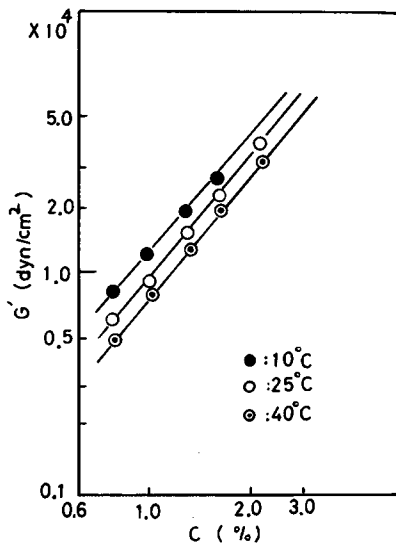
Fig. 16. Concentration dependence of G' measured at 78 kHz at various temperatures.

However, the concentration dependence of η_0 of a polyelectrolyte solution is small as the entanglement between polymer chains is depressed. For example, the values of η_0 in an aqueous solution are proportional to C^2 for sodium polyacrylate[24] and $C^{3.8}$ for sodium alginate.[3] In Figure 13, the slope n of the curves of log η_0 versus log C increases with increasing temperature. The value of n is 4.0 at 10°C, 4.4 at 25°C, and 4.8 at 40°C. These results indicate that the structural networks in a solution become closer with increasing temperature.

Concentration Dependence and Mechanism of Viscoelasticity

It was reported that the concentration dependence of G' is very characteristic for each aqueous solution.[1,25,26] From the slope of linear portion of the log G' versus log C plot, it is determined whether intermolecular secondary bondings or molecular orientations contribute to the mechanism of G'.

The concentration dependences of G' are shown in Figures 14, 15, and 16 for 0.625 Hz, 100 Hz, and 78 kHz, respectively. At lower frequencies, the concentration dependence of G' is more remarkable and becomes larger with increasing temperature. But at 78 kHz, the concentration dependence of G' shows the same tendency irrespective of temperature. The rigidity at the lower frequency ranges, which shows remarkable concentration dependence, can be explained by intermolecular entanglements, while that at higher frequencies, which shows small concentration dependence, cannot be explained by the entanglement mechanism.

In Figure 17, the concentration dependence of $\eta' - \eta_s$ at 78 kHz is shown together with that at 100 Hz. At 100 Hz, the concentration dependence is
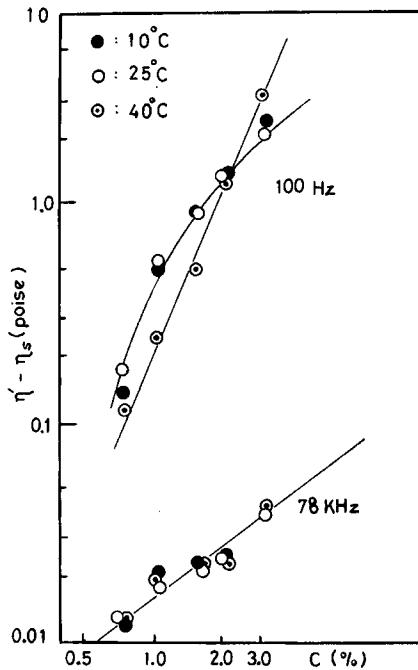
Fig. 17. Concentration dependence of $\eta' - \eta_s$ measured at 100 Hz and 78 kHz at various temperatures.

more remarkable at 40°C than that at other temperatures but is less than that of η_0. At 78 kHz, the concentration dependence of $\eta' - \eta_s$ becomes smaller, and its temperature dependence is not evident. From these tendencies it is concluded that the corresponding viscoelastic mechanism varies from intermolecular interaction such as entanglements to intramolecular motion with increasing frequency.

References

1. T. Amari and M. Nakamura, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*) **73,** 781 (1970).

2. M. Nakamura and T. Amari, *J. Soc. Mater. Sci. Japan,* **20,** 638 (1971).

3. T. Amari and M. Nakamura, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **74,** 2140 (1971).

4. A. B. Savage, *Encyclopedia of Polymer Science and Technology,* Vol. 3, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Ed., Wiley, New York, 1965, p. 500.

5. W. Kuhn, P. Mase, and H. Majer, *Helv. Chim. Acta,* **44,** 770 (1961).

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

7. S. Hayashi, *J. Phys. Soc. Japan,* **19,** 2306 (1964).

8. S. Kuroiwa, M. Ogawa, and M. Nakamura, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Eng. Sect.*), **70,** 1264 (1967).

9. W. P. Mason, *Trans. Amer. Soc. Mechan. Eng.,* **69,** 359 (1947).

10. Y. Wada, H. Sasabe, and M. Tomono, *Biopolymers*, **5**, 887 (1967).

11. P. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1953).

12. B. H. Zimm, *ibid.*, **24**, 269 (1956).

13. F. Bueche, *J. Chem. Phys.*, **20**, 1959 (1952).

14. S. Hayashi, *Kobunshi* (*High Polymers, Japan*), **14**, 49 (1965).

15. S. Onogi, T. Masuda, and K. Kitagawa, *Macromolecules*, **3**, 109 (1970).

16. F. Bueche, *Physical Properties of Polymers*, Wiley, New York, 1962.

17. J. D. Ferry, *Viscoelastic Properties of Polymer*, Wiley, New York, 1970.

18. J. F. Sanders, J. D. Ferry, and R. H. Valentain, *J. Polym. Sci. A-2*, **6**, 967 (1968).

19. T. Masuda, K. Kitagawa, and S. Onogi, *Polym. J.*, **1**, 418 (1970).

20. A. T. Walter, *J. Polym. Sci.*, **13**, 207 (1954).

21. J. D. Ferry, *Advan. Protein Chem.*, **4**, 1 (1948).

22. S. Onogi, T. Kobayashi, Y. Kojima, and Y. Taniguchi, *J. Appl. Polym. Sci.*, **7**, 847 (1963).

23. E. Fukada and M. Date, *Kobunshi* (*High Polymers, Japan*), **11**, 1284 (1962).

24. S. Kuroiwa and M. Nakamura, *Bull. Chem. Soc. Japan*, **39**, 1602 (1966).

25. S. Kuroiwa and M. Nakamura, *Kobunshi Kagaku* (*Chem. High Polymers*), **22**, 237 (1965).

26. J. D. Ferry, *J. Amer. Chem. Soc.*, **64**, 1330 (1942).