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Viscoelastic Properties of Aqueous Solutions of Amylose–Iodine Complex at Ultrasonic Frequencies

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Synopsis

The viscoelastic properties of aqueous solutions of amylose–iodine at ultrasonic frequencies have been investigated by a torsional method using quartz crystal resonators. The frequency dependences of the storage (G') and loss (G'') moduli show that the hydrodynamic interaction increases with the addition of iodine. The effects of the intermolecular hydrogen bonds could be observed from the concentration dependence of viscoelastic functions. The concentration dependences of G' and $G'' - \omega\eta_s$ were extremely large, but the concentration dependences decreased with the addition of 2 moles of urea since the effect of hydrogen bonds was minimized. The intramolecular hydrogen bonds seem to affect the tightness of the helical structure of the amylose–iodine complex in water. The frequency dependences of the intrinsic moduli at infinite dilution were compared with the hybrid model theory of Ferry et al. The helical structure of the amylose–iodine complex appears to be more rigid than that of other helical polymers such as poly(γ-benzyl-L-glutamate). However, the flexibility of the helix appears to become more prominent with the addition of urea. When the poor solubility of amylose in water was improved by the addition of ethanol, the conformation of amylose–iodine complex became similar to that in the noncomplex system, where amylose seems to assume a loose and extended helical conformation.

INTRODUCTION

It is well known that a characteristic blue color complex is produced on the addition of iodine to an amylose solution. Since Hanes[1] in 1937 suggested that the complex consists of a helical amylose molecule with iodine occupying the helical cavity, many investigations have been published concerning this material.

Rundle and French have determined the structure of the solid amylose–iodine complex by x-ray diffraction.[2] According to their conclusion, amylose exists in a helical conformation with 6 glucose residues per turn. In contrast, the nature of amylose–iodine complex in aqueous solution has not been well characterized. The conformation of the complex in an aqueous solution and the complexation mechanisms still appear to be a matter of some controversy. Furthermore, the relations between the dynamic viscoelastic properties and the conformation of the complex are not well established.

For the conformation of amylose in aqueous solution, Holló and Szejtli[3] have proposed a tight helix model which is essentially identical with the helical structure in the crystalline V-form of amylose. If amylose assumes the

tight helical structure before complexation, the dimension of complexed amylose should not be changed by the addition of iodine because the complexing agent may be expected to enter the preformed helical cavity.

In contrast to the conclusion of Holló and Szejtli, Banks and Greenwood[4] showed that the formation of complex resulted in a large decrease in viscosity number, namely, a decrease in hydrodynamic volume. From these results, they have proposed a random coil model for amylose in water.

On the other hand, Senior and Hamori[5] have proposed a loose and extended helical model for amylose in water and showed that the model is incompatible with the results of Banks and Greenwood. According to that model, the loose and extended helix is forced into the tight helical conformation as the V-form of amylose by a complexing agent, which enters the central cavity, and the hydrodynamic volume of amylose decreases. The interpretation of Senior and Hamori has been confirmed by the kinetic studies on the amylose-iodine reactions.[6]

Previously, we have reported the viscoelastic properties of dilute aqueous solutions of amylose in the absence of complexing agents and obtained the following results[7]: (1) the pH-dependent helix coil transition of amylose in water can be confirmed from the results of pH dependence of viscoelastic functions, and (2) amylose chain is thought to take a loose extended helical conformation which should be attributed to the C1 conformation of glucopyranose residue as suggested by Senior and Hamori[5] in the pH range below 10 without iodine.

It is our purpose here to determine the viscoelastic properties of amylose–iodine complex in water under various complexing conditions by a torsional method using quartz crystal resonators at ultrasonic frequencies and to examine the characteristic conformation of amylose–iodine complex in an aqueous solution.

EXPERIMENTAL

Measurements

Viscoelastic measurements at ultrasonic frequencies were carried out by the torsional method using quartz crystal resonators modified for an aqueous solution as described previously.[8] The values of the storage (G') and loss (G'') shear moduli and dynamic viscosity (η') were measured at frequencies of 13, 26, 39, 78, and 117 kHz. All measurements were carried out at temperature of 25 ± 0.01°C.

Material

Corn amylose ($\bar{M}_w = 3.70 \times 10^5$) fractionated in a dimethylsulfoxide/ethyl alcohol system was used throughout the experiments. The maximum amount of iodine bound by amylose was determined by an amperometric adaptation of the dead-stop titration developed by Larson and co-workers.[9]

Preparation of Sample Solutions

The aqueous solution of amylose–iodine complex (AI) was prepared by the following procedure: amylose was dispersed in a hot 0.001N NaOH solution

in a flask with a reflux condenser, then the solution was vigorously stirred for 1 hr in a boiling water bath under an atmosphere of nitrogen. The solution was filtered carefully through a fritted glass filter to remove undissolved particles, and the pH of the solution was adjusted to 10. An approximately 1*N* KI solution was added until the final concentration of KI became 0.05*N*, and a prescribed amount of I_2–KI solution (0.01*N* I_2, 0.05*N* KI) was added to an aqueous solution of amylose. The bound iodine–amylose ratio should be kept constant upon dilution of the solution. The amylose concentrations were determined by amperometric titration. To examine the effect of hydrogen bonds on the conformation and viscoelastic behavior, an aqueous solution of amylose–iodine complex with 2*M* urea (AIU) was prepared. To improve the poor solubility of amylose in water and examine the effect of ethanol on the conformation of amylose in water, the aqueous solution of the amylose–iodine complex containing a small amount of ethanol (AIE) was prepared by the following procedure. Amylose powder was wetted with a small amount of absolute ethanol (final concentration of ethanol was about 2%) and hot distilled water was poured upon the wetted amylose. The complexation with iodine was carried out by the same procedure as for AI.

RESULTS AND DISCUSSION

Determination of the Bound Iodine–Amylose Ratio

The amperometric titration curve for the amylose sample used in this study is shown in Figure 1, together with that for a reagent blank. The curve for amylose shows that as the amount of iodine in solution is increased, after an initial increase there is little change in the free iodine concentration until amylose has been saturated with iodine. The slope then increases abruptly and linearly. The total iodine bound up to the inflection point (A) can be calculated from the difference between total and free iodine in the system at that point according to the procedure by Larson and co-workers.[9] The amount of iodine required to form the complete amylose–iodine complex was calculated as 19.8 g per 100 g amylose. Viscoelastic measurements have been carried out at an amylose concentration above 0.002 g/ml in order to diminish some uncertainty which occurs when the values of relative viscosity are smaller than 1.1. However, under this condition, aggregation between the helical molecules occurred at iodine concentrations smaller than that required for the complete complexation, and a visible precipitate was formed. In this study, 0.085 g iodine per 1 g amylose, which corresponds to 43% of the amount of iodine required for the complete complexation, could be added to each aqueous amylose solution without precipitation.

Frequency Dependences of Viscoelastic Properties

Figures 2 and 3 show plots of G' and $\eta' - \eta_s$ for AI, AIU, and AIE at concentrations of approximately 0.3% and 0.5% as a function of angular frequency ω, where η_s is the viscosity of solvent. The results for the aqueous solution of amylose without iodine at pH 10 are also shown in Figures 2 and 3. For the solutions of amylose–iodine complex, the viscoelastic values of AIE are larger than those for AI and AIU. The values of $\eta' - \eta_s$ for AI and AIU seem

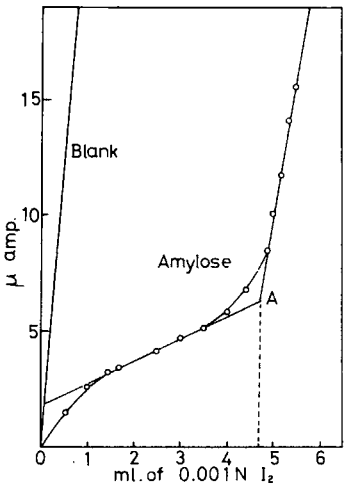

Fig. 1. Titration curves for a reagent blank and an aqueous solution of amylose. Initial amylose concentration = 0.000066 g/ml, initial volume = 100 ml.

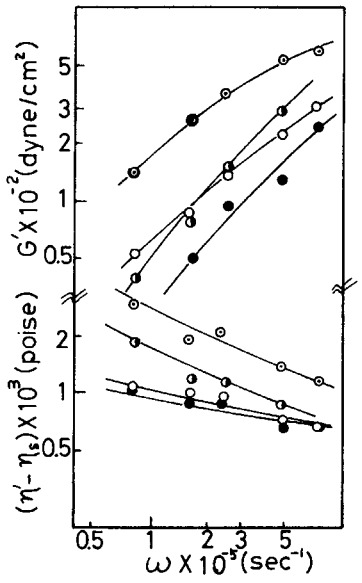

Fig. 2. Frequency dependences of G' and $\eta' - \eta_s$ for aqueous solutions of amylose–iodine complex: (○) for AI at a concentration of 0.294%, (●) for AIU at a concentration of 0.292%, (⊙) for AIE at a concentration of 0.294%, and (◑) for an aqueous solution of amylose without iodine at pH 10 at a concentration of 0.300%.

to approach nonvanishing limit which does not concern viscoelastic relaxation, while that for AIE decreases monotonously with frequency.

From these phenomena, the helical conformation and/or the relaxation mechanism of amylose–iodine complex for AIE is thought to be different from those for AI and AIU, in which the rigid behavior at high frequencies is observed. According to Banks and Greenwood,[10,11] if the molecule is forced into a helix by the addition of a complexing agent, all of the OH groups of the glucose units are found on the external surface of the amylose helix and the

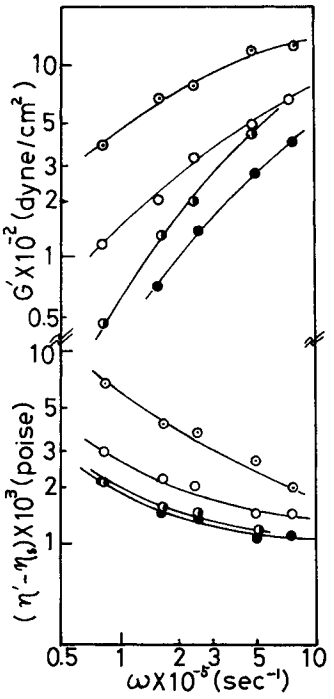

Fig. 3. Frequency dependences of G' and $\eta' - \eta_s$ for aqueous solutions of amylose–iodine complex: (○) for AI at a concentration of 0.464%, (●) for AIU at a concentration of 0.500%, (⊙) for AIE at a concentration of 0.476%, and (◑) for an aqueous solution of amylose without iodine at pH 10 at a concentration of 0.466%.

internal surface consists of CH groups and the glycosidic oxygen atoms depending upon the C1 conformation of glucose residue and the internal diameter becomes approximately 6 Å. In these circumstances, the role of hydrogen bonds cannot be neglected, therefore the helical structure may be stabilized by intramolecular bonding such as O_2—O_3' type hydrogen bonds as suggested by Erlander and Purvinas.[12] As Tobolsky[13] has pointed out, the conditions which enable an isolated helix to exist in solution free from intermolecular helix aggregation should be considered as unusual, namely, the intermolecular hydrogen bonds tend to interact with each other. For AIU in which the hydrogen bonds seem to be rather improbable, both G' and $\eta' - \eta_s$ show similar frequency dependences as observed for AI. However, the measured values for AIU, except the values of $\eta' - \eta_s$ for a concentration of 0.292%, are somewhat smaller than those for AI. In Figure 2, the values of $\eta' - \eta_s$ for AIU are almost as large as those for AI. Therefore, it is thought that the hydrodynamic volume of amylose molecule in each system may be similar, and in this concentration range the intermolecular hydrogen bonds do not take part in viscoelastic behavior of AI. However, in Figure 3 in the concentration range above 0.46%, the values of G' and $\eta' - \eta_s$ for AI are larger than those for AIU, so that the effect of intermolecular hydrogen bonds on the viscoelastic behavior seems to become larger in this concentration range. For an aqueous solution of amylose without iodine at pH 10 (noncomplex system), the frequency dependences of viscoelastic values are larger than those for aqueous

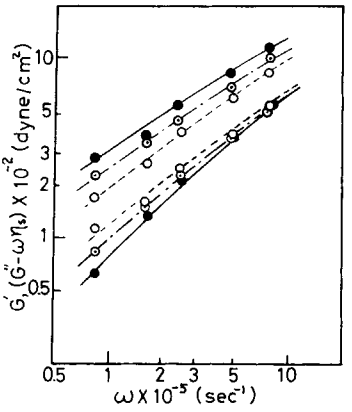

Fig. 4. Frequency dependences of G' and $G'' - \omega\eta_s$ for aqueous solutions of amylose–iodine complex at various iodine concentrations. Iodine concentration (mole/l.): (●) 0.00133; (⊙) 0.000667; (○) 0.000267.

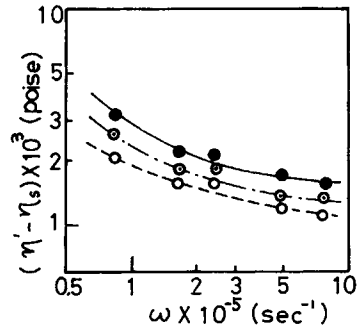

Fig. 5. Frequency dependences of $\eta' - \eta_s$ for aqueous solutions of amylose–iodine complex at various iodine concentrations. Iodine concentration (mole/l.): (●) 0.00133; (⊙) 0.000667; (○) 0.000267.

solutions of amylose–iodine complex. The values of $\eta' - \eta_s$ for the noncomplex system are larger than those for AI and AIU at the relatively dilute concentration as shown in Figure 2. This phenomenon seems to depend on the conformational change as a contraction in the linear dimension of the helix of the amylose molecule. However, at a concentration above 0.46%, the values of $\eta' - \eta_s$ for AI become larger than those for the noncomplex system, whereas those for AIU are still smaller. Therefore, it is thought that the intermolecular helix aggregation occurs in AI in this concentration range.

Effect of Iodine Addition on the Viscoelastic Properties

The values of G', $G'' - \omega\eta_s$, and $\eta' - \eta_s$ for AI with various amounts of iodine are plotted against ω at a amylose concentration of 0.41% in Figures 4 and 5. With increasing iodine concentration, the values of G' decrease, but those of $G'' - \omega\eta_s$ and $\eta' - \eta_s$ increase. The increase in the values of $G'' - \omega\eta_s$ and $\eta' - \eta_s$ reflects an incipient aggregation in this concentration range of amylose as pointed out by Banks and Greenwood.[4] The frequency dependence of G' somewhat increases with increasing iodine concentration. The

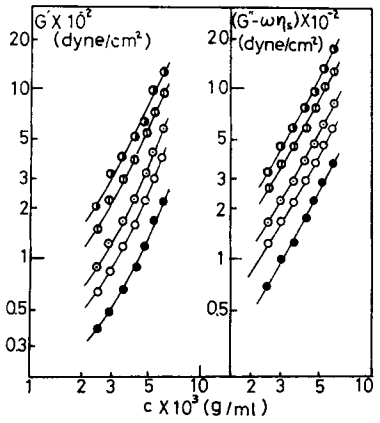

Fig. 6. Concentration dependences of G' and $G'' - \omega\eta_s$ for AI at various frequencies. Frequency (kHz): (●) 13; (○) 26; (⊙) 39; (Φ) 78; (◑) 117.

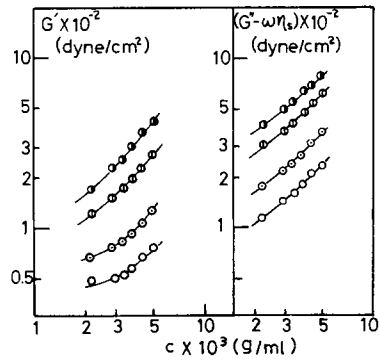

Fig. 7. Concentration dependences of G' and $G'' - \omega\eta_s$ for AIU at various frequencies. Frequency (kHz): (○) 26; (⊙) 39; (Φ) 78; (◑) 117.

ratio of $G'' - \omega\eta_s$ and G' increases with increasing iodine concentration. From the change of viscoelastic behavior, it is thought that the hydrodynamic interaction of amylose–iodine complex in an aqueous solution increases with the addition of iodine. This tendency can be explained by the conformational change of the amylose–iodine complex which is forced into a tight helix by the addition of iodine.

Concentration Dependences of Viscoelastic Properties

Plots of G' and $G'' - \omega\eta_s$ against amylose concentration c for AI, AIU, and AIE at various frequencies are shown in Figures 6, 7, and 8, respectively. As shown in Figure 6, the concentration dependences of G' and $G'' - \omega\eta_s$ for AI are extremely large and roughly proportional to c^2. As previously reported,[7] in aqueous solutions of amylose without iodine, the concentration dependences of G' and $\eta' - \eta$ at pH 10, where amylose exists essentially in a extended helical conformation, are larger than those in the pH range above 13, where amylose behaves as a random coil polymer, but even the concentration dependences of viscoelastic values at pH 10 are smaller than those for AI. The remarkable concentration dependences observed for AI, however, decrease

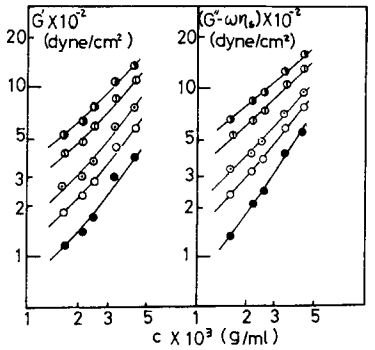

Fig. 8. Concentration dependences of G' and $G'' - \omega\eta_s$ for AIE at various frequencies. Frequency (kHz): (●) 13; (○) 26; (⊙) 39; (◐) 78; (◑) 117.

with the addition of urea as shown in Figure 7. Therefore, it is thought that the influence of intermolecular aggregation on the viscoelastic mechanisms can be seen in the concentration dependence of viscoelastic functions. On the other hand, for AIE the concentration dependences of G' and $G'' - \omega\eta_s$ become larger with decreasing frequency, and these concentration dependences agree well with those at pH 10 in the noncomplex system. These results may be explained by considering the corresponding helical conformation of amylose in aqueous systems, namely, the conformation of amylose in AIE differs from those in AI and AIU and is rather similar to that at pH 10 in the noncomplex system, where amylose seems to assume a loose and extended helical conformation.

Viscoelastic Properties at Infinite Dilution

As mentioned above, amylose exists in an imperfect helical conformation in aqueous solution. However, with the addition of a complexing agent such as iodine, the loose and extended helix is forced into a tight helical conformation by the complexing agent entrapped in the helical cavity.

On the other hand, polymer molecules in a helical form such as poly(γ-benzyl-L-glutamate) (PBLG) have been regarded as rigid rod-like shapes, and then the viscoelastic behavior has been compared quantitatively with the theory for thin rigid rods.[14–17] However, the viscoelastic behavior for such polymers could not be predicted by well-established theories for rigid rods. It seems difficult to apply the theories for rigid rods directly to the viscoelastic behavior for the helical polymers which have a rather rigid structure but exhibit some degree of flexibility. In the viscoelastic measurements for PBLG in a helicogenic solvent, Ferry and co-workers[18] reported that the frequency dependences of the storage and loss shear moduli at infinite dilution at low frequencies agreed well with the Ullman theory[19] for rigid rods depending on a single relaxation mechanism; but at higher frequencies, the behavior was intermediate between those predicted for rigid rods and flexible random coils. This behavior suggested that relaxation times besides rotational relaxation time in the Ullman theory[19] were involved. Therefore, they proposed "the hybrid model theory" in order to predict phenomenologically the viscoelastic behavior for the molecules with far less flexibility. According

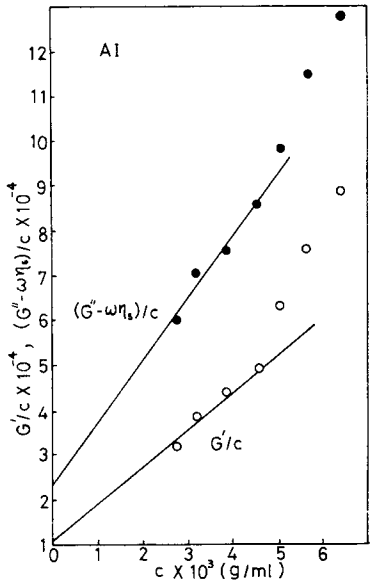

Fig. 9. Plots of G'/c and $(G'' - \omega\eta_s)/c$ vs. c at 39 kHz for AI: (○) G'/c; (●) $(G'' - \omega\eta_s)/c$.

to the hybrid model theory, by combining the single relaxation time corresponding to rigid end-over-end rotation in the rigid rod theory with a group of shorter times which are attributed to some kind of bending motions, a hybrid spectrum is obtained. According to Tanaka and co-workers,[20] the complex intrinsic rigidity at infinite dilution is defined as

$$[G^*] = \lim_{c \to 0} (G^* - i\omega\eta_s)/c. \tag{1}$$

Dimensionless functions of the real and imaginary parts of the complex intrinsic rigidity for the hybrid model may be expressed as follows:

$$[G']M/RT = \sum_p \omega^2\tau_p{}^2/(1 + \omega^2\tau_p{}^2) + B\omega^2\tau_k{}^2/(1 + \omega^2\tau_k{}^2) \tag{2}$$

$$[G'']M/RT = \sum_p \omega\tau_p/(1 + \omega^2\tau_p{}^2) + [A\omega\tau_k + B\omega\tau_k/(1 + \omega^2\tau_k{}^2)] \tag{3}$$

$$\alpha = \tau_{z1}/\tau_k \tag{4}$$

where M is the molecular weight, R is the gas constant, T is the absolute temperature, τ_p is the pth relaxation time in the Zimm sequence,[21] and τ_{z1} is tentatively identified as a maximum flex relaxation time in the Zimm sequence; τ_k is the rigid rotation relaxation time in the Kirkwood-Auer theory.[22] A and B are the coefficients of Kirkwood-Auer theory which approach asymptotic values of $\frac{1}{5}$ and $\frac{3}{5}$, respectively. α indicates the gap on the frequency scale between the rigid rod relaxation time and the longest relaxation time of the Zimm-like function. In order to apply the hybrid model theory to experimental data, B and α have been empirically determined. The constant A which is concerned with the rigid behavior at high frequencies has been set equal to zero in hybrid model for PBLG.[18] However, for an aqueous solution of amylose–iodine complex, especially for AI and AIU, the rigid behavior at

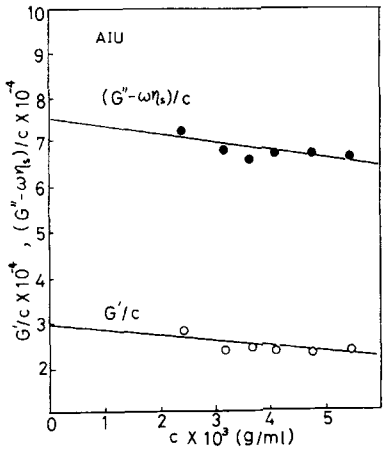

Fig. 10. Plots of G'/c and $(G'' - \omega\eta_s)/c$ vs. c at 39 kHz for AIU: (○) G'/c; (●) $(G'' - \omega\eta_s)/c$.

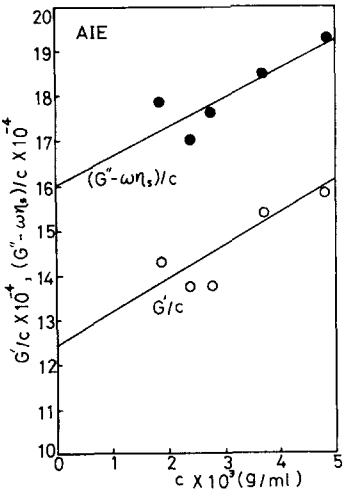

Fig. 11. Plots of G'/c and $(G'' - \omega\eta_s)/c$ vs. c at 39 kHz for AIE: (○) G'/c; (●) $(G'' - \eta)/c$.

high frequencies seems to appear as shown in Figure 2, so that the constant A was assumed to have the value of $B/3$ for convenience. The values of G'/c and $(G'' - \omega\eta_s)/c$ are plotted against c for AI, AIU, and AIE in Figures 9, 10, and 11, respectively. Although the exact chemical composition of the bound species is not clear, the values of G'/c and $(G'' - \omega\eta_s)/c$ are evaluated using the concentration of complex, in which the bound iodine is added to the weight of the amylose. For AI, the values of G'/c and $(G'' - \omega\eta_s)/c$ increase nonlinearly and abruptly with increasing concentration in the concentration range above 0.004 g/ml; these phenomena seem to be associated with the intermolecular aggregations which proceed with increasing concentration. On the contrary, for AIU, the values of G'/c and $(G'' - \omega\eta_s)/c$ increase slightly with decreasing concentration. These phenomena may be explained by the configurational change of the amylose–iodine complex in AIU. It is thought that not only intermolecular hydrogen bonds but also intramolecular ones which stabilize the helical structure of complex are difficult to exist in AIU.

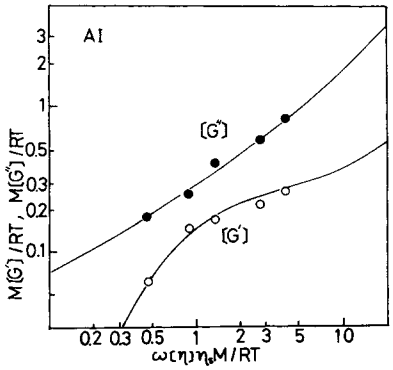

Fig. 12. Dimensionless plots of intrinsic rigidities vs. angular frequency for AI: (O) real part of the complex intrinsic rigidity; (●) imaginary part; (—) theoretical curves calculated from the hybrid model theory with $\alpha = 0.03$ and $B = 0.25$.

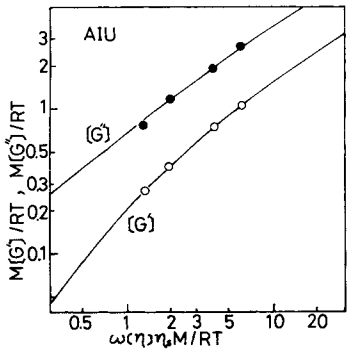

Fig. 13. Dimensionless plots of intrinsic rigidities vs. angular frequency for AIU: (O) real part of the complex intrinsic rigidity; (●) imaginary part; (—) theoretical curves calculated from the hybrid model theory with $\alpha = 0.15$ and $B = 0.3$.

Therefore, the helix becomes less stiff compared to that in AI, and the helical conformation bent by the intermolecular interaction seems to be restored to the extended rod-like conformation with decreasing concentration. Although Figure 11 for AIE shows some scattering, the concentration dependence is similar to that for an aqueous solution of amylose without iodine at pH 10.

The intrinsic rigidities reduced to the corresponding dimensionless values are plotted against normalized angular frequency in Figures 12, 13, and 14. In Figure 12 for AI, experimental values agree well with the theoretical curves with the following hybrid functions: $\alpha = 0.03$ and $B = 0.25$. The frequency dependences of normalized intrinsic rigidities for AI correspond to that for relatively rigid molecules in comparison with that for PBLG in a helicogenic solvent, and the gap between the rigid rotation relaxation time and a maximum flex relaxation time for AI is larger than that for PBLG. From these results, it is concluded that the helical structure for AI as an inclusion compound with an iodine molecule as a guest molecule is more rigid than that for PBLG.

In Figure 13, the frequency dependences of the intrinsic rigidities for AIU also fit the hybrid model theory very well with $\alpha = 0.15$ and $B = 0.3$. The de-

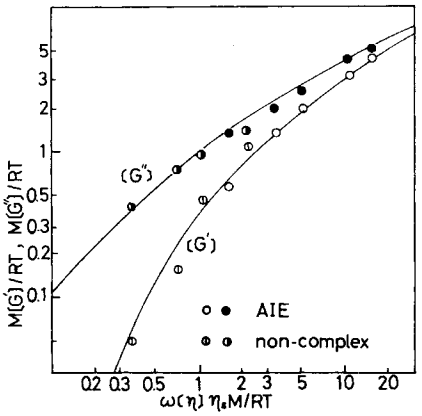

Fig. 14. Dimensionless plots of intrinsic rigidities vs. angular frequency for AIE, and noncomplex system at pH 10: (○), (⊖) real part of the complex intrinsic rigidity for AIE and noncomplex system, respectively; (●), (◑) imaginary part of AIE and noncomplex system, respectively; (—) theoretical curves calculated from the hybrid model theory with $\alpha = 0.35$ and $B = 0.2$.

gree of flexibility of helix appears to become more prominent with the addition of urea. It was suggested by Banks and Greenwood[11] that the intramolecular hydrogen bonds do not play a role in determining the conformation of amylose in an aqueous solution. However, from our results it can be concluded that the O_2—O_3' type hydrogen bonds between continguous residues stabilize the helical conformation and increase its stiffness as indicated by Erlander,[12] Sundararajan,[23] and Senior.[5]

In Figure 14, the results for AIE can be predicted by the hybrid model theory with $\alpha = 0.35$ and $B = 0.2$, in which the constant A concerning the persistence of rigid behavior at high frequencies has been put equal to zero as used by Ferry.[20] In this figure, the results for an aqueous solution of amylose at pH 10 without iodine are also plotted, and these results fit the same theoretical curves very well. From these results, the conformation of the amylose–iodine complex in AIE is similar to the loose and extended one in the noncomplex system. According to Senior and Hamori,[5] the iodine-binding capacity of amylose in an aqueous solution is not affected by the addition of a small amount of ethanol. Therefore, it is thought that the interactions between amylose and water are increased by the addition of small amount of ethanol, so that the linear dimension of the helical conformation of the amylose–iodine complex and its flexibility in AIE are larger than those in AI and AIU.

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