$$R=k[S:SbBr_3]^2[RBr] \quad (15)$$

The first order kinetics with respect to antimony tribromide in the region of lower $[SbBr_3]$ concentration could not be well explained by this reaction mechanism. Hence, a different mechanism has to be considered in this case. The following reaction schemes are assumed to occur in the region of lower $[SbBr_3]$ concentrations:

$$S+SbBr_3 \rightleftharpoons S:SbBr_3 \quad (11)$$

$$RBr+S:SbBr_3 \rightleftharpoons R^{\delta+}Br^{\delta-}SbBr_3+S \quad (12)$$

$$R^{\delta+}Br^{\delta-}SbBr_3 \xrightarrow{slow} R^+SbBr_4^- \quad (13)'$$

$$S+R^+SbBr_4^- \rightleftharpoons RBr+S:Sbr_3 \quad (14)'$$

In this reaction scheme, the breaking of the carbon-bromine bond (step 13′) in the polarized molecules of the addition compound of antimony tribromide with benzyl bromide is also assumed to be the slowest step among other reaction steps. This mechanism would lead to the following kinetic expression:

$$R=k[S:SbBr_3][RBr] \quad (15)'$$

In these two reaction mechanisms, the reaction steps (13) and (13)′ are considered as the rate-determining steps of the exchange reaction. The reason for reaction (13)′ to occur instead of (13) in the region of lower $[SbBr_3]$ concentrations is not clearly known. It is hoped that further investigations should be carried out in order to solve this question.

It has also been assumed that the addition compound of antimony tribromide with benzyl bromide is formed in solution. Although direct evidence has not been obtained for the formation of the addition compound, this has been assumed by the analogy with similar systems of gallium bromide with alkyl bromides in solution.[1-6]

Acknowledgement. The neutron irradiation of ammonium bromide was carried out in the nuclear reactor, TRIGA-III, of the Korea Advanced Energy Research Institute, Seoul, Korea. This assistance is gratefully acknowledged. One of the authors (S.H.R.) wishes to express his sincere appreciation to the Korea Science and Engineering Foundation for granting a Graduate Scholarship to him.

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Effect of Poly(vinyl alcohol) on the Thermally Induced Conformational Change of Poly(D-Glutamic acid)

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In relation to denaturation of proteins, thermally induced conformational change of poly(D-glutamic acid) was studied in the presence of poly(vinyl alcohol) at low pH, where poly (D-glutamic acid) undergoes a helix-to-β transition without any other polymer. In a dilute solution, poly(vinyl alcohol) enhanced the α-to-β_1 transition of poly(D-glutamic acid) due to intermolecular interaction between the two polymers. On the other hand, this conformational change was interrupted to a large extent in a concentrated solution, due to the interpenetration of poly(vinyl alcohol) chain into poly(D-glutamic acid) chain which prevented the intramolecular association of poly(D-glutamic acid) chain. A conformational change from β_1 to β_2 of poly(D-glutamic acid) was observed for the films obtained by casting during annealing the mixture solutions. The β_2 content in the cast film increased with increasing poly(vinyl alcohol) content in the mixture.

Interoduction

In the previous paper[1], we reported the interaction between PGA and PVA as a model for polypeptide/polysaccharide complex formed in biological systems. It was found that the interaction due to hydrogen bonding and the mutual in-

terpenetration of PGA and PVA occurred during aging and casting the mixture solution. This result added an important information on the intermolecular interaction between biopolymers to other works on the ionic interaction between polymers in very dilute solutions[2-27]. In other words, the interpolymer interaction due to hydrogen bondings may play an important role in rather concentrated solution or gel of such biological systems as connective tissues in which ionic polymer interactions are also acting to some extent. The interpolymer interaction due to hydrogen bonding in a concentrated solution or in gelly state can be examined during casting a dilute solution to the solid state where the interaction in question may be enhanced. We are also interested in the thermal behavior of polypeptides which is well known as denaturation of proteins. From this viewpoint, we studied the thermal-induced conformational transition of PGA in the presence of PVA during annealing and casting the solution.

Experimental Part

Poly(D-glutamic acid) (PGA). PGA was prepared from γ-methyl-D-glutamate as the starting material in the following way. γ-Methyl-D-glutamate N-carboxy anhydride [D-methyl 3-(2,5-dixo-1-oxa-3-aza-4-cyclopentyl) propionate] was first prepared by the reaction of γ-methyl-D-glutamate and trichloromethyl chloroformate in dry tetrahydrofuran at 45° C according to the method reported previously[28]. The amino acid N-carboxy anhydride (*M*) was polymerized in dioxane at 30 °C using triethylamine as the initiator (*I*) at the mole ratio, [*M*]/[*I*] of 50. A given amount of the as-polymerized solution was used for the characterization of the resultant poly (γ-methyl-D-glutamate) which was collected as precipitate by pouring the solution into a large amount of methanol. The other portion of the as polymerized solution was diluted with dioxane to 500 cm³ of 2 wt% polymer solution, into which 3.64 g of sodium hydroxide [1.3 times of the residual moles of poly (γ-methyl-D-glutamate)], which had been dissolved in 30 cm³ of water and 50 cm³ of methanol, was dropwise added with stirring. Immediately the hydrolysis product, poly(D-glutamic acid) sodium salt began to precipitate and the turbidity increased with addition of the sodium hydroxide solution. The reaction was carried out for 24 h at room temperature. Then the precipitate was collected by filtration, washed with methanol several times and dried in vacuo. About 10 g of PGA sodium salt thus obtained was dissolved in 200 cm³ of water. After filtrating the insoluble fraction off, the filtrate solution was adjusted to pH 3 by slow addition of 1 *N* HCl aqueous solution with stirring, which gave rise to the precipitation of PGA. The PGA was collected by centrifugation after keeping the above solution for 24 h, washed with a small amount of water. This washing and centrifugation were repeated several times, having given rise to gellike PGA, which was then freeze-dried and used for the study. The molar mass of the poly (γ-methyl-D-glutamate) was estimated as 1.0×10^5 from the following equation[29] and accordingly the degree of polymerization was calculated as *ca.* 700. $[\eta]^{25}_{DCA}=2.24\times10^{-3}$ $Mw^{0.58}$, where DCA denotes dichloroacetic acid.

Poly(Vinyl Alcohol) (PVA). PVA with degree of polymerization of ca. 2000 and OH content of 98.5 mole% was purchased from Wako Pure Chemicals Co.

Preparation of PVA/PGA mixed Solution. 0.2g of PGA was dissolved in 14.2 cm³ of aqueous solution of 0.1 *N* NaOH with stirring for 24h. The resulting solution gave rise to pH 7.9-8.0 and the degree of neutralization of *ca.* 0.9. Solutions with certain pH values for the subsequent uses were prepared by adding aqueous solution of 0.1 *N* HCl to the above mother solution. 100 cm³ of aqueous solution 2 wt% PVA was prepared by dissolving the polymer at 80-90° C and used as another mother solution for the subsequent uses. Equal volumes of the PGA solution and the PVA solution, which had been diluted and adjusted to a given pH, were mixed so as to give a constant concentration of PGA independent of the concentration of PVA. The mixing of the two solutions underwent a slight increase of 0.05~0.1 in pH due to dilution of the PGA solution, indicating that PVA did not affect pH upon mixing the solutions. Thus, the pH of the PGA solution before mixing was adjusted 0.05~0.1 lower than pH to be obtained after mixing.

Heat Treatment of the Solution of the Polymer Mixture. The heat treatment was carried out in an glass ample using *ca.* 0.1 cm³ of the solution for the CD and IR measurements and 20 cm³ of the solution for the viscometry.

IR Measurement. The heat-treated solution was cooled for 1 h to room temperature and cast onto a AgCl disk, using *ca.* 0.15 cm³ of the solution, in a dark room. The IR spectrum was recorded in a JASCO IR-G Spectrophotometer under a condition of *ca.* 95% transmittance at 1900 cm^{-1} to estimate quantitatively optical densities of the absorption bands of PGA.

CD Measurement. The CD spectrum was recorded for the heat-treated and cooled solution using a quartz cell with a path length of 0.10 mm in a JASCO J-20 Spectropolarimeter.

Viscometry. The viscosity of the heat-treated solution was measured using an Ostwald viscometer at 25 °C.

Electron Microscopy. A drop of heat-treated solution was put and dried on carbon film coated onto a copper sheet mesh and Pt-Pd was shadowed at an angle of 30 °C. The morphology was observed in a JEOL JEM-7 electron microscope.

Results and Discussion

The Effect of PVA in the α-Helical Region

1. PGA Conformations in Solution. CD spectra shown in Figure 1 were recorded for the solutions of the PVA/PGA mixture with various residual mole ratios of the two polymers, [VA]/[GA] annealed at 105 °C for 0, 1 and 5h. The concentration of PGA in the solution was chosen as 0.016 residual moles/*l* in all cases studied in the α-helix region, *i.e.*, pH of 4.0. All the CD spectra before annealing indicate the α-helical PGA with 100 % helicity estimated from the ellipticity at 222 nm, $[\theta]_{222}$ of *ca.* 4.0×10^4 deg·cm²·dmol⁻¹. However, the maximum value of the ellipticity, $[\theta]_{max}$ decreases and the wavelengh for $[\theta]_{max}$ shows blue-shifts from 222 nm to 216 nm with increasing annealing time. This

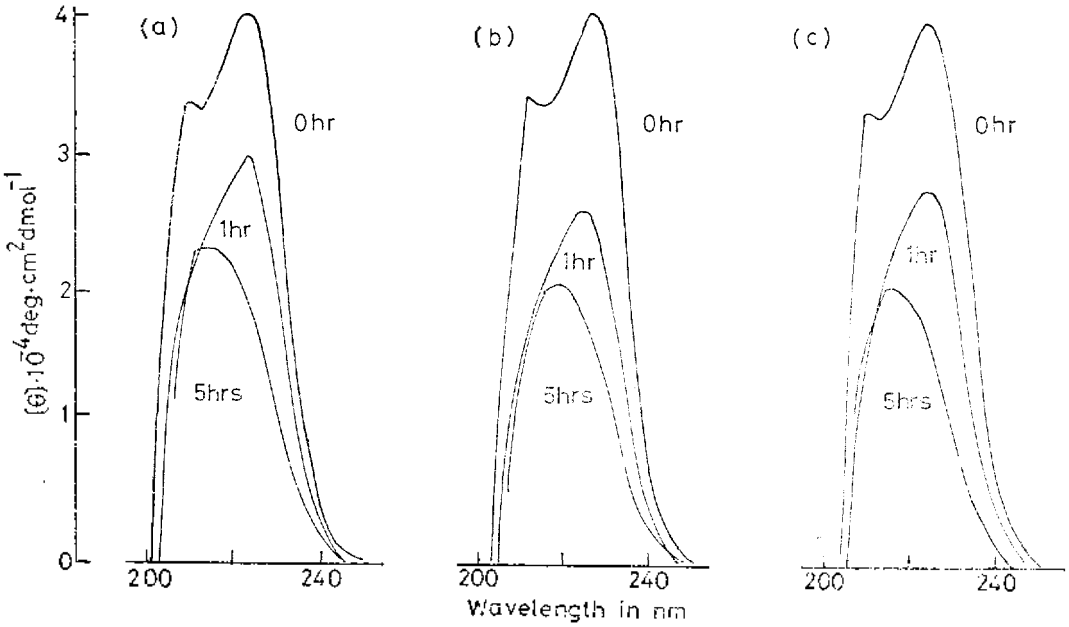

Figure 1. CD spectra of the pH 4.0 poly (vinyl alcohol) (PVA)/poly (**D**-glutamic acid) (PGA) mixed solutions after keeping the solutions at 105°C for various times. Concentration of PGA was 0.016 unit mol/**1**. Residual mole ratio, [VA]/[GA]=0/1 (a), 0.5/1 (b), and 2/1 (c).

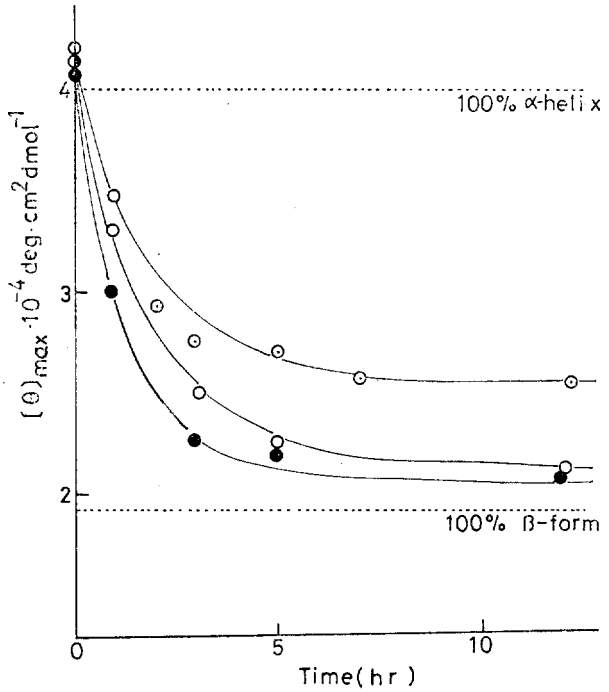

Figure 2. Ellipticity $[\theta]_{max}$ of poly (**D**-glutamic acid) (PGA) plotted against the annealing time at 105°C for the pH 4.0 PGA/poly(vinyl alcohol) (PVA) mixed solutions. Concentration of PGA was 0.016 unit mol/*1*. Residual mole ratio, [VA]/[GA]= 0/1 (○), 0.5/1 (●), and 2/1 (⊙). Wavelength for $[\theta]_{max}$ was from *ca.* 222 nm to 215 nm.

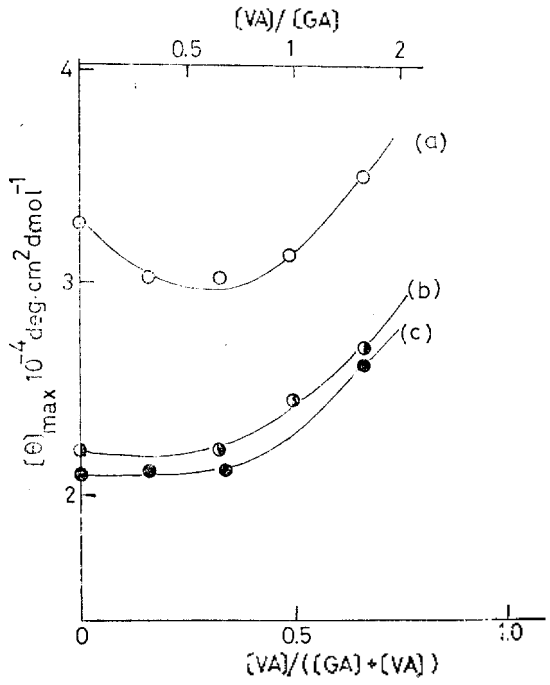

Figure 3. $[\theta]_{max}$ of poly (**D**-glutamic acid) (PGA) plotted against the fraction of poly(vinyl alcohol) (PVA) as a function of annealing time at 105°C for the pH 4.0 PVA/PGA mixed solutions. Concentration of PGA was 0.016 unit mol/*1*. Annealing time: 1 h (a), 5h(b), and 12 h (c).

indicates a conformational transition of PGA from the α-helix to the β_1-structure during annealing, which is dependent on [VA]/[GA]. The thermo-induced conformational transition of PGA from the α-helix to the β_1-form at pH 4.0 is consistent with the IR result reported by Itoh *et al.*[30] on poly (**L**-glutamic acid) itself in a gel state.

The CD spectra obtained were tried to be analyzed in terms of a linear combination of three reference conformations (α-helix, β-form denoted as β_1-form in this paper, and random coil) of poly (**L**-lysine) as was applied to several proteins[31] and poly (β-benzyl-L-aspartate)[32]. The fit to the

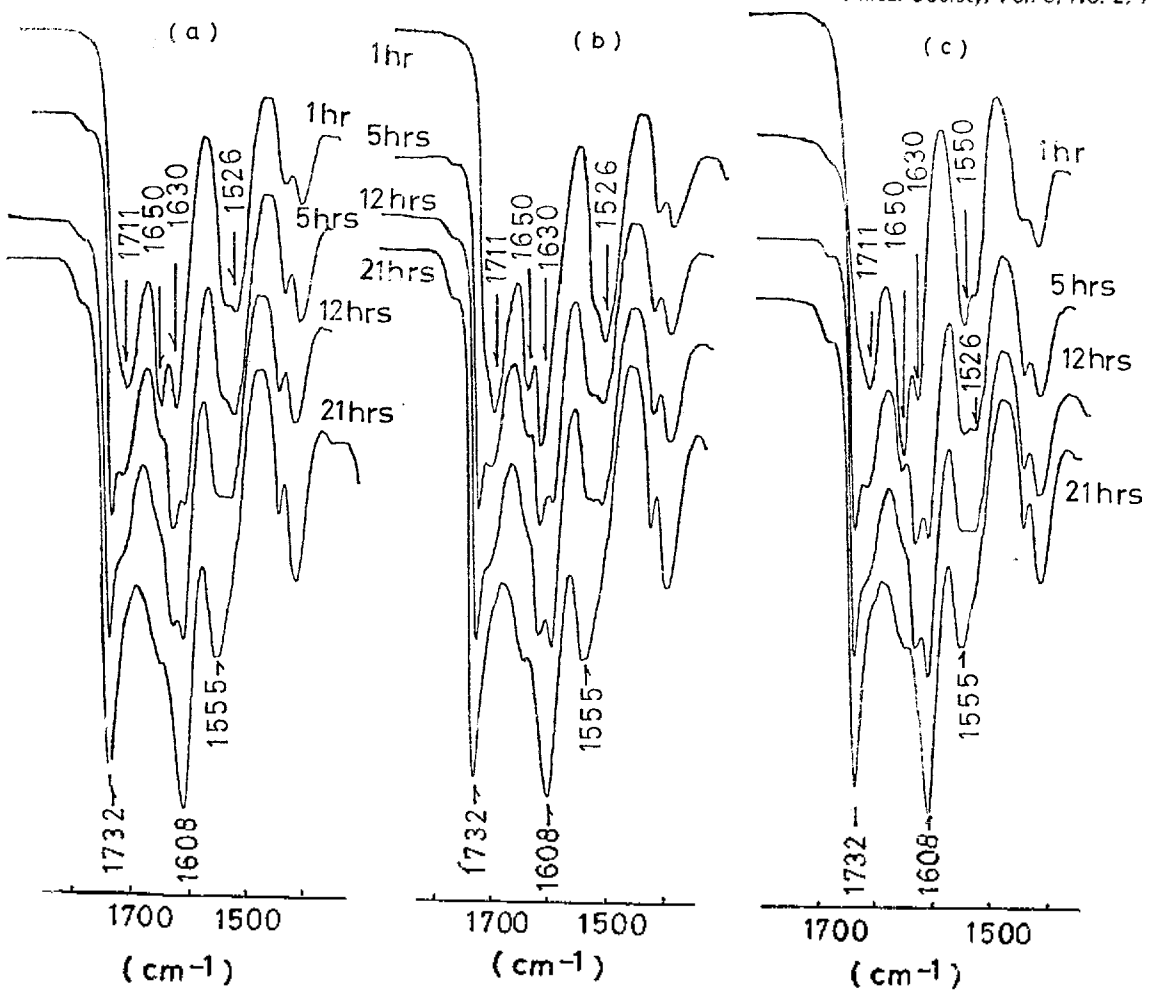

Figure 4. IR spectra of the films cast from the pH 4.0 poly (vinyl alcohol) (PVA)/poly (**D**-glutamic acid) (PGA) mixed solutions after keeping the solutions at 105°C for various times. Concentration of PGA was 0.016 unit mol/*l*. Residual mole ratio, [VA]/[GA]=0/1 (a), 0.5/1 (b) and 2/1 (c)

experimental curve, however, was not good in the present case, probably due to a trace of precipitates observed during annealing. Therefore, the α-helix and β_1-form contents were semiquantitatively estimated from the $[\theta]_{max}$ value and are plotted against annealing time in Figure 2 for the ratios [VA]/[GA] values. $[\theta]_{max}$ decreases drastically from the value of *ca.* 4.0×10^4 in the beginning with annealing time and becomes almost constant after 5 h, the value being *ca.* 2.1×10^4 for [VA]/[GA] of 0/1 and 0.5/1 and *ca.* 2.5×10^4 for [VA]/[GA] of 2/1. This implys that the transition of the PGA chains from the α-helix to the β_1-form takes place rather slowly during the annealing. It is of interest that the transition in the initial stages of annealing occurrs faster for [VA]/[GA] of 0.5/1 than for PGA.

The polymer composition dependence of $[\theta]_{max}$ was examined in more detail as a function of annealing time and the results are shown in Figure 3. As is evident from Figure 3(a), the conformational transition of PGA accompanied by the annealing within 1h is accelerated by PVA in the systems of [VA]/[GA] less than 1.3 and $[\theta]_{max}$ after 1 hr of annealing is as low as *ca.* 3.0×10^4 for [VA]/[GA] of 0.2 and 0.5. At annealing times longer than 5 h, $[\theta]_{max}$ is independent of the composition of the two polymers up to [VA]/[GA] of 0.5 and then increased with increasing [VA]/[GA] [Figure 3(b) and (c)]. This result may suggest that the nucleation of the β_1-structure is accelerated by a small amount of PVA, but the nucleation and growth of the β_1-structure are significantly retarded by PVA chains in the systems with high [VA]/[GA] values.

2. Conformations of PGA in Cast Films. Figure 4 shows IR spectra of the films of the various PVA/PGA compositions cast onto AgCl disks after annealing the solutions. In all the cases, the IR spectra clearly indicate that the conformational transition is depending on the annealing time before the casting as revealed by the relative intensities of the absorptions characteristic of the α-helix (at 1650 cm^{-1}), the β_1-form (at 1630 cm^{-1}) and the β_2-form (at 1608 cm^{-1}). As for the β_2-form, Itoh *et al.*[10] reported from the X-ray study that the wet slurries of PGA with the β_1 and β_2 forms in water gave the 001 spacings between pleated sheets of 0.903 nm and 0.783 nm, resp., indicating the difference in the PGA side chain packing between the two β conformation.

In Figure 5 are plotted against the annealing time for the various compositions. It is obvious from the OD_{1630}/OD_{1650} ratios that the β_1 contents in the cast film increase with increasing annealing time before the casting and are in the following order of [VA]/[GA] for all the annealing times: 0.5/1>0/1>2/1. This result is quite consistent with the just mentioned results of the α to β_1 transition observed in the solution. The OD_{1630}/OD_{1650} ratio was not estimated for

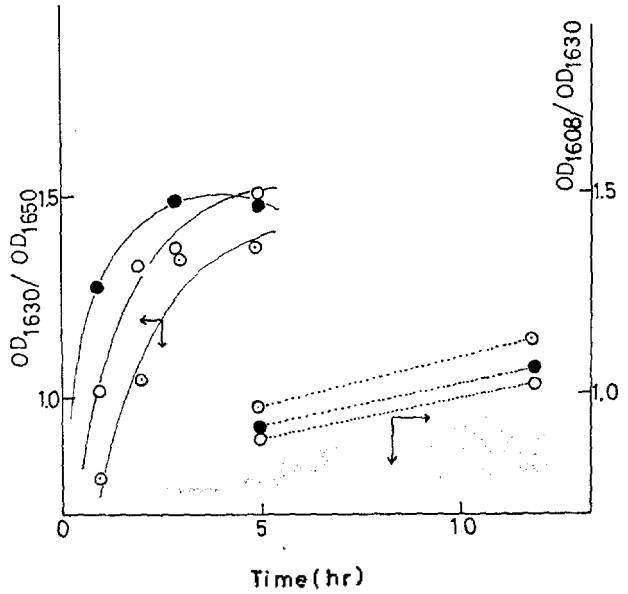

Figure 5. Plots of optieal density (OD) ratios of 1630 Cm^{-1} to 1650 cm^{-1}, and of 1607 cm^{-1} to 1630 cm^{-1} for the films obtained by casting the pH 4.0 poly (vinyl alcohol) (PVA)/poly (**D**-glutamic acid) (PGA) mixed solutions after annealing the solutions at 105°C for various times. Concentration of PGA was 0.016 unit mol/*l*. Residual mole ratio,[VA]/[GA]=0/1(○), 0.5/1 (●) and 2/1(⊙)

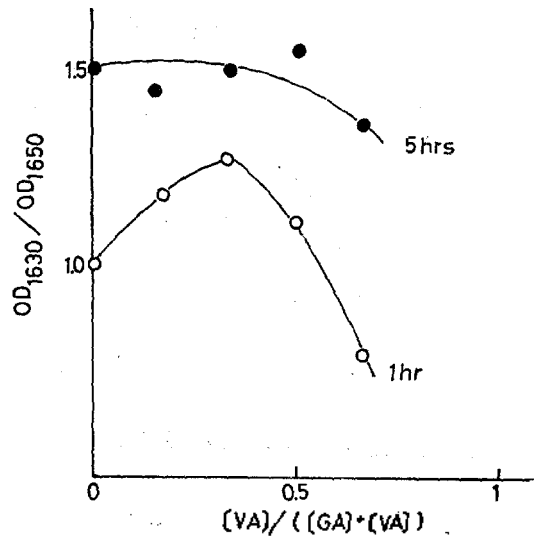

Figure 6. Plots of optical density (OD) ratio of 1630 cm^{-1} to 1650 cm^{-1} for the films cast from the aqueous pH 4.0 poly (vinyl alcohol) (PVA)/poly (**D**-glutamic acid) (PGA) mixed mixed solutions after annealing the solutions at 105°C for 1 h (○)and 5 h (●).Concentration of PGA was 0.016 unit mol/*l*.

the annealing times longer than 5 h since the IR absorption at 1650cm^{-1} became a very weak shoulder. On the other hand, the OD_{1608}/OD_{1630} ratios could be estimated for the samples cast after annealing the solutions for 5 and 12h, resp. The absorption at 1630 cm^{-1} became unobservable for the cast sample of the annealing time of 21 h, indicating the formation of only the β_2-structure. The change in OD

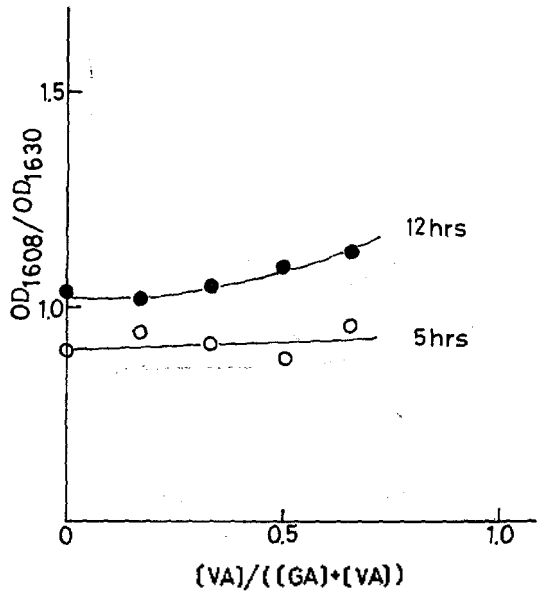

Figure 7. Plots of optical density (OD) ratio of 1608cm^{-1} to 1630 cm^{-1} for the films cast from the pH 4.0 poly-(vinyl alcohol) (PVA)/poly (**D**-glutamic acid) (PGA) mixed solutions after annealing the solutions at 105°C for 5 h and 12 h.Concentration of PGA was 0.016 unit mol/*l*.

$_{1608}/OD_{1630}$ with the annealing time indicates that the β_1 to β_2 transition of PGA is accelerated by the coexisting PVA.

The above changes of the optical density ratios with the annealing time are also evident from Figure 6 and 7. Figure 6 shows the OD_{1630}/OD_{1650} ratios for the cast films plotted against the polymer composition for the various annealing times before the casting. It is seen that OD_{1630}/OD_{1650} shows a maximum at [VA]/[GA] of 0.5 for the annealing time of 1 h and decreases monotonously with increasing [VA]/[GA] for the annealing time of 5 h. On the other hand, OD_{1608}/OD_{1630} shows a monotonous increase with the increasing [VA]/[GA] ratio.

3. Morphology of Precipitate. The precipitation of the polymer mixtures occurred and the amount of the precipitate increased with time during annealing their solution. The effect of PVA on the conformation of PGA during the annealing may imply that an interaction is acting between the two polymers. In order to clarify this, the morphology of the precipitates was examined by electron microscopy. Figure 8 shows the electron micrographs of the precipitates formed after 32 h-annealing at 105° and subsequent 5 h-keeping at room temperature. From the IR measurement, the precipitates are considered to take the β_2-structure irrespectively of the polymer composition. The precipitates consisted of in all the cases are seen from Fgirue 8, which may be characteristic of the β-structure. It is also evident from the micrographs that PVA and PGA are completely mixed with each other, since the precipitates are seen to contain more PVA in the case of [VA]/[GA] of 2/1 than in the case of 0.5/1.

4. Mechanism of Conformational Changes During Annealing and Casting. In order to discuss the mechanism of the conformational changes of the PGA/PVA mixture during annealing and casting, the sizes and numbers of PGA and

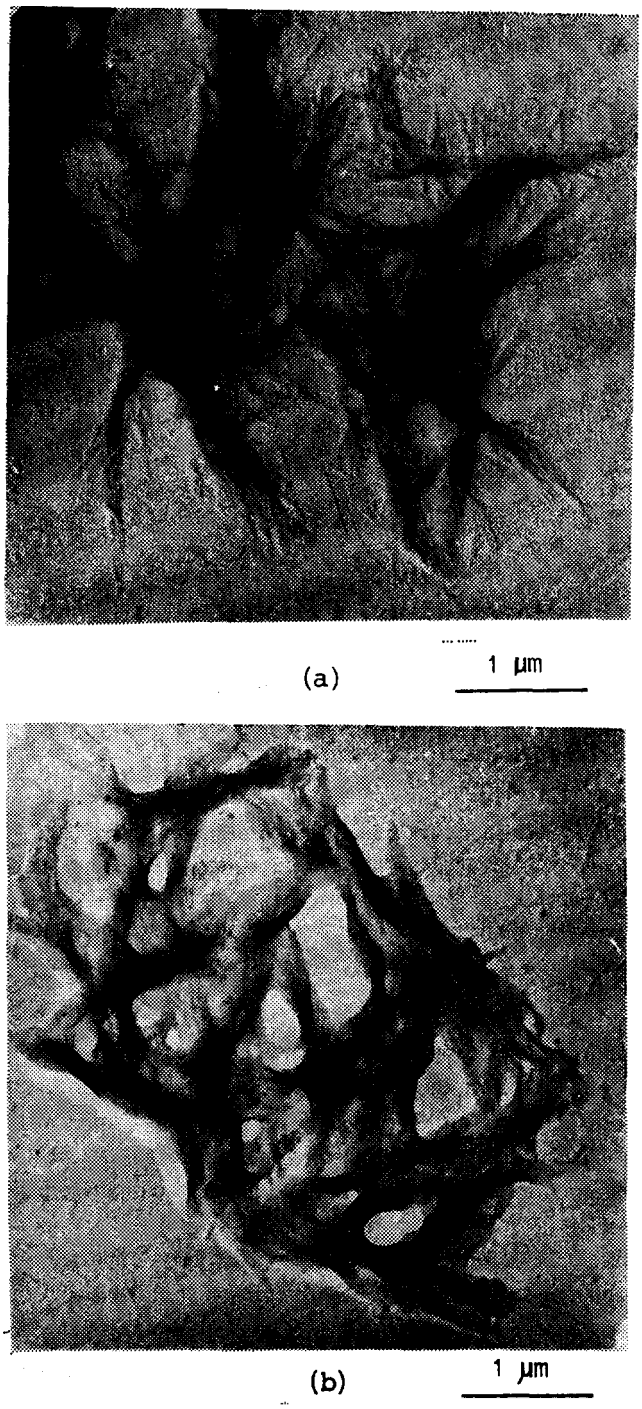

Figure 8. Electron micrographs of precipitates formed after keeping the pH 4.0 poly (vinyl alcohol) (PVA)/poly (D-glutamic acid) (PGA) mixed solutions for 32 h at 105°C and 5 d at room temperature. Concentration of PGA in solution was 0.016 unit mol/*l*. Residual mole ratio. [VA]/[GA]=0.5/1 (a) and 2/1 (b)

PVA molecules in the solution should be taken into consideration. The extended chain lengths of the α-PGA and PVA molecules are calculated as *ca.* 1000 Å and *ca.* 5000 Å, resp. from the degrees of polymerization (*ca.* 700 and *ca.* 2000, resp.) and the residual translations (1.5 Å and 2.5 Å[33], resp.) of the two polymer. The α-PGA chain is dissolved as a rod-like molecule in the solution of pH 4.0, while the PVA chain is assumed to be in a random coil conformation, suggesting that the radius of gyration of PVA is less than the extended length of PGA. In the solution of the mixture of [VA]/[GA] of 1/1, for example, the ratio of the numbers of PVA chain molecules to those of PGA is *ca.* 7/20. Taking into consideration the probability of the PVA and PGA chains to be found in a small volume of the solution, therefore, one PVA molecule is surrounded with many PGA molecules.

During annealing the solution of this mixture, the PGA molecules change their conformation from the α-helix to the β_1-form due to the destabilization of the intramolecular hydrogen bonding of the α-helix and the stabilization of the intermolecular hydrogen bondings of the β_1-form. This α-to-β_1 transition was apparently accelerated by a small amount of PVA in the initial stages of annealing. This may be accounted for by the association of the PGA molecules by the longer PVA molecules (through the intermolecular hydrogen bonding) in the solution, where the intermolecular collision occurrs more frequent between the neighboring PGA molecules than between the PGA and PVA molecules, which may enhance the nucleation of the β_1-structure of PGA.

Contrarily, the α-to-β_1 transition was retarded to some extent in the cases of high [VA/([GA] ratios. This can be accounted for by the decrease in the frequency of the collision between the PGA molecules themselves with increasing [VA]/[GA] ratio.

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Direct Observation of an Antihomoaromatic Bicyclooctadienyl Cation

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The question of the bicyclohomoaromatic stabilization and destabilization is examined. The chemistry of bicyclo (3. 2. 1.) octa-3, 6-dienide anion has been studied on order to test these concepts. The bicyclooctadienide anion is shown to be stable delocalized ion which undergoes a facile proton-deuterium exchange reaction. The solvolysis of bicyclo (3.2.1) octa-3,6 -dienyl p-nitrobenzoate is much slower than the monoene analog. We have made direct observation of the bicycloocata-dienyl and octenyl cations by ^{19}F-nmr spectroscopy, and were able to demonstrate that the bicyclooctadienyl cation was bishomoantiaromatic.

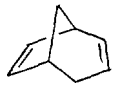
Introduction

The stabilization of carbonium ions and carbanions by means of cyclic charge delocalization or aromaticity is well documented and universally accepted.

The cyclopropyl cation **1**[1] and the cyclopentadienyl anion **2**[2] are just two examples of a large number of the wellknown carbonium ions and carbanions whose unusual stability is thought to be due to this effect.


1


2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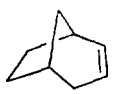
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Recently many evidences have been presented in support of a new stabilization mechanism for carbonium ions and carbanions, generally known as homoaromaticity[3].

The 7-norbornenyl cation **3** and the bicyclooctadienyl anion **4** are considered to be homologs of **1** and **2**, respectively, and their unusual stability has been attributed to homoaromaticity.

Since the early work on the solvolysis of the cholestryl chloride[4], Winstein and his coworkers have been concerned about the long-range stabilization of ionic centers by remote carbons. One of the most fascinating concepts to develop from this interest was the theory of homoaromaticity[5]. Goldstein[6] used MO symmetry arguments to extend the concept of the homoaromatic ions to bicycloaromatic species.

Bicyclo(3.2.1)octa-3,6-diene(5), previously reported by Brown and Occolowitz[7], is more reactive compared with the monoene analog **6** in allylic proton-deuterium exchange in DMSO-*t*-BuOK. Molecular orbital symmetry arguments have suggested that anion **4** should also have enhanced stability. The ^{1}H-nmr spectrum of the bicyclohomopentadienide anion **4** has been reported by Winstein[8], and all of the features are in accordance with the delocalized six-π-electron bishomaromatic species with appreciable ring currents. The rates of the solvolysis of the *p*-nitrobenzoates of bycyclo[3.2.1]octa-3,6-dienyl(7) and bicyclo[3.2.1] octenyl (8) in aqueous acetone have been studied by Diaz and his coworkers[9].

Here, the 6,7-double bond in **7** makes the intermediate cation a four-π-electron antiaromatic species and, therefore, retards the reaction in contrast with monoene analog **8**.

It occured to us that a study of the ^{19}F-nmr and ^{13}C-nmr spectra of the *p*-fluorophenyl bicyclooctadienyl cation **9** and especially comparison of these spectra with those of the *p*-fluorophenyl bicyclooctenyl cation **10** would be ideally suited in providing the information about long-