furan are near those predicted earlier from the melting of poly[$(Ala)_2$-Lac]. We are currently reexamining our theoretical predictions of the circular dichorism thought to be exhibited by polymers in the R_{10} helical conformation.

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Registry No. poly(Ala-Lac) (homopolymer), 53777-54-1; poly(Ala-Lac) (SRU), 53745-64-5; poly(Val-Lac) (homopolymer), 54664-24-3; poly(Val-Lac) (SRU), 54711-82-9; poly[$(Leu)_2$-Lac] (homopolymer), 78426-69-4; poly[$(Leu)_2$-Lac] (SRU), 78426-76-3; poly(Ala-Hiv) (homopolymer), 78426-67-2; poly(Ala-Hiv) (SRU), 78437-72-6.

References and Notes

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Conformational Transition of a Water-Soluble Poly(diacetylene): Potassium Salt of Poly[4,6-decadiyne-1,10-diol bis([carboxymethyl]urethane)]

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ABSTRACT: The conformational transition of poly(diacetylene), $(=RC-C\equiv C-CR=)_x$, was studied on a poly(electrolytic diacetylene), poly(3KAU) (R = $-(CH_2)_3OCONHCH_2COOK$), in aqueous solution by measurements of visible absorption spectra, potentiometric titration, and shear rate dependence of intrinsic viscosity. Visible absorption spectra for the 10^{-2} M solutions of poly(3KAU) showed that the effective conjugation length of the main chain becomes longer as the degree of neutralization α' decreases. Correspondingly, the color of the solutions changed from yellow to violet with decreasing α'. Potentiometric titrations resulted in distinct conformational transition curves similar to those observed for poly(methacrylic acid) and poly(α-glutamic acid). The enthalpy change ΔH of the conformational transition was estimated from the titration experiments to be −8 kJ per carboxylic acid group. These results are interpreted by a planar–nonplanar conformational transition proposed by Patel. The intrinsic viscosity $[\eta]$ for the violet solutions of poly(3KAU) in the low-α' region strongly depended on the shear rate, while $[\eta]$ for the yellow solutions in the high-α' region did not. This may be explained by the fact that the whole chain conformation is rodlike in the low-α' region and coillike in the high-α' region.

Introduction

Poly(diacetylenes) have conjugated backbones of a resonance admixture of acetylenic $(=RC-C\equiv C-CR=)_x$ and butatriene $(-RC=C=C=CR-)_x$ structures, exhibiting a characteristic color.[1] Although poly(diacetylenes) had been thought to be insoluble in common organic solvents because of their conjugated backbone, Patel succeeded in synthesizing a series of soluble poly(diacetylenes), in which R = $-(CH_2)_nOCONHCH_2COO(CH_2)_mCH_3$ with n = 1–4 and m = 1 or 3.[2] They are referred to as poly(nACMU), standing for the number of methylene groups, n, and [(alkoxycarbonyl)methyl]urethane side chains. Patel et al. also found that the yellow to orange color of the solution of poly(3BCMU) (n = 3, m = 3) and poly(4BCMU) (n = 4, m = 3) changes to blue and red on addition of a poor solvent, respectively. They attributed this color change to a conformational transition of poly(nACMU). The conformation in a poor solvent such as $CHCl_3/n\text{-}C_6H_{14}$ mixture was thought to be planar, maintained by hydrogen bonds between the —NH and —C=O groups in neighboring side chains, while the conformation in a good solvent such as $CHCl_3$ was believed to be nonplanar because of the destruction of the hydrogen bonds. This conformational transition influences the effective conjugation length of the main chain and is visible as a color change of the solution. In addition, Patel et al. suggested that the color transition is a purely single-chain phenomenon, since it is completely independent of polymer concentration.[3] However, Wenz and Wegner measured the molecular weight of poly(3BCMU) by light scattering and observed an extremely high value in the blue solution as compared with that in the yellow solution.[4] From this result, they concluded that the transition to the blue form should be attributed to an aggregation phenomenon and not a transition occurring within a single molecule.

On the other hand, several studies have been carried out with respect to the overall conformation of poly(diacetylene) in solution. First, Patel and Walsh reported that poly(3BCMU) has an extended chain conformation in the yellow solution as well as in the blue solution on the basis of their finding that the reduced viscosities of 0.05% solutions in $CHCl_3$ and $CHCl_3/n\text{-}C_6H_{14}$ mixtures are the same.[5] In contrast, our study of non-Newtonian intrinsic viscosities of these solutions showed that poly(3BCMU) assumes a more extended conformation in $CHCl_3/n\text{-}C_6H_{14}$ mixtures than in $CHCl_3$.[6] Recently, Lim et al. carried out quasi-elastic light scattering and spectroscopic studies on poly(4BCMU) and reported that the red-to-yellow change of poly(4BCMU) solutions corresponds to the rod-to-coil conformational transition, which is interpreted as a single-chain phenomenon.[7] As mentioned above, there are some contradictions with regard to the solution properties of poly(*n*ACMU) examied so far.

Poly(3BCMU) can be converted to a polyelectrolyte, poly[4,6-decadiyne-1,10-diol bis([carboxylmethyl]urethane)] [abbreviated as poly(3HAU), R = $-(CH_2)_nOCONHCH_2COOH$], by hydrolyzing the ester bonds of the side chains. Patel et al. reported that the potassium salt of poly(3HAU), i.e., poly(3KAU), R = $-(CH_2)_3OCONHCH_2COO^-K^+$, is soluble in water and that the solution changes its color from yellow to violet by adding salt and/or by lowering pH.[8] This means that poly(3KAU) in aqueous solution undergoes a conformational transition similar to that of poly(3BCMU). Since this poly(electrolytic diacetylene) is highly soluble in water, it is a convenient model system for studying the solution properties of poly(diacetylenes) with urethane-substituted side chains. In this article, the conformational transition of poly(3KAU) is studied by measurements of visible absorption spectra, potentiometric titration, and shear rate dependence of intrinsic viscosity. Furthermore, we carry out thermodynamic analysis of the titration data and evaluate some thermodynamic quantities in order to elucidate the nature of the conformational transition.

Experimental Section

Materials. The synthesis of 3BCMU monomer has been described elsewhere.[6] The monomer was sealed in ampules after degassing under vacuum of 10^{-4} mmHg and allowed to polymerize by ^{60}Co γ-ray at room temperature. The dose rate was 0.3 Mrad/h and the total dose was 50 Mrad. The unreacted monomers were removed by extracting with acetone. The polymer was observed on a gel permeation chromatograph (GPC; Model 801A, Toyo Soda Manufacturing Co.) to estimate its average molecular weight and molecular weight distribution by using $CHCl_3$ as a carrier solvent and narrow-distribution polystyrenes (TSK polystyrene, Toyo Soda Manufacturing Co.) as elution standards. The polystyrene (PS) reduced number-average molecular weight M_n and weight-average molecular weight M_w were 6.80×10^4 and 6.84×10^6, respectively. The M_w/M_n was about 100, and the poly(3BCMU) sample has a very broad molecular weight distribution.

Poly(3KAU) was prepared by hydrolyzing the side chains of the poly(3BCMU) with 0.2 N KOH methanol solution under continuous stirring.[8] The produce was recovered by filtration as red precipitates. The precipitates were redissolved in distilled and reionized water, freeze-dried, and stored under N_2 atmosphere. The poly(3HAU) was obtained as violet precipitates by adding excess HCl to the poly(3KAU) aqueous solution.

The degree of hydrolysis of poly(3BCMU) was determined to be 0.946 by potentiometric titration. A similar value has been reported for poly(acrylic acid) obtained by the hydrolysis of ester groups.[9]

Visible Absorption Measurements. Visible absorption spectra of poly(3KAU) aqueous solutions with 10^{-2} M KCl were measured at various degrees of neutralization. The measurements were carried out on a Jasco spectrometer (Nihon Bunko Co., Model UVDEC-5A) or a recording spectrometer (Hitachi Seisakusho Ltd., type 323) with a quartz cell of 1-cm optical path length.

The degree of neutralization α' was controlled by adding a known amount of HCl to the completely neutralized polymer solution. The required value of HCl was calculated on the basis of the weight of dry poly(3KAU). The concentration was about 2.3×10^{-5} mol/L. All the solutions were prepared under a nitrogen atmosphere.

Potentiometric Titrations. Potentiometric titration experiments were carried out under CO_2-free nitrogen with a SelectIon analyzer (Beckman Instrument Co., type 5000) equipped with a Futura 10-mm combination electrode (39504). Standardization was checked with pH 4.01 and 6.86 buffer solutions at 25 °C. The temperature was controlled to within ±0.1 °C of the desired value by circulating thermostated water around the titration vessel.

For titration experiments, poly(3KAU) was first dissolved in 10^{-3} M KOH solution, to which water or aqueous KCl solution was added to adjust the added-salt concentration. The polymer concentration was $(7.4 \pm 0.2) \times 10^{-3}$ mol/L. Distilled water was deionized by passing it through an ion-exchange resin column before use. The polymer solutions were titrated with 0.2 N HCl with a microhand buret (Metrohm AG, E457).

The degree of dissociation α was estimated from the degree of neutralization α' according to the equation

$$\alpha = \alpha' + ([H^+]_{BL} - [OH^-]_{BL})/[COOH] \qquad (1)$$

where [COOH], $[H^+]_{BL}$, and $[OH^-]_{BL}$ refer to the concentrations of carboxylic acid groups in the polymer, free hydrogen, and hydroxyl ions, respectively, of which the latter two were determined by a blank titration for the salt solution containing no polymer.

Viscometry. Intrinsic viscosities were determined as a function of shear rate and the degree of neutralization for poly(3KAU) aqueous solutions at 25 °C by using a four-bulb spiral viscometer. The shear rates for each bulb were 91, 65, 35, and 13 s^{-1} for pure water at 25 °C, respectively.

Solutions were prepared by the same procedure as those for visible absorption spectroscopy, stirred for 3 days under a nitrogen atmosphere, and filtered through a Teflon filter of 2.0-μm pore size to remove dust just before use.

Results and Discussion

Degree of Neutralization Dependence of Absorption Spectra. Figure 1 shows absorption spectra of 10^{-2} M KCl solutions of poly(3KAU) with different degrees of neutralization α'. The color of poly(3KAU) solution at α' = 1.0 is yellow, while it changes to red around $\alpha' \simeq$ 0.8–0.9, to red violet at α' = 0.7, and finally to violet at α' = 0.6. In the spectrum of the solution at α' = 1.0, there are three characteristic absorption maxima at 480, 510–530, and 590 nm. As α' decreases, the height of the peak at 480 nm decreases, but the wavelength at the maximum does not vary. On the other hand, the height of the peak at 510 nm increases and the peak shifts from 510 to 530 nm as α' decreases. As α' decreases further, an additional peak

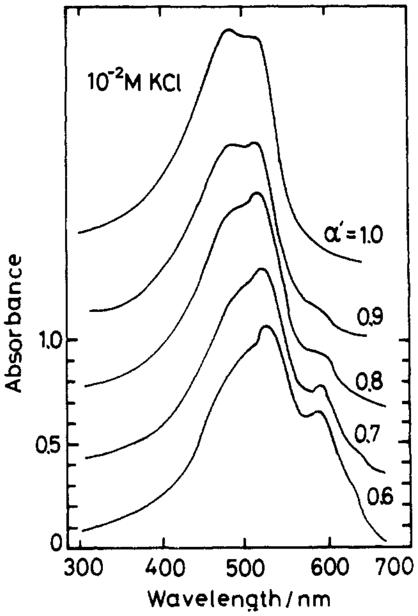

Figure 1. Absorption spectra of poly(3KAU) in 10^{-2} M KCl aqueous solution at various α'.

appears at 590 nm. This color change of poly(3KAU) solutions may be attributable to the change in the effective conjugation length, as pointed out by Patel et al.[8] In general, the wavelength of absorbed light becomes longer with increased conjugation length. Therefore, the above results mean that the conjugation length of the poly(3KAU) in solution becomes greater as α' decreases.

Dependence of Titration Curves on Added-Salt Concentration. The pH of a polyelectrolyte solution is given by[10,11]

$$\mathrm{pH} = \mathrm{p}K_0 + \log\,(\alpha/(1-\alpha)) + 0.434F(\alpha)/kT \qquad (2)$$

where $\mathrm{p}K_0$ is the intrinsic ionization constant of the ionizable group in the polyelectrolyte, and $F(\alpha)$ is a function of α, which represents an increase in the electrostatic free energy caused by addition of one more unit charge to the polyelectrolyte of α. The apparent pK can then be defined as

$$\mathrm{p}K \equiv \mathrm{pH} - \log\,(\alpha/(1-\alpha)) \qquad (3)$$

A plot of the pK against α has been found more informative than the titration curve of pH vs. α in examining a pH-dependent conformational transition. Figure 2 shows plots of pK vs. α for the solutions with added-salt concentrations, C_s, of 1.0×10^{-3}, 1.0×10^{-2}, 5.0×10^{-2}, and 1.0×10^{-1} M KCl. In all the curves, the pK value increases sharply in the region of $\alpha \leq 0.5$ and levels off in the range of $\alpha \geq 0.5$. The $\mathrm{p}K_0$ values obtained by extrapolating pK to $\alpha = 0$ are 4.30, 4.30, 4.20, and 4.10 for 1.0×10^{-3}, 1.0×10^{-2}, 5.0×10^{-2}, and 1.0×10^{-1} M KCl solutions, respectively. These values are close to those reported for poly(methacrylic acid)[12] and poly(α-glutamic acid).[13] The pK values of the 1.0×10^{-3} M KCl solution in the range of low α merge into those of the 1.0×10^{-2} M KCl solution, because C_s of the former becomes almost the same as that of the latter in the region of low α as the titration proceeds. The effect of C_s on the titration curves in Figure 2 stems from the change in the electrostatic interaction due to the shielding effect by small ions.

The pH of a polyelectrolyte solution may be also described by a modified Henderson–Hasselbalch equation[14]

$$\mathrm{pH} = \mathrm{p}K_a + n \log\,(\alpha/(1-\alpha)) \qquad (4)$$

where $\mathrm{p}K_a$ is the value of pH at $\alpha = 0.5$, and n an empirical parameter related to the intramolecular electrostatic interactions. The values of $\mathrm{p}K_a$ and n have been found to depend on the nature of the concentration of the polymer itself, and the concentration of the neutral salt in the system. The n value reflects the magnitude of the interaction between ionic groups, increasing as the interaction becomes stronger. Ordinarily, the n value is about 2 for common polyelectrolytes without neutral salts.[14] For a polyelectrolyte which exhibits a conformational transition, it is known that the n value changes at the points where the conformational transition begins and becomes complete.[15]

To study the conformational transition of poly(3KAU), we replotted the titration results by a Henderson–Hasselbalch plot, pH vs. log ($\alpha/(1-\alpha)$) plot, as shown in Figure 3. All the curves have one or two bends. That is, the curves are divided into two or three regions, I–III, from the left-hand side of the curves. Behavior similar to this is found in many polyelectrolytes such as poly(methacrylic acid) and poly(α-glutamic acid), which show a globule–coil transition and a helix–coil transition, respectively.[15,16] We

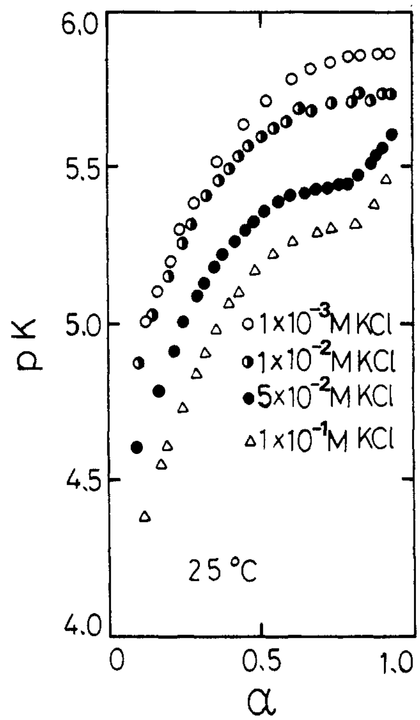

Figure 2. pK vs. α plots of poly(3KAU) aqueous solutions at 25 °C.

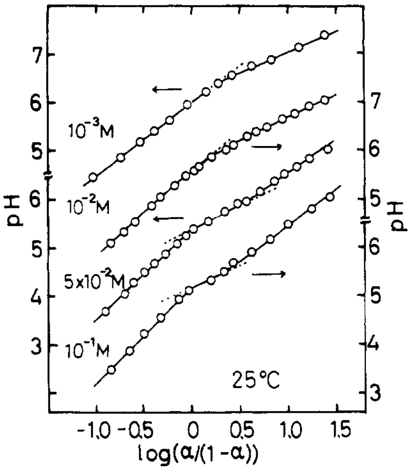

Figure 3. Henderson–Hasselbalch plots for poly(3KAU) solutions with various C_s at 25 °C.

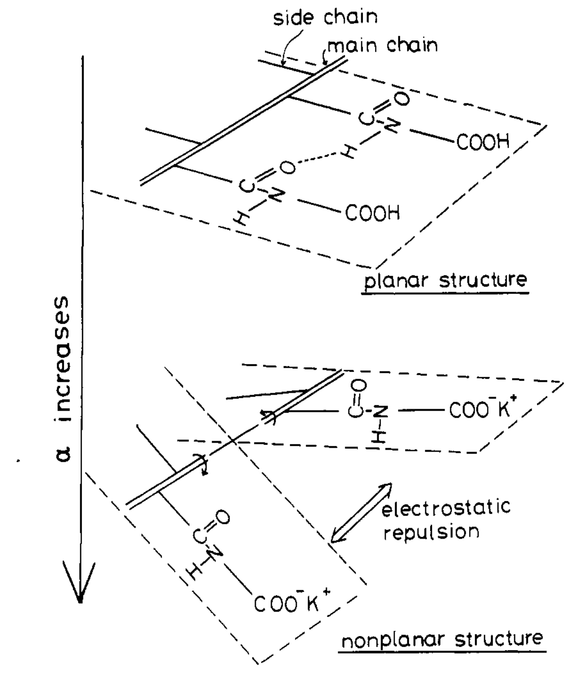

Figure 4. Schematic figure of a model of the conformation transition of poly(3KAU).

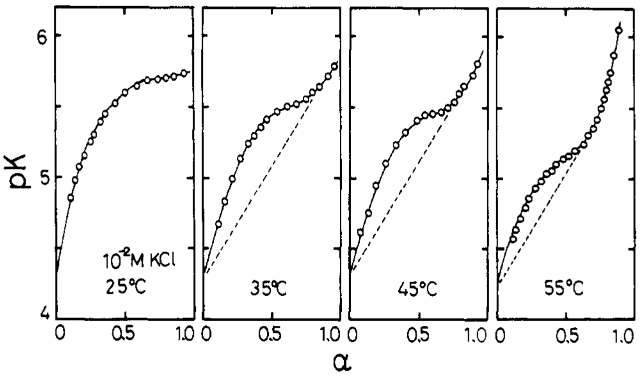

Figure 5. pK vs. α plots of poly(3KAU) in 10^{-2} M KCl solutions at various temperatures.

consider that region II may be a transition region.

Model of the Conformation Transition. The color change in poly(3KAU) aqueous solution is quite similar to that of a poly(3BCMU) in $CHCl_3/n\text{-}C_6H_{14}$ mixture. This analogy suggests that the conformational transition of poly(3KAU) is also similar to that of poly(3BCMU). A schematic figure of this model is shown in Figure 4.

When α is low, the urethane groups form hydrogen bonds between —NH and —C=O groups of the neighboring side chains. In this state, the backbone of poly(3KAU) has a planar structure and the carboxyl groups are aligned as shown in Figure 4. As α increases, the carboxyl groups dissociate and the electrostatic repulsion between the carboxyl groups becomes stronger. When the electrostatic repulsive force becomes larger than that of the hydrogen bonding, the hydrogen bonds break, followed by the twisting of the side chains around the main chain. Thus, the electrostatic potential becomes lower. In this state, the structure is nonplanar. In addition, the increase in the hydrophilic atmosphere around the side chains at high α promotes the breaking of the hydrogen bonds.

Temperature Dependence of the Titration Curves. To examine the effect of temperature on this rather unusual transition behavior, we carried out titrations at 25, 35, 45, and 55 °C for 10^{-2} and 10^{-1} M KCl solutions at a polymer concentration of $(7.4 \pm 0.2) \times 10^{-3}$ mol/L. The results are shown in Figures 5 and 6, respectively. The pK_0 varies from 4.30 to 4.20 for 10^{-2} M KCl solution, decreasing as the temperature is raised. The pK_0 value for 10^{-1} M KCl solutions is 4.10 at all temperatures. For all the solutions, the pK value at which the conformational tran-

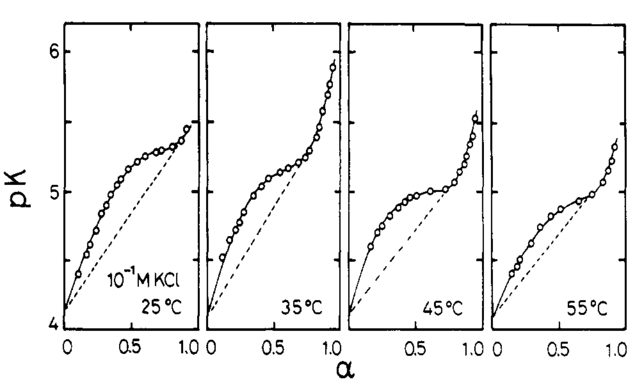

Figure 6. pK vs. α plots of poly(3KAU) in 10^{-1} M KCl solutions at various temperatures.

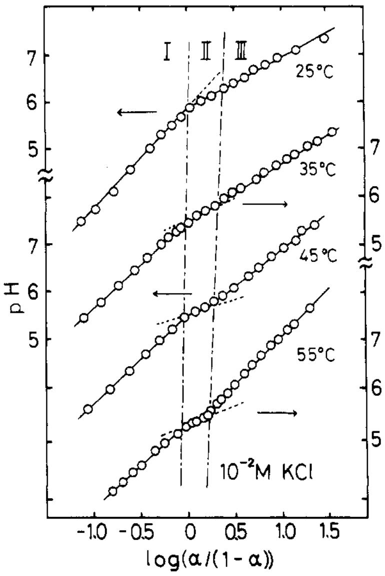

Figure 7. Henderson–Hasselbalch plots of poly(3KAU) in 10^{-2} M KCl solutions at various temperatures.

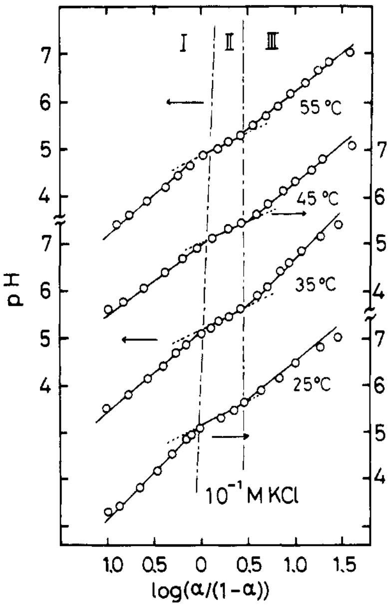

Figure 8. Henderson–Hasselbalch plots of poly(3KAU) in 10^{-1} M KCl solutions at various temperatures.

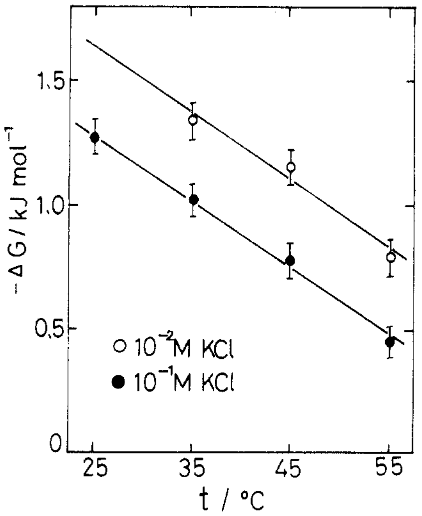

Figure 9. Temperature dependence of ΔG for the conformational transition in 10^{-1} and 10^{-2} M KCl solutions.

sition completes decreases with rising temperature. Figures 7 and 8 show Henderson–Hasselbalch plots for the two solutions at different temperatures. The curves, except that at 25 °C of 10^{-2} M KCl solution, have two bends at $\alpha_1{}^*$ and $\alpha_2{}^*$ ($\alpha_1{}^* < \alpha_2{}^*$) and consist of three regions, designated as I–III from the lower α side. The slopes of the curves in region I are nearly the same, while those in region III increase from 1 to 2 as the temperature is raised. As the temperature is raised, the value $\alpha_2{}^*$ decreased and the region II becomes narrower, corresponding presumably to the fact that the hydrogen bonds between side chains become weaker.

Free Energy of the Conformational Transition. The standard free energy change ΔG per carboxylic acid group of poly(3KAU) for the transition between planar and nonplanar structures in un-ionized states is given by[17]

$$\Delta G = -2.314RT\int_0^1 (\mathrm{p}K - \mathrm{p}K')\,\mathrm{d}\alpha \qquad (5)$$

where pK' is the hypothetical pK value for poly(3KAU) which assumes the nonplanar structure over the entire range of α. In Figures 5 and 6, the dashed lines extrapolated from the curves in the range of higher α show the hypothetical pK' curves for poly(3KAU) with nonplanar structure. The ΔG at various temperatures are calculated by eq 5 from the area between these two curves.

Figure 9 shows the plots of ΔG vs. the temperature t. The ΔG for the 10^{-2} M KCl solution at 25 °C could not be estimated, because the Henderson–Hasselbalch curve exhibited no end-point $\alpha_2{}^*$ of the transition. The plots are approximately straight lines for both 10^{-1} and 10^{-2} M KCl solutions. From the slope of ΔG vs. t plots, we estimated the change in entropy ΔS to be −22.0 J/(mol K) and then, from ΔG and ΔS, the value of the change of enthalpy ΔH to be −7.80 and −8.17 kJ/mol for 10^{-1} and 10^{-2} M KCl solutions, respectively. The difference presumably originates from the error involved in the estimation of the pK_0 values and the difference in the environment around the urethane groups between the two systems. The ΔH values obtained are smaller than that evaluated from the heat of dissolution of poly(3BCMU) and poly(4BCMU) gels in *o*-dichlorobenzene, which is −14.5 kJ per 1 mol of hydrogen bonds.[18] This is reasonable because the permittivity of H_2O is higher than that of *o*-dichlorobenzene. On the other hand, a much smaller value is reported for the ΔH per 1 mol of hydrogen bonds in H_2O, which varies from 2.1 to 4.2 kJ/mol.[13] Accordingly, we can guess that the environment around the hydrogen bonds of poly(3KAU) is rather hydrophobic because of the conjugated main chains and bulky hydrophobic side chains.

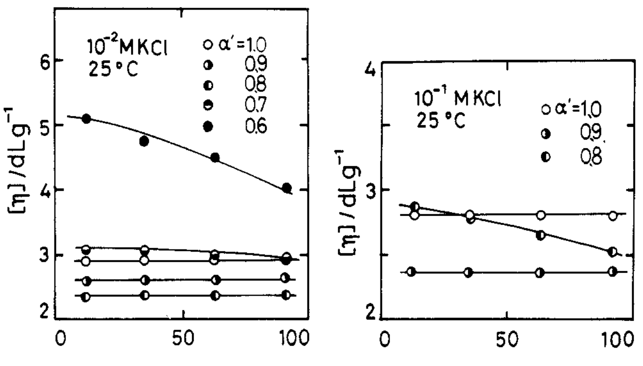

Figure 10. Shear rate dependence of [η] for 10^{-1} and 10^{-2} M KCl solutions of poly(3KAU) at various α' at 25 °C.

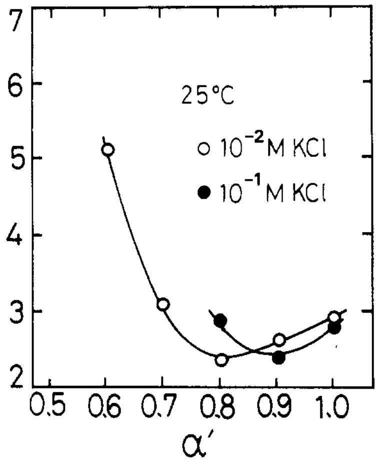

Figure 11. α' dependence of $[\eta]_0$ for 10^{-1} and 10^{-2} M KCl solutions of poly(3KAU) at 25 °C.

Intrinsic Viscosities and Their Shear Rate Dependence. As mentioned above, poly(3KAU) undergoes a conformational transition in aqueous solutions. Potentiometric titration and absorption spectra give information only on the local change in the chain conformation. In order to obtain information on the conformational transition of the whole chain, the shear rate dependence of intrinsic viscosities at varied α' was examined. Although we attempted to measure the viscosity over the entire range of α', we limited the measurement to the region of $\alpha' \geq 0.6$ for 10^{-2} M KCl solution and $\alpha' \geq 0.8$ for 10^{-1} M KCl solution, because in the region of low α' violet precipitates formed.

The shear rate dependences of [η] are shown in Figure 10. In 10^{-2} M KCl solutions at α' = 1.0, 0.9, and 0.8 and in 10^{-1} M KCl solutions at α' = 1.0 and 0.9, the [η] does not depend on the shear rate $\dot{\gamma}$, while in 10^{-2} M KCl solutions at α' = 0.7 and 0.6 and in 10^{-1} M KCl solution at α' = 0.8, the [η] does. The α' dependence of the zero-shear viscosity $[\eta]_0$ is shown in Figure 11. The $[\eta]_0$ decreases from 2.9 dL/g for 10^{-2} M KCl solution at α' = 1.0 to 2.35 dL/g at α' = 0.8. Then, the $[\eta]_0$ increases to 5.22 dL/g for that at α' = 0.6. For 10^{-1} M KCl solutions, the behavior of $[\eta]_0$ is similar, but the $[\eta]_0$ reaches the minimum for that at α' = 0.9. For solutions of an ordinary flexible polyelectrolyte such as poly(acrylic acid), the $[\eta]_0$ increases smoothly as α' increases by expansion of the chain caused by electrostatic repulsion between dissociated carboxylic groups.[19]

For flexible macromolecules as well as rigid ellipsoids, the dependence of [η] on shear rate has been theoretically

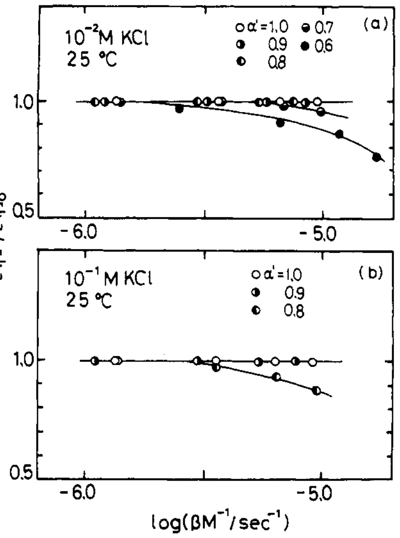

Figure 12. $[\eta]/[\eta]_0$ vs. log (β/M) plots at 25 °C: (a) results for 10^{-2} M KCl solutions and (b) those for 10^{-1} M KCl solutions.

elucidated[20,21] and tested by experiment.[22,23] All the available theories may be cast into a form

$$[\eta] = [\eta]_0(1 - A\beta^2 + \text{higher terms in even powers of } \beta) \quad (6)$$

with

$$\beta = (M[\eta]_0\eta_s/RT)\dot{\gamma} \quad (7)$$

Here, $[\eta]$ and $[\eta]_0$ are the intrinsic viscosities at an apparent shear rate $\dot{\gamma}$ and at the limit of zero-shear rate, respectively; A is a factor dependent on the shape of the polymer (e.g., the axial ratio for ellipsoid); β is the reduced shear rate defined by eq 7; η_s is the solvent viscosity; M is the solute molecular weight; and RT has the usual meaning.

The values of $[\eta]/[\eta]_0$ as a function of β/M are shown in Figure 12, because we do not determine M of poly(3KAU). The intrinsic viscosities for 10^{-2} M KCl solutions in the range of $\alpha' \geq 0.8$ and 10^{-1} M KCl solutions in the range of $\alpha' \geq 0.9$ are Newtonian. However, the $[\eta]$ was non-Newtonian for 10^{-2} M KCl solutions in the range of $\alpha' \leq 0.7$ and 10^{-1} M KCl solutions in the range of $\alpha' \leq 0.8$. $[\eta]_0$ for the 10^{-2} M KCl solution at $\alpha' = 0.6$ is larger than that at $\alpha' = 0.7$. This shows that the polymer form at $\alpha' = 0.6$ is more rigid than that at $\alpha' = 0.7$.

From the results described above, we conclude as follows. In the region of high α', in which $[\eta]$ values are independent of $\dot{\gamma}$, and the $[\eta]_0$ values are rather small, the poly(3KAU) chains are coillike. In this coillike region, the chain is expanded by electrostatic repulsion between the carboxyl groups, and the $[\eta]_0$ values decrease as α' decreases, because the electrostatic repulsion becomes weak as α' decreases. However, in the region of lower α' in which $[\eta]$ depend on $\dot{\gamma}$ and the $[\eta]_0$ values are large, the chains are rigid rodlike. The color of the solutions in the rodlike region is dark red or violet, indicating that the local conformation is planar. Therefore, we may conclude that the hydrogen bonds between the side chains make the local conformation planar and the whole chain conformation semirigid rodlike.

Figure 13 compares our results on the non-Newtonian $[\eta]$ with the theoretical ones calculated for prolate ellipsoids of various axial ratio p by Scheraga.[21] The values of p for poly(3KAU) of $\alpha' = 0.7$ and 0.6 in 10^{-2} M KCl solutions were estimated to be 5 and 300, respectively, and that of $\alpha' = 0.8$ in 10^{-1} M KCl solution 300. These p values have only a relative meaning for a sample with a broad molecular weight distribution as in the present case because the A value of eq 5 depends greatly on the molecular weight distribution.[23] However, we may say that the chains in the violet solution are long rods.

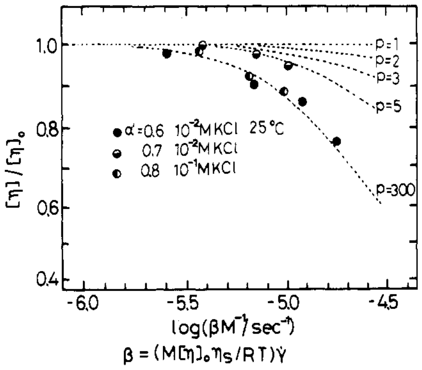

Figure 13. Non-Newtonian intrinsic viscosity behavior of poly(3KAU) solutions at 25 °C. Theoretical curves for prolate ellipsoids with various axial ratio p are indicated by the broken lines.

Concluding Remarks

In this article, we have analyzed our experimental data on the basis of an intramolecular conformational transition model (planar-to-nonplanar transition). All the phenomena, and the derived thermodynamic and hydrodynamic quantities, can be reasonably explained in this context. Although we cannot completely deny the possibility of aggregation pointed out by Wenz and Wegner,[4] there is some indirect evidence against it in the case of poly(3KAU). For example, the viscosity measurement for the completely blue solution of poly(3BCMU) was difficult because of aggregation, as previously reported by us,[6] but we could easily measure the shear rate dependence of $[\eta]$ for the violet solutions of poly(3KAU). In addition, the concentration dependence of reduced viscosity was normal even in the violet solution. However, in order to clarify this problem, we need further study, which is in progress in our laboratory.

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Mesophase Formation and Chain Rigidity in Cellulose and Derivatives. 3. Aggregation of Cellulose in *N,N*-Dimethylacetamide–Lithium Chloride

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ABSTRACT: Light scattering and viscosity measurements on diluted and moderately concentrated solutions of several cellulose samples dissolved in *N,N*-dimethylacetamide (DMAc) containing 5% or 7.8% (w/w) LiCl are reported. Cellulose samples include regenerated cellulose, sulfate pulps, and HCl hydrolyzates having DP between 60 and 760. Solubilization without chain degradation was achieved by using a method reported in the patent literature involving activation of cellulose by DMAc at the reflux temperature followed by addition of LiCl. Cellulose was dissolved either as a molecular dispersion (I) or as stable aggregates (II) consisting of ca. 7 fully extended cellulose molecules with a side-by-side organization. Concentration-dependent association equilibria (III) involving single molecules or aggregates were also observed. The occurrence of said situations depends upon the concentration, C_p, of stock solutions prepared with the method indicated above, the concentration, c, to which stock solutions are diluted, the LiCl concentration, the DP, and the treatment performed by the producer. In particular, acid hydrolysis favors situation II. This complex situation is considered in the accompanying paper in order to establish a relationship between the size of polymer particles and the critical concentration for mesophase formation.

In preceding papers of this series we investigated the relationship between chain rigidity and mesophase formation for (hydroxypropyl)cellulose (HPC) in *N,N*-dimethylacetamide (DMAc)[1] and in dichloroacetic acid (DCA).[2] The persistence length q was used to evaluate the axial ratio of the Kuhn segment. The latter was used for testing the prediction of a theory[3] for mesophase formation by semirigid mesogens. Satisfactory agreement between experiment and theory was verified in the high molecular weight range when the Kuhn chain model more likely applies and provided both hard and soft interactions contribute to mesophase formation.

A recurring problem in the above, and in most other studies with polymer liquid crystals,[4] has been the proper evaluation of the axial ratio of the rigid segment, which is inversely related[2] to the critical concentration at which the mesophase appears. In fact, the persistence length can only be determined from dilute solution studies. The chain diameter is often affected by a significant indetermination, which also poses limitations to a test of the various theories.[2] Moreover, the possibility has been considered that *aggregated* polymer species, and not molecularly dispersed entities, occur in the concentrated solutions at which mesophases are observed. In such a case, it would be extremely difficult to assess the length and diameter of the unit related to the critical concentration.

Table I
Characteristics of Samples Investigated[a]

sample	producer	$[\eta]_{\mathrm{CED}}$, dL/g	DP[b]	M_w[b]
A	Snia Fibre (regenerated cellulose II)	1.61	288	46 700
B	Snia Fibre (prehydrolyzed Kraft pulp)	2.52	474	76 800
C	Buckeye Corp. V68 (prehydrolyzed Kraft pulp)	2.40	449	72 800
D	Avicel (microcrystalline for TLC hydrolyzed)	0.92_5	155	25 100
E	Mischia Latifoglia Snia (Kraft pulp, not hydrolyzed)	3.85	760	123 100
F	obtained by hydrolysis of sample E	0.94	159	25 700
G	obtained by hydrolysis of sample E	0.63	102	16 500
H	obtained by hydrolysis of sample E	0.41_5	64	10 400
I	SSCC, Milan, (regenerated cellulose II)	2.45	460	74 500
L	Snia Fibre (regenerated cellulose II)	1.62	290	47 000

[a] "Hydrolyzed" refers to HCl treatments. [b] Determined from $[\eta]_{\mathrm{CED}}$ (M_0 = 162) using eq 1.

In the studies so far reported,[1,2,4] no definite proof has been given for the absence of aggregation in concentrated solutions. On the other hand, no evidence of such an aggregation was suggested by dilute solution studies. Due to the difficulties in solubilizing cellulose and to other features of its phase diagram in DMAc + LiCl prelimi-

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