

광활성 Poly(*trans*-5-methyl-*L*-proline)의 변광회전에 대한 반응속도와 활성화에너지

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The Kinetics and Activation Energy for the Mutarotation of Optically Active Poly(*trans*-5-methyl-*L*-proline)

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요 약. 여러 농도와 온도에서 Poly(*trans*-5-methyl-*L*-proline)을 trifluoroethanol 용매에서 정방향 변광회전, trifluoroethanol-*n*-butanol (1 : 4) 용매에서 역방향 변광회전을 시키면서 변광회전속도를 측정하였다. 이 두 방향의 변광회전 현상은 폴리머농도에 대하여 1차 반응이었다. 활성화에너지를 측정하기 위하여 변형된 Arrhenius식을 유도하였는데 이식은 물리적 성질과 농도와의 관계나 반응차수가 불확실한 반응에 이용할 수 있다. 정방향과 역방향 변광회전의 활성화에너지는 잔기몰당 각기 32.5와 33.5 kcal이었고 이 값은 polyproline 변광회전의 활성화에너지 (아미드결합의 공명에너지) 보다 잔기몰당 10 kcal가 높다. 이 과량의 활성화에너지는 폴리머아미드 결합이 시스-트란스 이성질화현상이 일어날 때 카르보닐기와 메틸기 사이에 생기는 입체장애에 의한 것이다.

ABSTRACT. The rates of the forward mutarotation of poly(*trans*-5-methyl-*L*-proline) in trifluoroethanol and of the reverse mutarotation in trifluoroethanol-*n*-butanol (1 : 4 v/v) have been measured at a number of temperatures and polymer concentrations. It was found that both mutarotations are of first-order with respect to the polymer concentration. A modified Arrhenius equation to evaluate the activation energy was derived for the reaction kinetics, in which the relation between the measured physical properties and concentration, and the order of the reaction are uncertain. The activation energies for the forward and reverse mutarotation were found to be 32.5 and 33.5 kcal per residue mole, respectively, which are about 10 kcal per residue mole higher than the E_a for the mutarotation of polyproline (the resonance energy of amide bonds). The excessive quantity of the activation energy was attributed to the steric barrier between carbonyl and methyl groups during the *cis-trans* isomerization of amide bonds in the polymer.

INTRODUCTION

In the previous paper we reported that poly(*trans*-5-methyl-*L*-proline) (PTMP) exists in

two conformations in the solid state and in solution in appropriate solvents¹. The two forms of PTMP are interconvertible by changing the solvents. The forward mutarotation, from form

I to form II, occurred in strong organic acids such as methanesulfonic acid, trifluoroacetic acid, dichloroacetic acid and trifluoroethanol (TFE), whereas the reverse mutarotation resulted by dilution of TFE solution with excess aliphatic alcohols such as *n*-butanol (*n*-BuOH) and *n*-propanol. The changes in CD, ORD and uv-spectra during the mutarotation were also reported. Since all solution properties of PTMP are similar to those found for polyproline (PP), it was proposed that the two conformations of PTMP are the same conformations as polyproline form I and form II; *i.e.*, a right-handed helix with all *cis* amide bonds and a left-handed helix with all *trans* amide bonds.

Randall and Downie² and Katchalski³ investigated the kinetics of the mutarotation of PP in acetic acid by optical rotation at *D*-line. Bovey⁴ *et al.* measured the same kinetics in aqueous solution by nmr spectroscopy using the different resonance values of α -protons in form I and form II. While the former suggested that the forward mutarotation and reverse mutarotation obey the first-order kinetics with regard to the polymer concentration, the latter found that the forward mutarotation is of zero-order reaction. The mechanisms of the mutarotation were also proposed^{3,4}. However, the reported activation energy for the mutarotation was 20~24 kcal per residue mole, which is similar to the resonance energy of the amide bond and hence contributed to the conclusion that the mutarotation of PP is a *cis-trans* isomerization of amide bonds in the polymer.

PTMP differs from PP in that a methyl group was introduced in the *trans*-5-position relative to the carbonyl group on pyrrol ring of PP. Due to the steric hindrance of the methyl group, only low molecular weight polymers were obtained by the polymerization of *trans*-5-methyl-

proline-N-carboxyanhydride. However, once the polymers were formed, the methyl groups remained in place in the helical structure of the polymer so as not to disturb the formation of the same conformation as PP form I and form II. Studies of space-filling models indicated that the rotation around the amide bonds of the polymer was hindered because of steric interaction of the introduced methyl group and it was found that the rate of the mutarotation of PTMP was much slower than that of PP¹. Consequently, it was expected that the activation energy of the mutarotation should be influenced by the steric interaction.

The increase in viscosity during the forward mutarotation of PTMP indicated that the mutarotation is a *cis-trans* isomerization of amide bonds in the polymer⁵. In order to verify the isomerization and the steric influence of the methyl group on the mutarotation, the kinetics and activation energy for the mutarotation were investigated. Since the forward mutarotations of PTMP in strong organic acids, such as methanesulfonic, trifluoroacetic and dichloroacetic acids were found to be too fast to be followed by any optical measurements, TFE was chosen as solvent for the forward mutarotation and TFE-*n*-BuOH (1 : 4 v/v) for the reverse mutarotation. Both solvent systems are also suitable for optical measurements in the far ultraviolet region.

Changes of many physical properties were observed during the mutarotation of PTMP,⁵ which enabled us to measure the kinetics; such as changes in CD, ORD, uv, nmr-spectra and viscosity. The change of the differential dichroic absorption at the wave length 217 m μ ($\Delta\epsilon_{217}$) was utilized for the measurement of the forward and reverse mutarotation of PTMP, since the range of its change was superior to the rest.

EXPERIMENTAL

Polymerization. PTMP was synthesized as described previously.¹ The two polymers in Table 1 were used in this investigation.

CD-Measurements. CD-measurements were made with a Jasco ORD, CD, UV-5 spectropolarimeter. A 0.1 mm cell equipped with a temperature control jacket was used. During measurement the wavelength was fixed at 217 m μ and temperature of the mutarotation solution was measured with a thermocouple.

RESULTS

The Forward Mutarotation. The order of the forward mutarotation. The changes in the CD-spectra of PTMP for the forward and reverse

Table 1. PTMP's and their physical data.

Polymer No.	Mn ^a	$[\eta]^b$
1	600	0.14
2	820	0.15

^a Measured by VPO in trifluoroethanol.

^b Measured in trifluoroethanol at 25°C.

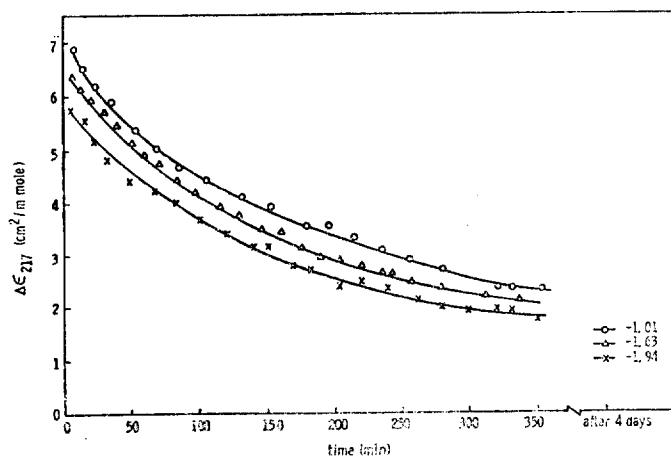


Fig. 1. Change of the differential dichroic absorption ($\Delta\epsilon_{217}$) of poly(*trans*-5-methyl-*L*-proline) during the forward mutarotation in trifluoroethanol at 40.3°C at 3 different concentrations; 1.35 mg/ml (\circ), 1.88 mg/ml (Δ) and 2.46 mg/ml (\times).

mutarotation has been described in a previous communication⁵. The rate of these reactions were determined by measuring the change in differential dichroic absorption at the wavelength 217 m μ ($\Delta\epsilon_{217}$) as a function of time. Since the relation between $\Delta\epsilon$ and concentration of form I or form II was not known, some different concentration of polymer were measured, in order to find out the order of reaction. The change in $\Delta\epsilon_{217}$ during the forward mutarotation of PTMP in TFE at 40.3°C at three different concentrations (1.35 to 2.46 mg/ml) is given in Fig. 1. The course of the reaction is seen to be practically independent of concentration in the range studied. A higher concentration of polymer gives a lower value of $\Delta\epsilon$ and *vice versa*. The effects of concentration on $\Delta\epsilon$ are nearly equal at any given time during whole mutarotation, so that three curves run parallel.

Fig. 2. shows the plot of $\log(\Delta\epsilon_t - \Delta\epsilon_\infty)$ vs. time at 40.3°C at three different concentrations. Until 30% conversion of $\Delta\epsilon$ we obtain a linear relationship between $\log(\Delta\epsilon_t - \Delta\epsilon_\infty)$ and time. The plots of three different concentrations put

one upon another yielding one straight line. The fact that the apparent rate constants, slope of the line, are independent of the concentrations would indicate that the mutarotation obeys first order kinetics. This result is in agreement with the order of PP mutarotation in organic solvents.^{2,3}

Activation Energy. In the mutarotation of PP, the order of reaction was uncertain and the plot of $\log [\alpha]_D$ vs. time gave a linear relationship only until about 30% of conversion.

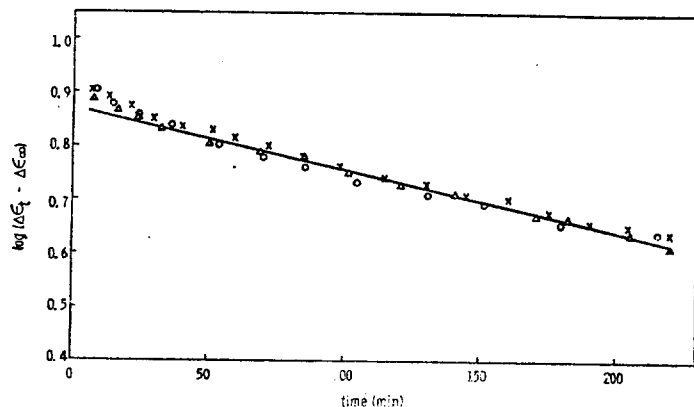


Fig. 2. Plot of $\log(\Delta\epsilon_t - \Delta\epsilon_\infty)$ vs. time for the forward mutarotation of poly(*trans*-5-methyl-*L*-proline) in trifluoroethanol at 40.3°C at 3 different concentrations; 1.35 mg/ml (○), 1.88 mg/ml (×) and 2.46 mg/ml (Δ).

As a result, the activation energies, measured by Arrhenius plot of the apparent rate constants of first order, fluctuated about 12%; 22.9 kcal per residue mole was calculated by Randall², who considered whole reaction for the calculation, whereas 20.9 kcal per residue mole was found by Katchalski *et al.*³ who considered only the linear part of the logarithm plot at the beginning of the mutarotation for the evaluation of activation enthalpy.

In order to avoid such deviations, a new equation for the evaluation of activation energy, which is independent on the reaction orders, was developed. The reaction rate of a single component:

$$-\frac{dc}{dt} = kc^n \quad (1)$$

The integration gives:

$$\text{for } n=1 \quad \ln \frac{C_0}{C} = kt \quad (2)$$

for $n \neq 1$ in general

$$\frac{1}{(n-1)} \left[\frac{1}{C^{n-1}} - \frac{1}{C_0^{n-1}} \right] = kt \quad (3)$$

For the case of the forward mutarotation of PTMP C_0 and C are the concentrations

of *cis* amide bonds at starting ($t=0$) and at time t , respectively. If we set the mole fraction of *cis* amide bond at time t as α and at two different temperatures (T_a and T_b), we obtain:

$$T_a : \frac{1}{(n-1)} \left[\frac{1}{(\alpha_a C_{0a})^{n-1}} - \frac{1}{(C_{0a})^{n-1}} \right] = k_a t_a \quad (4)$$

$$T_b : \frac{1}{(n-1)} \left[\frac{1}{(\alpha_b C_{0b})^{n-1}} - \frac{1}{(C_{0b})^{n-1}} \right] = k_b t_b \quad (5)$$

Fig. 3 shows the change in $\Delta\epsilon$ as a function of time for two different temperatures. At a given value of $\Delta\epsilon$ ($\Delta\epsilon_i$ in Fig. 3) the composition of form I and form II, *i.e.*, concentrations of *cis* and *trans* amide bonds, in the both curves should be the same. Since this system is under the course of reaction and not under the equilibrium state, the temperature effect on $\Delta\epsilon$ is negligible. The solvent expansion at a higher temperature could cause the dilution of the solution resulting in a low $\Delta\epsilon$ value. The error caused by the solvent expansion in a narrow temperature interval will remain within experimental error.

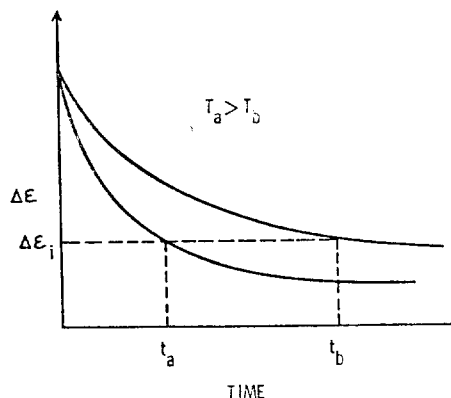


Fig. 3. Change in $\Delta\epsilon$ as a function of time for two different temperatures.

When we start with a constant initial concentration, the effect of concentration in $\Delta\epsilon$ can be avoided. Under these conditions, *i.e.*, a constant initial concentration and at a given $\Delta\epsilon$ ($\Delta\epsilon_i$ in Fig. 3), we obtain:

$$\begin{aligned} C_{0a} &= C_{0b} \\ \alpha_a &= \alpha_b \end{aligned} \quad (6)$$

By substitution of (6) in equations (4) and (5), we obtain:

$$k_a t_a = k_b t_b \text{ and } \frac{k_a}{k_b} = \frac{t_b}{t_a} \quad (7)$$

In the same manner the equation (7) can be derived from equation (2) which is for the first order reaction. The ratio of two rate constants is inversely proportional to the ratio of times required to be mutarotated to a given $\Delta\epsilon$ at two different temperatures.

According to Arrhenius, equation (8) is obtained for two different temperatures:

$$\ln\left(\frac{k_b}{k_a}\right) = \frac{E_a}{R} \left(\frac{1}{T_a} - \frac{1}{T_b} \right) \quad (8)$$

Where k_a and k_b are the rate constants at the temperature T_a and T_b , and E_a is the activation energy of the reaction. By substitution of equation (7) in equation (8):

$$\ln\left(\frac{t_a}{t_b}\right) = \frac{E_a}{R} \left(\frac{1}{T_a} - \frac{1}{T_b} \right) \quad (9)$$

When we measure the time-dependent change of $\Delta\epsilon$ at several different temperatures and plot $\log(t_a/t_b)$ vs. $(1/T_a - 1/T_b)$, the activation energy for the reaction can be evaluated from the slope of the straight line, regardless of the orders of the reactions. This equation (9) is especially useful for the measurement of activation energy in the case that the order of reaction and the relation between the measured physical properties and concentrations are uncertain. The validity of the equation is not

restricted to the differential dichroic absorption, but all the physical properties which are changing monotonically in the course of the reaction.

The changes of $\Delta\epsilon_{217}$ during the forward mutarotation of PTMP at constant initial concentration at four different temperatures are shown in Fig. 4. By elevating the reaction temperature about 10 °C, the half-life was shortened from 120 minutes (44.6 °C at $\Delta\epsilon=2.7$) to 28 minutes (54.4 °C at $\Delta\epsilon=2.7$). In order to plot equation (9), the values of t_a/t_b were measured every 0.5 $\Delta\epsilon$ change in the range of $\Delta\epsilon=2\sim5$ and averaged. Fig. 5 shows the plot of $\log(t_a/t_b)$ against $(1/T_a - 1/T_b)$. The plot satisfies the equation, as it shows a linear relationship and passes through the origin. The activation energy was found to be 32.5 kcal per residue mole from the slope.

In order to measure the activation energy by an Arrhenius plot, $\log(\Delta\epsilon_t - \Delta\epsilon_\infty)$ against time is plotted in Fig. 6. As mentioned previously, a linear relationship was obtained only up to 35 % conversion of $\Delta\epsilon$. After evaluation of the apparent rate constants (k') from the slopes, an activation energy 29.6 kcal per residue mole was obtained from the usual Arrhenius plot of $\log k'$ vs. the reciprocal of the absolute temperatures (Fig. 7).

In comparison with the previous activation energy evaluated by equation (9), this E_a is *ca.* 3 kcal smaller. This difference seemed to be caused by the fact that the evaluation of former E_a covered all of the reaction, whereas the latter E_a was based on about the first 35% of $\Delta\epsilon$. A similar difference was found in the forward mutarotation of PP in acetic acid. An E_a of 22.9 kcal was obtained by Randall², whose evaluation covered the whole mutarotation, while an E_a of 20.6 kcal was found by calculation with the first straight part of $\log[\alpha]_D$ vs.

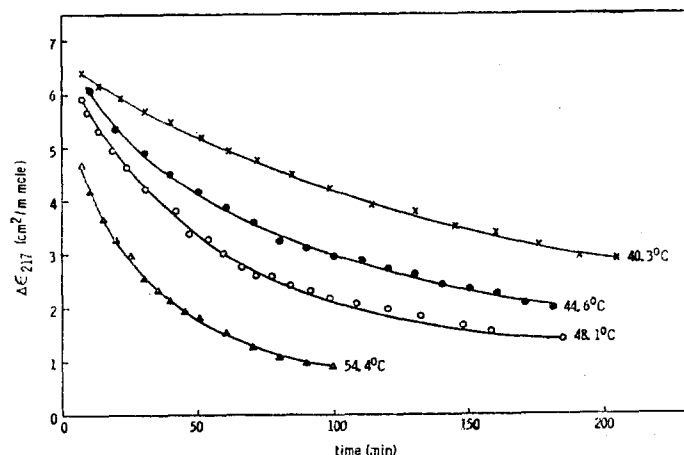


Fig. 4. Change of the differential dichroic absorption ($\Delta\epsilon_{217}$) of poly(*trans*-5-methyl-*L*-proline) during the forward mutarotation in trifluoroethanol at 4 different temperatures, with a constant initial concentration of 1.88 mg/ml.

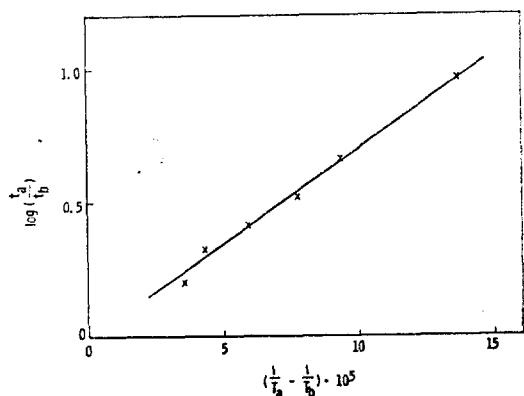


Fig. 5. Plot of $\log t_e/t_b$ vs. $(1/T_e - 1/T_b)$ for the forward mutarotation.

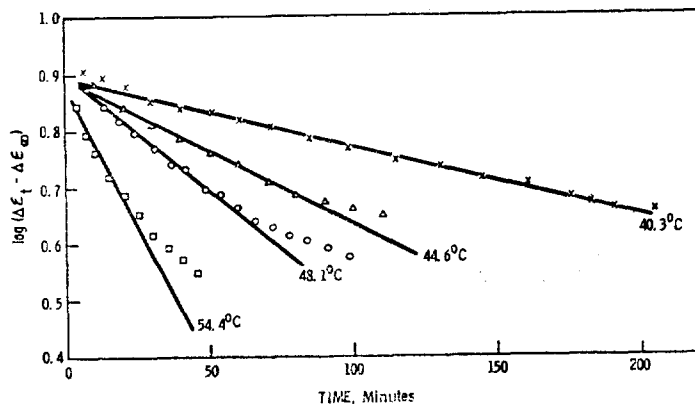


Fig. 6. Plot of $\log(\Delta\epsilon_t - \Delta\epsilon_\infty)$ vs. time for the forward mutarotation of poly(*trans*-5-methyl-*L*-proline) in trifluoroethanol at four different temperatures with constant initial concentrations of polymer.

time plot, which covered only *ca.* 30 % of conversion³.

Reverse Mutarotation. The reverse mutarotation of PTMP (form II \rightarrow form I) was carried out in a solvent mixture, TFE-*n*-BuOH (1 : 4 v/v). The changes in CD-spectra during the reverse mutarotation has been shown in the previous paper.⁵ The change of $\Delta\epsilon_{217}$ during the reverse mutarotation of PTMP at constant temperature (44.0°C) at three different concentrations is given in Fig. 8. Contrary to

the forward mutarotation, the effect of concentration on $\Delta\epsilon$ in this reverse mutarotation is negligible at low value of $\Delta\epsilon$ and it increases as $\Delta\epsilon$ increases.

Fig. 9 shows the plot of $\log(\Delta\epsilon_\infty - \Delta\epsilon_t)$ vs. time at 44.0°C at three different concentrations. The linear relationships are obtained for the whole course of the reaction. This fact would, therefore, indicate that $\Delta\epsilon$ is inversely proportional to the concentration of *trans* amide bonds and that the reverse mutarotation obeys first order kinetics. The slight differences in the slopes of the straight lines would be due to the different concentration effects.

Changes of $\Delta\epsilon_{217}$ as a function of time during the reverse mutarotation of PTMP at constant initial concentration at four different temperatures are shown in Fig. 10. By increasing the temperature 10°C the half-life time (half conversion of $\Delta\epsilon = 3.0$) of the mutarotation

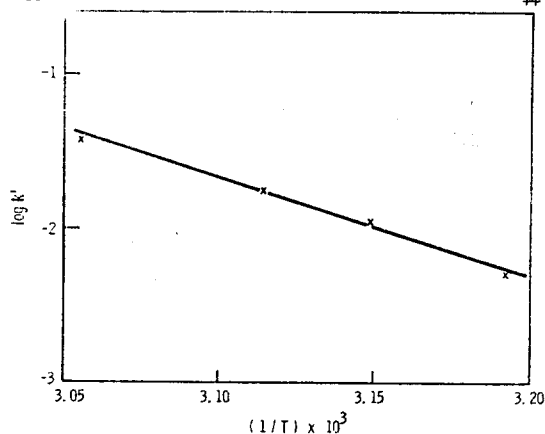


Fig. 7. Arrhenius plot for the forward mutarotation.

was decreased by a factor of five ($37.5^{\circ}\text{C} : 112$ minutes, $47.6^{\circ}\text{C} : 22$ minutes). The accelerations of reaction rates by temperature are similar in the forward and reverse mutarotations, suggesting that the activation energies of both reactions would be nearly equal.

In the same manner as mentioned previously, $\log (t_a/t_b)$ are plotted against $(1/T_a - 1/T_b)$ in Fig. 11 according to equation (9). This plot also satisfies equation (9), since it has a linear relationship and passes through the origin. The activation energy of 33.5 kcal per residue mole

was evaluated from the slope.

This amount is 1 kcal higher than the activation energy for the forward mutarotation.

In order to evaluate the activation energy by Arrhenius method, two plots are shown in Fig. 12 and 13. The plots of $\log (\Delta\epsilon_{\infty} - \Delta\epsilon_t)$ vs. time are linear almost the whole course of the reaction. The activation energy for the reverse mutarotation was found to be 33.6 kcal per residue mole from Fig. 13, which is in good agreement with E_a evaluated by equation (9) within experimental error. While the activation energies for the forward mutarotation calculated by equation (9) and by the Arrhenius method are not the same due to the deviation from a linear relationship in the logarithm plot after 35% conversion, the good agreement of both energies of activation for the reverse mutarotation is due to the fact that both

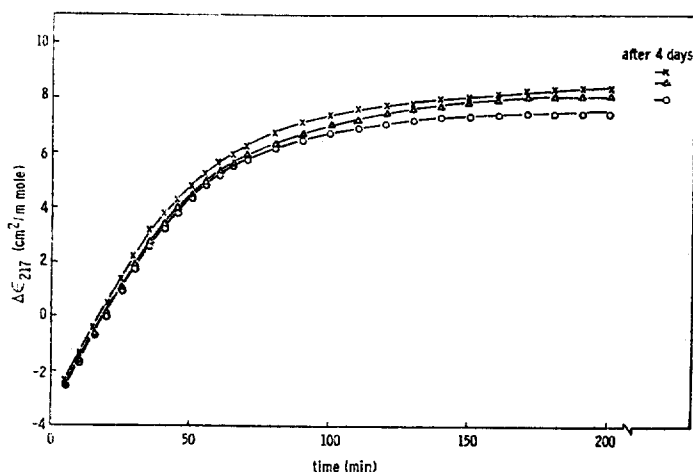


Fig. 8. Change of the differential dichroic absorption ($\Delta\epsilon_{217}$) of poly(*trans*-5-methyl-*L*-proline) during the reverse mutarotation in trifluoroethanol-*n*-butanol (1 : 4 v/v) at 44.0°C at 3 different concentrations; 1.58 mg/ml (\times), 1.87 mg/ml (Δ) and 2.68 mg/ml (\circ).

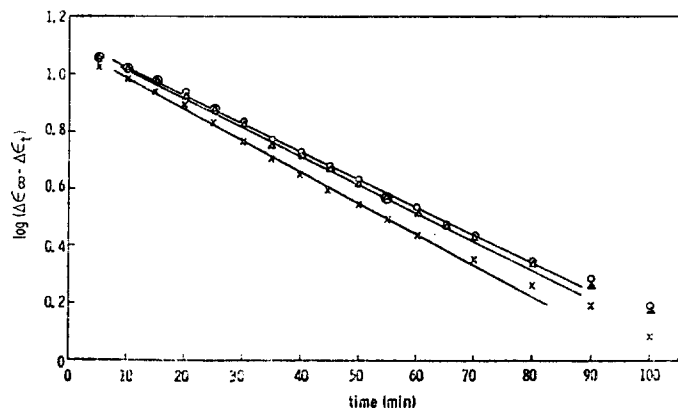


Fig. 9. Plot of $\log (\Delta\epsilon_{\infty} - \Delta\epsilon_t)$ vs. time for the reverse mutarotation of poly(*trans*-5-methyl-*L*-proline) in trifluoroethanol-*n*-butanol (1 : 4 v/v) at 44.0°C at 3 different concentrations; 1.58 mg/ml (Δ), 1.87 mg/ml (\circ) and 2.68 mg/ml (\times).

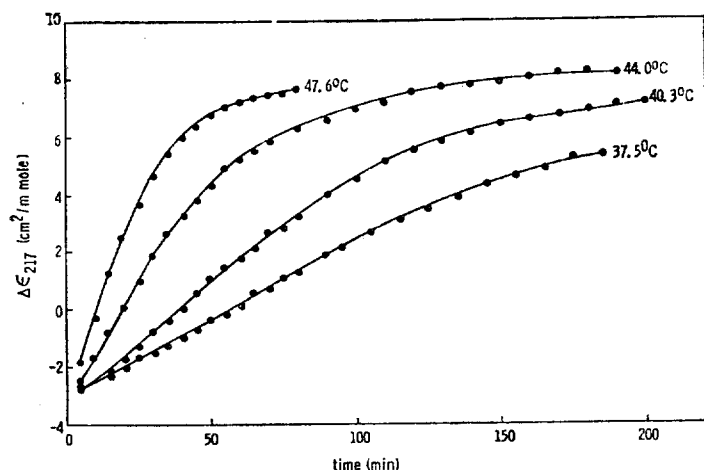


Fig. 10. Change of the differential dichroic absorption ($\Delta\epsilon_{217}$) of poly(*trans*-5-methyl-*L*-proline) during the reverse mutarotation in trifluoroethanol-*n*-butanol (1:4 v/v) at 4 different temperatures, with a constant initial concentration of 1.87 mg/ml.

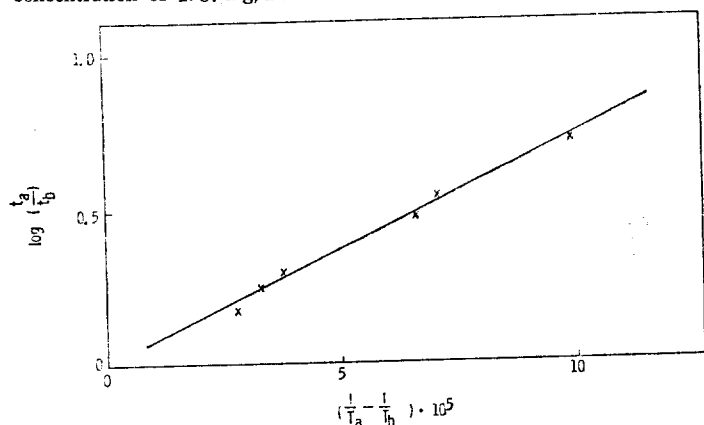


Fig. 11. Plot of $\log(t_a/t_b)$ vs. $(1/T_a - 1/T_b)$ for the reverse mutarotation.

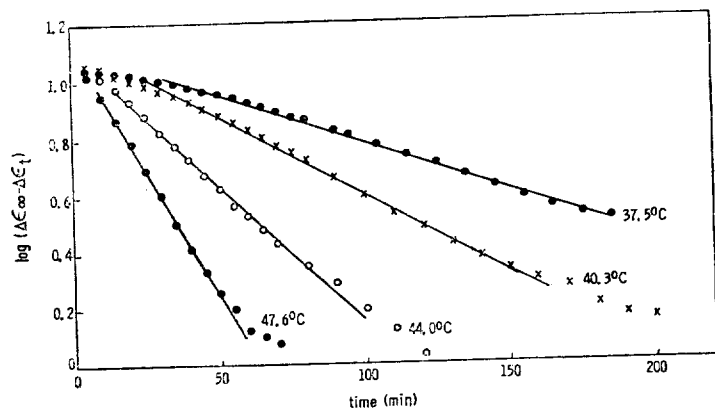


Fig. 12. Plot of $\log(\Delta\epsilon_\infty - \Delta\epsilon_t)$ vs. time for the reverse mutarotation of poly(*trans*-5-methyl-*L*-proline) in trifluoroethanol-*n*-butanol (1:4 v/v) at 4 different temperatures, with constant initial concentration of 1.87 mg/ml.

methods cover the whole course of the reaction.

The coincidence of activation energies for the reverse mutarotation lead us to the conclusion that $\Delta\epsilon$ is inversely proportional to the concentration of *trans* amide bonds of the polymer and the reverse mutarotation obeys the first order kinetics, since the activation energy obtained by Arrhenius plot was evaluated by the rate constants of first order kinetics.

DISCUSSION

The forward mutarotation in TFE and the reverse mutarotation in TFE-*n*-BuOH (1:4 v/v) were both found to obey first order kinetics. This is in agreement with the order of PP mutarotation in organic solvents reported in literature^{2,3}. Since there are many factors which make the kinetics very complicated, the obtained kinetic order contributes little to the determination of mutarotation mechanisms. However, three mechanisms might be feasible for the mutarotation of polyproline derivatives: 1) the mutarotation starts at the terminal amide bond and propagates along the peptide chain; 2) the mutarotation starts at one internal amide bond and propagates along the peptide chain; and 3) *cis-trans* iso-

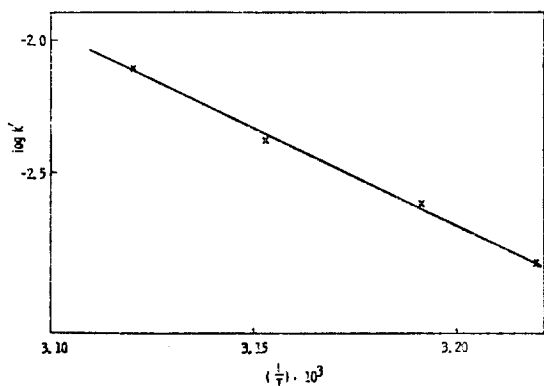


Fig. 13. Arrhenius plot for the reverse mutarotation.

merization occurs randomly at all over the peptide chain independently.

The last mechanism seems to be pertinent for the mutarotation of very low molecular weight polymer, because the cooperative character becomes more important with increasing molecular weight. In this case a first order reaction is expected. Zero-order kinetics will result in mechanism 1, when the distribution of molecular weight of the polymer is very narrow and the rate of initiation is the same as the rate of propagation, as observed in the mutarotation of PP in aqueous solution⁴. In the case that the rates of initiation and propagation are different and the distribution of molecular weight of the polymer is broad, the order for mechanisms 1 and 2 might be very complex.

However, if the initiation rate is much slower than the rate of propagation, as expected, and the molecular weight of the polymer is very low, first order kinetics might be the result of mechanisms 1 and 2, since the propagation can be proceeded only by few amide bonds along the chain and the rate of mutarotation is consequently determined by the initiation. Since the polymers used in these kinetics have very low molecular weights ($M_n=600\sim 820$), the measured first order of this investigation seems to be the case discussed above or of mechanism 3.

The activation energy of the mutarotation of PTMP was evaluated by a modified Arrhenius equation (9), which was derived under the assumption that, at a given differential dichroic absorption, the concentration of *cis* and *trans* amide bonds are the same in reactions at different temperatures. The validity of the equation was demonstrated in the case of the reverse mutarotation of PTMP. Since it is not necessary to know the order of reaction or the relation between the measured physical properties and concentration to apply the equation, it can be utilized for the evaluation of activation energies of some complicated biological reactions such as protein denaturation. This equation is valid not only with the changes of differential dichroic absorption but with any physical property, which changes monotonically during the reaction. The activation energy evaluated by this equation using the change of optical rotation was found to be in good agreement with the corresponding value measured by other methods.

The activation energies for the forward and reverse mutarotation were found to be 32.5 and 33.5 kcal per residue mole, respectively. The activation energy of reverse mutarotation is 1 kcal higher than that found for the forward mutarotation. This difference can be ascribed to either one or both of the two factors: one is the different solvent systems for each mutarotation, which may have different solvation energies with both forms I and II, and may also influence the energy barrier of the transition states during the mutarotation. The other is that PTMP forms I and II have inherently different enthalpies due to the introduced methyl groups, as observed in the case of poly(*cis*-5-methyl proline).⁵

The measured activation energies are about 10 kcal per residue mole higher than that found for PP (the resonance energy of amide bond).

The mutarotation is a *cis-trans* isomerization of amide bonds in PTMP and the activation energy, as it was found for the mutarotation of PP, should be similar to the resonance energy of amide bond provided that there is no appreciable steric resistance. This result leads us to conclude that the excessive quantity of the activation energy (10 kcal) is due to the steric barrier between the introduced methyl group and the other groups in polymer. Fig. 14 shows a rough Newman projection of one amide bond in PTMP in the direction from amino to carbonyl terminal. In one turn of the amide bond there are two steric barriers; between methyl and carbonyl group, and between methyl group and pyrrolyl ring. Studies of space-filling models indicate that the steric hindrance between methyl and carbonyl groups is smaller than that between methyl and pyrrolyl ring. Since *cis-trans* iso-

merization is required only 180° rotation and the rotation should occur thermodynamically over the low energy barrier, the *cis-trans* isomerization is expected to result around the carbonyl group, as indicated with arrows in Fig. 14. The excessive activation energy (10 kcal) in the mutarotation of PTMP is attributed to the steric barrier between methyl and carbonyl groups during the mutarotation.

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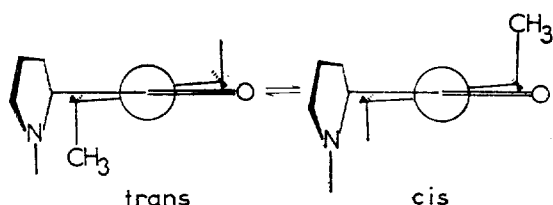


Fig. 14. The Newman projection of amide bond in PTMP.