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# Conformation of Methacryloyl-L-proline

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Many conformational studies have been made on the hindered internal rotation about amide bonds since the first investigation by Pauling.[1] However, very few investigations have been reported on that of $\alpha,\beta$-unsaturated acid amide except for the work by Rogers and Woodbrey.[2] They determined the activation free energy for the hindered internal rotation about the amide bond of N,N-dimethylacrylamide to be 16.1 kcal/mol at 25.2 °C. The alternating photocopolymerization of methacryloyl-L-valine methyl ester (MAVM) with maleic anhydride suggested that the amide compounds has a specific planar conformation.[3] For the purpose of elucidating the participation of the amide proton in this specific conformation, we synthesized methacryloyl-L-proline (MAP) and examined the effect of the temperature on its NMR and CD spectra. The results indicate that the following two isomeric

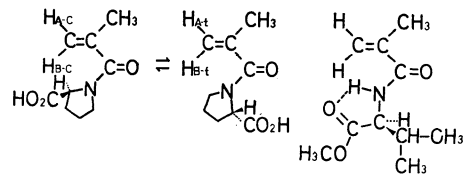


Fig. 1. Conformations of MAP and MAVM.

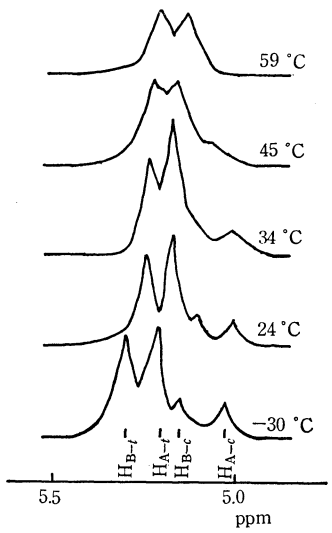


Fig. 2. The NMR spectra assigned to the vinyl protons of MAP from HMDS at 100 MHz in $CDCl_3$.

MAP, *cis* and *trans* conformers exist at lower temperature.

Temperature dependence of the NMR signals assigned to the vinyl protons of MAP is shown in Fig. 2. The four signals at −30 °C are seen to decrease to the two signals with the rise in temperature. The results suggest the coexistence of the rotational isomers. $H_A$ and $H_B$ of the *cis* and *trans* isomers were assigned on the basis of the study by Bovey *et al.* on polysarcosine.[4] In deutero methanol and dimethyl sulfoxide-$d_6$, the vinyl protons gave a similar NMR pattern to that in $CDCl_3$. For example, in deutero methanol at −50 °C, they gave four resonance peaks at 5.09, 5.21, 5.28, and 5.36 ppm assigned to $H_{A-c}$, $H_{B-c}$, $H_{A-t}$ and $H_{B-t}$ respectively, and at 42 °C they gave only three peaks at 5.06, 5.20, and 5.26 ppm assigned to $H_{A-c}$, an overlapped signal of $H_{B-c}$ and $H_{A-t}$, and $H_{B-t}$ respectively.

The activation free energy ($\Delta F^{\neq}_{T_c=318}$) for the transformation between the two isomers of MAP was calculated to be 16.4±0.2 kcal/mol from the NMR data in deutero chloroform by the equation

$$\Delta F_{Tc}^{\neq} = 2.303RT_c \log \frac{\sqrt{2}\kappa kT_c}{\pi \Delta \nu h} \qquad (1)$$

where $T_c$ is the coalescence temperature, and $\Delta\nu$ is the difference between the chemical shifts of the two isomers. Transmission coefficient $\kappa$ was assumed to be unity. The enthalpy change for the *cis–trans* transformation was calculated to be −1.5±0.2 kcal/mol by the temperature dependence of the equilibrium constant ($K$) in Table 1, where $K$ values obtained from the *cis–trans* area ratio of NMR spectra were used.

Figure 3 indicates the positive CD maximum of L-proline at 219 nm, and the negative CD maximum at 227 nm with a shoulder at about 246 nm for MAP

Table 1. Equilibrium constants for the *cis–trans* transformation between the two isomers of MAP ($CDCl_3$)

| Temperature (°C) | Equilibrium constant $K=[trans]/[cis]$ |
|---|---|
| −30 | 4.39[a] |
| 0 | 3.05[a] |
| 15 | 2.42[a] |
| 24 | 2.48[a] |
| 28 | 2.26[a] |
| 55 | 2.45[b] |
| 59 | 2.42[b] |

a) obtained from the area ratio of NMR spectra.
b) obtained from chemical shifts.

1) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornel University Press, Ithaca, N.Y. (1940), p. 1.
2) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).
3) K. Nishihara and N. Sakota, *J. Polym. Sci.*, in preparation.
4) F. A. Bovey, J. J. Ryan, and F. P. Hood, *Macromolecules*, **1**, 305 (1968).

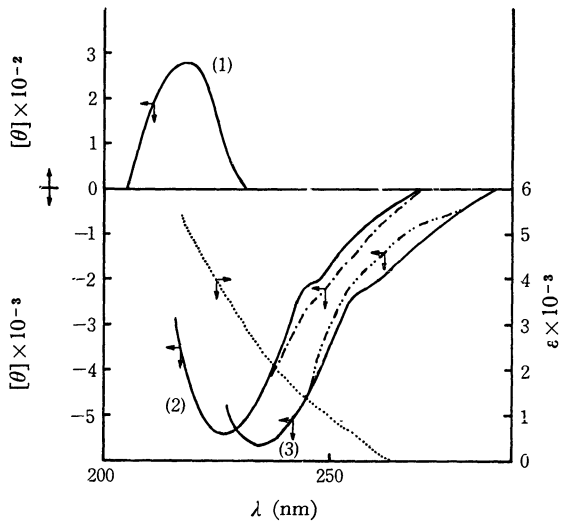


Fig. 3. The UV spectrum of MAP in methanol at 25 °C (·····) and the CD spectra of L-proline and MAP.
(1) The CD spectrum of L-proline in methanol at 25 °C.
(2) The CD spectra of MAP in methanol at 25 °C (——) and −50°C (—·—).
(3) The CD spectra of MAP in dioxane at 25°C (——) and 52°C (—··—).

in methanol at 25 °C. The negative CD maximum of MAP is presumably associated with the n→$\pi^*$ transition of the methacryloyl amide group. The CD spectra of MAP measured at 52 °C in dioxane and at −50 °C in methanol differ from those obtained at 25 °C in the corresponding solvents. The difference in the CD curve near the shoulder of absorption might be ascribed to the coexistence of the two different conformations of MAP.

## Experimental

MAP was prepared by the reaction of methacryloyl chloride with L-proline according to the method of Sakota.[5] mp 103.0—104.5°C; $[\alpha]_D^{29}$ −79.2 ($c=1$, methanol).

NMR spectra were recorded with a JEOL Model JNM-4H-100 Spectrometer operating at 100 MHz. CD spectra were measured with a Jasco Model ORD/UV 5 Spectropolarimeter. UV spectrum was measured with a Shimadzu Double Beam Spectrophotometer UV-200.

5) N. Sakota, *Nippon Kagaku Zasshi*, **88**, 1087 (1968).