dioxide and a nitrile end group. This reaction has been demonstrated by a reaction between dimethylketene and isocyanic acid to yield carbon dioxide and isobutylonitrile.[7] The reaction between isocyanic acid and the ketene end group will account for the CO_2 formation from the irradiated polyimide prepared via cyclopolymerization. In the polyimide prepared by the ammonia modification of the polyacid a small amount of the residual acid group is present,[8] and it acts as a catalyst in the hydrolysis of isocyanic acid to give carbon dioxide and ammonia.[5,9] Thus, the hydrolysis of isocyanic acid, photodecarboxylation from the residual acid or acid anhydride groups, and reaction between isocyanic acid and the ketene end group will explain the CO_2 formation from the irradiated polyimide prepared by the ammonia modification. The volatile photoproducts of poly(dimethacrylimide) measured with a mass spectrometer and a gas chromatograph were carbon dioxide, carbon monoxide, ammonia, and a trace amount of isocyanic acid.

The exposed part of the polymer films became more soluble in an organic solvent such as 2-methoxyethanol. Poly(diacrylimide) prepared in the ammonia modification did not show any trace of isocyanic acid under the same photolysis condition as for poly(dimethacrylimide). The polymer films became insoluble even in dimethylformamide after the photolysis, indicating that cross-linking was taking place in the polymer. Contrary to poly(diacrylimide), no cross-linking took place in the photolysis of poly(acrylic anhydride).[1] The cross-linking took place only between the NH group and the tertiary CH group in the main chain upon the elimination of hydrogen; the formation of hydrogen was confirmed by mass spectrometric analysis.

N-Alkyl-substituted polyimides such as poly(*N*-methyldiacrylimide), poly(*N*-ethyldiacrylimide), poly(*N*-methyldimethacrylimide), and poly(*N*-ethyldimethacrylimide) were prepared by heating polymer films of the corresponding poly(acrylic acid) or poly(methacrylic acid) at 200 °C for 1 h under about 30 cm of pressure of methylamine or ethylamine.[3] For this purpose polymer films were cast on sodium chloride plates from a 2-methoxyethanol solution of the polyacid. After the above amination the resulting polyimide had an infrared absorption spectrum identical with the one reported for the polyimide made via free-radical initiated cyclopolymerization of *N*-alkyl diacrylimide or *N*-alkyl dimethacrylimide.[4,10] The polymer films were irradiated exactly in the same way as described for poly(dimethacrylimide) at low temperature. The sharp band at 2340 cm^{-1}, a rather broad band at 2280 cm^{-1}, and a sharp band at 2110 cm^{-1} from poly(*N*-alkyl diacrylimide) or at 2140 cm^{-1} from poly(*N*-alkyl dimethacrylimide) appeared. The first band at 2340 cm^{-1} may belong to carbon dioxide; the second band can be assigned to methyl or ethyl isocyanate in agreement with previously reported spectra.[11] The infrared bands at 2110 and 2140 cm^{-1} are due to the ketene end groups.[1] The mass spectrometric measurement of the volatile photoproducts also confirms the formation of these products. Thus, all the *N*-alkyl-substituted polyimides show the same kind of photodegradation by eliminating alkyl isocyanate with simultaneous formation of ketene and olefin end groups.

In conclusion, all glutarimide type polymers except poly(diacrylimide) show a photodegradation pattern which is similar to that of glutaric anhydride type polymers except for the elimination of isocyanic acid or of alkyl isocyanate instead of carbon dioxide from the latter polymers.

Acknowledgments. The author wishes to thank Drs. J. Bargon, E. Gipstein, and T. Nogami for stimulating discussions and also Mr. L. W. Welsh, Jr., for his technical help.

References and Notes

(1) H. Hiraoka, *Macromolecules*, **9**, 359 (1976).
(2) H. Hiraoka, *IBM J. Res. Dev.*, **21**, 121 (1977).
(3) J. Bargon, E. Gipstein, and H. Hiraoka, United States patent 3 964 908 (July 1976); A polymer consisting partially of dimethacrylimide unit is reported to be an electron beam resist and photoresist by S. Matsuda, M. Honda, K. Hasegawa, G. Nagamatsu, and T. Asano, Technical Papers presented in Fourth Photopolymer Conference, Society of Plastic Engineering, Inc., Oct. 15, 1976, p 284.
(4) F. Götzen and G. Schröder, *Makromol. Chem.*, **88**, 133 (1965).
(5) G. Hertzberg and C. Reid, *Discuss. Faraday Soc.*, **9**, 92 (1950); M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, **40**, 2457 (1964).
(6) The radiation chemistry and photochemistry of the poly(dimethacrylimides) prepared by the cyclopolymerization of dimethacrylimides will be reported later by T. Nogami and H. Hiraoka.
(7) The reaction may proceed through an intermediate, $(CH_3)_2CH(=O)NCO$. We are undertaking a detailed mechanistic study of this kind of reaction.
(8) An elementary analysis of the nitrogen in the polyimide showed that about 85% of the imide conversion had been accomplished in the ammonia modification.
(9) For instance, see J. March, "Advance Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hall, New York, N.Y., 1968, p 658.
(10) G. Schröder, *Makromol. Chem.*, **96**, 227 (1966).
(11) R. P. Hirschmann, R. N. Kniseley, and V. A. Fassel, *Spectrochim. Acta*, **21**, 2125 (1965).

Hiroyuki Hiraoka

IBM Research Laboratory
San Jose, California 95193

Received November 11, 1976

β-Structure Formation and Its Stability in Aqueous Solutions of α-L-Glutamic Acid Oligomers

The formation of a β structure in aqueous solution, particularly of poly(L-lysine), has been extensively studied and its stability with regard to temperature, ionic strength, and pH has been investigated.[1] The formation in solution of such a structure with poly(α-L-glutamic acid) has never been demonstrated. Recently, Zimmerman et al.[2,3] have shown two distinct regions of precipitation with poly(Glu) in aqueous solutions at low pH, corresponding to α-helix and β-structure formation. To interpret the $\alpha \rightarrow \beta$ transition, they suggested a random-coil intermediate and a schematic mechanism proceeding through the following steps:

$$\alpha(\text{solution}) \leftrightarrow \text{random coil(solution)} \leftrightarrow \beta \leftrightarrow \beta\text{i}^* \rightarrow \beta(\text{ppt})$$

where β is the isolated β conformation and βi* is an aggregation type preceding the irreversible β precipitation β(ppt).

Using circular dichroism (CD) experiments on a series of α-L-glutamic acid oligomers with the general structure $CH_3\text{–}CO\text{–}(Glu)_n\text{–}NH\text{–}CH_2\text{–}CH_3$, we have made clear the existence of a critical range of DP (8 to 10) for β-structure formation in solution.[4] This paper is an extension of our previous work.

Experimental. The optical rotatory dispersion (ORD) spectra were obtained with a FICA spectropolarimeter (Spectropol 1b) using a 5-mm thermostated quartz cell with stepwise temperature variation from 25 to 80 °C and a 1-mm quartz cell at ambient temperature. The solutions were prepared as previously described.[4,5]

Results and Discussion. The formation and stability of β structure in solution as a function of temperature and concentration has been studied by optical rotatory dispersion (ORD). Recently we have demonstrated that the transition from one ordered structure to another necessarily passed through an unordered structure whose CD spectra can be observed for all DP > 5 when the degree of neutralization (α') is close to 0.4.[4] In Figure 1a, a confirmation of this choice is provided if we consider the absence of an isorotation point in the ORD spectra when the temperature of a solution of DP = 12 at $\alpha' \simeq 0.4$ is increased. For polymers of degrees of polymerisation of 8 and 9 at ambient temperature, the β structure slowly appears, followed by precipitation. The precipi-

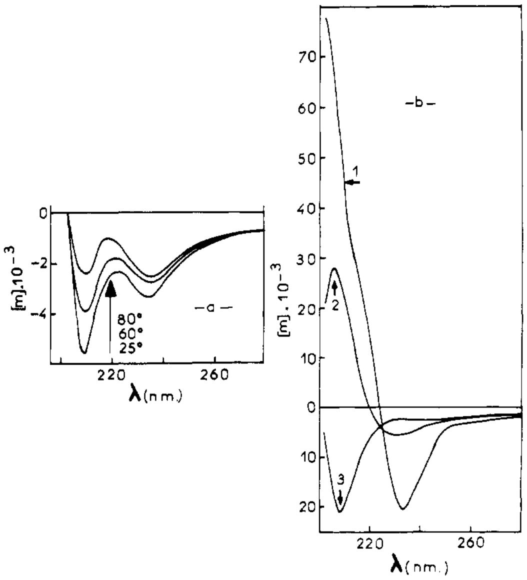

Figure 1. (a) Temperature dependance on ORD spectra for DP = 12 ($C = 10^{-3}$ equiv L^{-1}; $\alpha' = 0.4$). (b) Characteristic ORD spectra[5] for: (1) α helix; (2) β form; (3) extended structure.

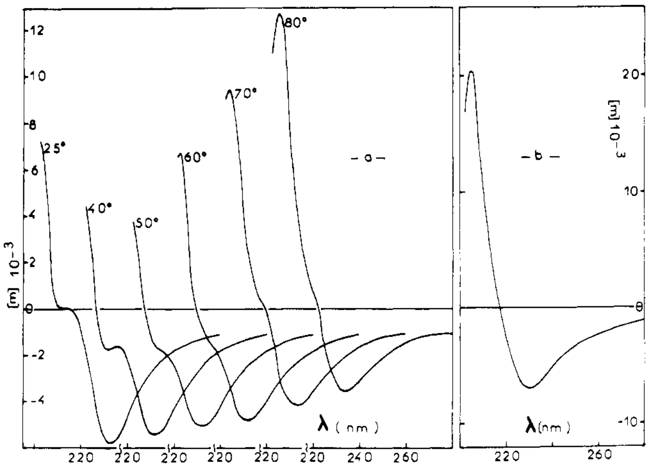

Figure 2. (a) Temperature dependance on ORD spectra for DP = 12 ($C = 10^{-3}$ equiv L^{-1}; $\alpha' = 0$). (b) ORD spectra for the same solution after a decrease of the temperature from 80 to 25 °C.

tation is almost instantaneous at 40 °C, showing the important effect of temperature on this kinetic process.

The interpretation of the ORD spectra is made possible by using the characteristics of the different peaks reproduced in Figure 1b and by resorting to the same process of combination as for CD on the four limiting spectra.[4] For the polymer of DP = 12, under acidic conditions, the ORD spectra given in Figure 2a for various temperatures clearly demonstrate that the $\alpha \rightarrow \beta$ transition proceeds through an unordered form with maximum yield at 50 °C. This process is fully reversible up to 60 °C.

At 80 °C, the spectrum corresponds to a perfectly stable equilibrium between β and unordered structures. When the temperature decreases to 25 °C (Figure 2b), the spectrum becomes characteristic of the pure β form followed by precipitation.

For a DP greater than 12 it is impossible to induce a complete β-structure formation at 10^{-3} equiv L^{-1}, whatever the time, pH, and ionic strength may be. Thus for $DP_n = 16$, the process starts in the same way as for DP = 12, but only a small amount of β form is obtained at 80 °C (Figure 3a). Therefore, the equilibrium is entirely reversible when the temperature is lowered to 25 °C. Nevertheless, as one increases the concentration to 1.84×10^{-3} equiv L^{-1} an irreversible β structure can be observed at ambient temperature (Figure 3b) with apparent precipitation after 6 h. When the DP is larger than 16 no experimental conditions allow us to separate β-structure formation from precipitation.

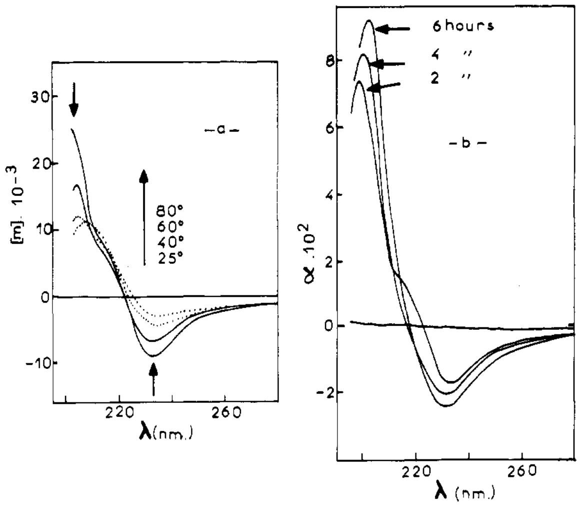

Figure 3. (a) Temperature dependance on ORD spectra for $\overline{DP}_n$ = 16 ($C = 10^{-3}$ equiv L^{-1}; $\alpha' = 0$). (b) Time dependance on ORD spectra for $\overline{DP}_n$ = 16 at 25 °C ($C = 1.84 \times 10^{-3}$ equiv L^{-1}; $\alpha' = 0$).

Conclusion. In this work we demonstrate that the β-structure formation induced by an increase of temperature necessarily passes through an unordered form and that the $\alpha \rightarrow \beta$ transition is reversible when the proportion of β form is lower than a critical value.

Finally, the different steps of the mechanism proposed by Zimmerman et al. are proved.

References and Notes

(1) B. Davidson and G. D. Fasman, *Biochemistry*, **6**, 1616 (1967).
(2) S. S. Zimmerman and L. Mandelkern, *Biopolymers*, **14**, 567 (1975).
(3) S. S. Zimmerman, J. C. Clark, and L. Mandelkern, *Biopolymers*, **14**, 585 (1975).
(4) M. Rinaudo and A. Domard, *J. Am. Chem. Soc.*, **98**, 6360 (1976).
(5) A. Domard, Thesis, Grenoble, France, 1976.

M. Rinaudo* and A. Domard
Centre de Recherches sur les Macromolécules Végétales,
53 X-38041 Grenoble, Cedex, France

Received December 3, 1976

Nuclear Magnetic Resonance and X-Ray Study of the Mesomorphic Transition in Poly[bis(2,2,2-trifluoroethoxy)phosphazene]

A number of polyphosphazene polymers, which have the general formula $[(RO)_2PN]_n$, exhibit two first-order transition temperatures. The lower temperature, denoted $T(1)$, appears to involve transformation from a crystalline to a mesomorphic phase, while the upper temperature, T_m, involves transformation to the true melt.[1,2] In poly[bis(2,2,2-trifluoroethoxy)phosphazene], for which RO = CF_3CH_2O, $T(1) \approx 80$ °C, and $T_m = 240$ °C.[1] The transition temperatures appear to be reproducible on samples from several different preparations, though $T(1)$ depends on thermal history.[2]

X-ray diffraction work by Allen, Lewis, and Todd[3] showed the $T(1)$ transition in $[(CF_3CH_2O)_2PN]_n$ involves loss of order along the direction of the polymer backbone. The presence at 90 °C of a single equatorial diffraction line corresponding to an 11 Å spacing was taken to indicate that order in the lateral plane, perpendicular to the backbone, is retained. Subsequently, Desper and Schneider observed as many as three sharp lines in the mesomorphic phase of the meta and