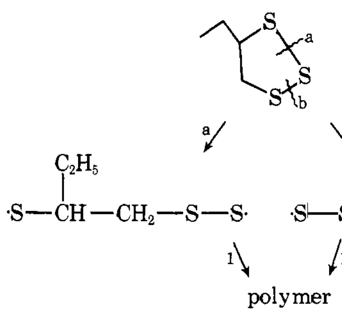


Figure 1.

We are continuing to study the physical properties of these and related compounds, as well as aspects of catalyzed polymerizations (solution and solid state). Work is also directed not only toward structure elucidation, but also toward obtaining structurally regular, as well as stereoregular polymers of this class of materials.

Acknowledgment. We thank Professor B. Wunderlich for the use of his calorimeter and D.N.H. and T.G.B. are indebted to the National Research Council of Canada for financial support of this work.

References and Notes

(1) E. J. Goethals, Proceedings of the NATO Advanced Studies Institute, J. A. Moore, Ed., Reidel Press, Boston, 1973, p 30.
(2) R. H. Gobran, "Encyclopedia of Polymer Science and Technology", Vol. 10, Wiley, New York, N.Y., 1969, p 325.
(3) H. A. Smith, ref 2, Vol. 10, p 653.
(4) (a) J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Am. Chem. Soc.*, **76,** 4348 (1954); (b) J. A. Affleck and A. Dougherty, *J. Org. Chem.*, **15,** 865 (1950); (c) N. A. Hiatt, *Adv. Chem. Ser.*, **No. 123,** 92 (1973).
(5) M. B. Berenbaum, ref 2, Vol. 11, p 425.
(6) D. S. Breslow and H. Skolnik, "The Chemistry of Heterocyclic Compounds", Interscience, New York, N.Y., 1965, Part 1, and references therein.
(7) C. G. Krespan and W. R. Brasen, *J. Org. Chem.*, **27,** 3995. These authors prepared and polymerized the tetrafluoro-1,2,3,4-tetrathiane, as well.
(8) (a) B. Milligan and J. M. Swan, *J. Chem. Soc.*, 2901 (1965); (b) H. Fritz and C. D. Weis, *Tetrahedron Lett.*, 1659 (1974); (c) T. C. Shields and A. N. Kurtz, *J. Am. Chem. Soc.*, **91,** 5415 (1969).
(9) D. N. Harpp and T. G. Back, McGill University, unpublished results.
(10) (a) A 41% yield of 1 was obtained (10 mmol scale): bp 40–44 °C (0.09 mm) (oil bath 150 °C); ms 152 (P^+). NMR: (CCl_4) δ 1.17 (t, 3 H), ~1.9 (m, 2 H), ~3.5 (m, 3 H). (b) Anal. Calcd for $C_4H_8S_3$: C, 31.5; H, 5.3; S, 63.2. Found: C, 31.5; H, 4.9; S, 63.5.
(11) A Du Pont Model 900 Thermal Analyzer was employed using a heating rate of 10 °C/min starting from 30 °C.
(12) See ref 11; the heating rate was 20 °C/min starting from −80 °C.
(13) The absolute molecular weight of this material may, in fact, be considerably larger than indicated because polystyrene is probably a stiffer chain than the poly"(trisulfide)".
(14) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry", W. A. Benjamin, new York, N.Y., 1965.

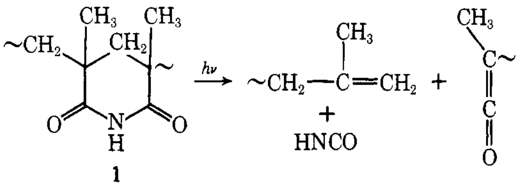
J. A. Moore* and J. E. Kelly
Department of Chemistry
Rennselaer Polytechnic Institute
Troy, New York 12181

David N. Harpp* and Thomas G. Back
Department of Chemistry
McGill University, Montreal, Quebec, Canada

Received August 30, 1976

Photolysis of Poly(dimethacrylimide) and Related Polymers

Poly(acrylic anhydride) and poly(methacrylic anhydride) have been shown to undergo decarboxylation to yield olefin and ketene end groups under UV irradiation[1] and electron beam exposure.[2] Poly(dimethacrylimide) and its copolymers have been disclosed to be a useful resist under electron and x-ray irradiation.[3] We wish to report here that poly(dimethacrylimide) 1 decomposes in a similar way as poly(methacrylic anhydride) by elimination of isocyanic acid which results in main chain scission with formation of olefin and ketene end groups as shown below:



1

(1)

Photochemical elimination of isocyanic acid has never been reported in the literature to our knowledge.

An ammonia treatment of poly(acrylic acid) and poly(methacrylic acid) at an ammonia pressure of 25 cm and 200 °C for 1 h yielded the structures of poly(diacrylimide) and poly(dimethacrylimide), respectively.[3] The polymer films thus obtained have identical infrared absorption spectra to the polymer obtained by the cyclopolymerization of dimethacryimide initiated by free radicals.[4] The same polyimide structures are also obtained by a similar ammonia treatment of poly(acrylic anhydride) and poly(methacrylic anhydride). Thin films of poly(dimethacrylimide) prepared on a sodium chloride plate were irradiated at low temperature (ca. −120 °C) with two medium pressure mercury lamps. When the poly(dimethacrylimide) prepared by the ammonia modification was irradiated for 5 h, an intense band at 2270 cm^{-1} (indicated by A) appeared in addition to a sharp band at 2345 cm^{-1} due to carbon dioxide, and a very weak band at 2135 cm^{-1} belonging to the ketene end group,[1] as shown in Figure 1. The band at 2270 cm^{-1} can be assigned to isocyanic acid in accordance with the data in the literature.[5] With the poly(dimethacrylimide) prepared by the cyclopolymerization of dimethacrylimide, the CO_2 band at 2345 cm^{-1} became much weaker, and the maximum peak of HNCO band shifted to 2245 cm^{-1}, while the ketene band at 2135 cm^{-1} became more intense.[6] The shift of HNCO band is probably due to the absence of the strong neighboring band in the latter case. Because the HNCO band appeared as a broad band with a half-band width of 50 cm^{-1}, the shift of the peak position from 2270 to 2245 cm^{-1} represents only the change of the absorption band shape.

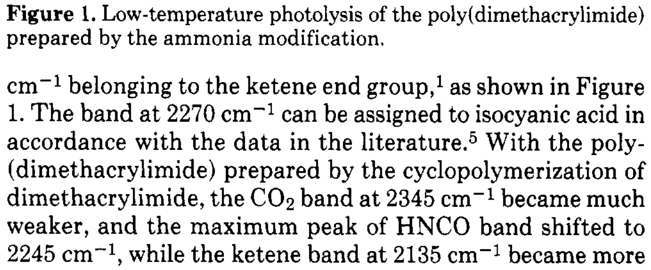


Figure 1. Low-temperature photolysis of the poly(dimethacrylimide) prepared by the ammonia modification.

The weak ketene band in comparison with the one from poly(methacrylic anhydride)[1] is due to the high reactivity of the ketene toward a labile hydrogen such as the one in the NH group, particularly in the polyimides prepared by the ammonia modification. The small but appreciable ketene band from the polyimide made by the cyclopolymerization may partially be explained by the rigid polymer structure, as revealed by a high glass transition temperature and a long lifetime of some radicals trapped in the polymer.[6] When the irradiated polymer films were warmed up, isocyanic acid and the ketene end group reacted with each other to yield carbon 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–CO–$(Glu)_n$–NH–CH_2–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-