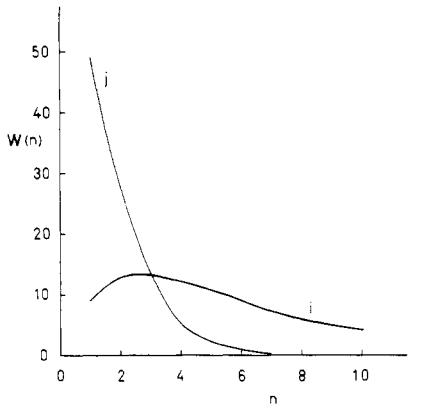

Figure 3. Weight fraction % sequences of length n for the structures i and j of Chart I.

bonds of type i and j, respectively. The probability of occurrence of a dyad will be determined by the equations

$$P(ii) = P(i)P(i) = P(i)^2$$

$$P(ij) = P(i)P(j) = P(ji)$$

The resonance data of Figure 1 in conjunction with these equations were used to estimate the values of $P(i)$ and $P(j)$, shown in Table II, where bond scission through bonds of type i was arbitrarily considered more probable than through bonds of type j. These data suggest the microstructure of poly(3-methyltetrahydrofuran). For illustrative purposes, the weight fractions of sequences of length n for structures of type i and j in the polymer prepared at lower temperature (polymer B) are shown in Figure 3. It can be observed that 49% of the structures of type j are isolated whereas the sequences of type i present a wide distribution with a maximum for $n = 3$.

The similarity of values of $P(i)$ for the two polymers prepared at −4 and −25 °C should not lead to the conclusion that the k_i/k_j ratio is independent of the reaction temperature. In fact, owing to the low ceiling temperature of poly(3-methyltetrahydrofuran) ($T_c = 4$ °C), the polymerization can only be carried out over a very limited interval of temperature, which precludes reaching any reliable conclusion regarding the influence of temperature on the structure of the polymer, although it can be expected that more regular polymers form at lower temperatures. The data at hand suggest that the ring opening occurs preferably through one of the bonds (70% of the total scission), but they do not allow one to establish which carbon is preferentially attacked over the interval of temperature that we have studied. It can be argued that the steric hindrance of the methinic carbon presumably influences a preferential attack at the methylenic carbon, adjacent to the oxonium ion, situated further away from the methinic carbon, in a way similar to that which occurs in poly(propylene oxide), where the cationic ring opening takes place between oxygen and the methinic carbon to the extent of 30%.[15] This conclusion is highly speculative since the steric factor is not predominant in all the cases. For example, in the cationic polymerization of bicyclic ethers such as 2-oxabicyclo[2.2.2]octane,[16] the ring opening occurs predominantly by attack on the tertiary carbon adjacent to the oxonium ion. However, for *trans*-7-oxabicyclo[4.3.0]none[17] and *trans*-2-oxabicyclo[3.3.0]octane,[18] where severe steric hindrances are present, the attack of the monomer takes place preferably at the methylenic carbon.

Acknowledgment. Thanks are due to Dr. M. Rico from the Instituto de Estructura de la Materia (CSIC) for helpful discussions on the ^{13}C NMR spectra.

Registry No. 3-Methyltetrahydrofuran, 13423-15-9; poly(3-methyltetrahydrofuran), 25607-91-4.

References and Notes

(1) Dainton, F. S.; Ivin, K. J. *Q. Rev., Chem. Soc.* **1958**, *12*, 61.
(2) Chiang, R.; Rhodes, J. H. *Polym. Lett.* 1969, *7*, 643.
(3) Garrido, L.; Guzmán, J.; Riande, E. *Macromolecules* **1981**, *14*, 1132.
(4) Dreyfuss, P.; Dreyfuss, M. P. *Adv. Polym. Sci.* **1967**, *4*, 528.
(5) Rozenberg, B. A.; Lyudvig, E. B.; Gantmakher, A. R.; Medvedev, S. S. *J. Polymn. Sci., Part C* **1967**, *16*, 1917.
(6) Saegusa, T.; Imai, H.; Matsumoto, S. I. *J. Polym. Sci., Part A-1* **1968**, *6*, 459.
(7) Croucher, T. G.; Wetton, R. E. *Polymer* **1976**, *17*, 205.
(8) Matyjaszewski, K.; Slomkowski, S.; Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 69.
(9) Matyjaszewski, K.; Slomkowski, S.; Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2413.
(10) Kops, J.; Hvilsted, S.; Spanggaard, H. *Macromolecules* **1980**, *13*, 1058.
(11) Oguni, N.; Hyoda, J. *Macromolecules* **1980**, *13*, 1687.
(12) Pretsh, E.; Clerc, T.; Scibl, J.; Simon, W. "Strukturanfklärung Organischer Verbindungen"; Springer-Verlag: Berlin, 1976.
(13) Garrido, L.; Guzmán, J.; Riande, E., work in progress.
(14) Iving, K. J. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 62*, 89.
(15) Searles, S.; Pollart, K. A.; Lutz, E. F. *J. Am. Chem. Soc.* **1957**, *79*, 948.
(16) Saegusa, T.; Hodaka, T.; Fujii, H. *Polym. J.* **1971**, *2*, 670.
(17) Kops, J.; Larsen, E.; Spanggaard, H. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 56*, 91.
(18) Kops, J.; Hvilsted, S. *Macromolecules* **1979**, *12*, 889.

Vacuum-Ultraviolet Circular Dichroism of Poly(γ-ethyl *N*-methyl-L-glutamate)

RICHARD T. COFFEY

Lever Research, Inc., Edgewater, New Jersey 07020

EUGENE S. STEVENS*

Department of Chemistry, State University of New York, Binghamton, New York 13901

ALESSANDRO COSANI and EVARISTO PEGGION*

Biopolymer Research Center of CNR, Institute of Organic Chemistry, University of Padova, 35100 Padova, Italy.
Received October 28, 1982

We report here the vacuum-ultraviolet circular dichroism (VUCD) of poly(γ-ethyl *N*-methyl-L-glutamate).

The polymer was synthesized as previously described by Cosani et al.[1,2] Purity was established by amino acid analysis and infrared spectroscopy, and the degree of polymerization was determined to be greater than 500. The polymer was dissolved in 2,2,2-trifluoroethanol (TFE) (Gold Label, Aldrich Chemical Co.) to form 5.2 mg/mL solutions. Films were cast by applying 0.03 mL of solution to a circular CaF_2 disk 1 mm thick and 1.9 cm in diameter and drying under nitrogen. The VUCD spectrometer has been described previously.[3,4] Spectra were insensitive to repeated 90° rotations of the disk in the light path, indicating an absence of linear birefringence.

The film spectrum is shown in Figure 1. The negative and positive bands at 229 and 200 nm, respectively, are 1–4 nm red shifted relative to the CD spectra of TFE solutions.[2] We also find a positive band at 175 nm not previously reported. We observed apparent negative ellipticity in the region 145–160 nm, but the signal–noise ratio was unacceptably small (<4) so those data are not included in Figure 1. In our previous VUCD studies of peptide films[3,4] we were able to obtain satisfactory spectra

0024-9297/83/2216-1243$01.50/0

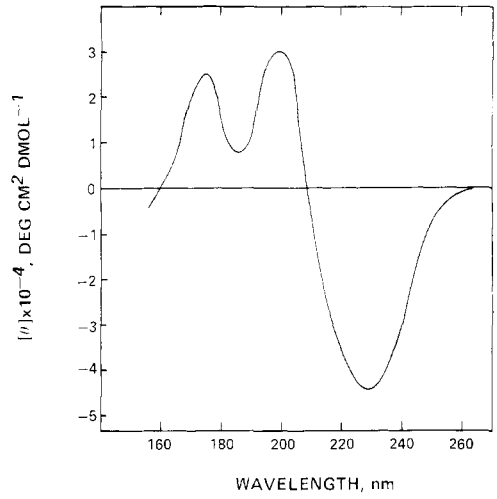

Figure 1. Vacuum-ultraviolet circular dichroism of poly(γ-ethyl *N*-methyl-L-glutamate) film.

to 135 nm. Those studies were of peptides with saturated side chains, and we attribute the higher wavelength cutoff experienced here to particularly strong film absorptivity caused by the oxygen-containing chromophore in the side chain. For purposes of presentation the intensity of the 229-nm band in Figure 1 is scaled to its intensity in solution.[2] A direct measure of that band's intensity in the film gave an apparent intensity 65% less than in solution, which likely resulted from a nonuniform film thickness.

We also obtained a solution spectrum on the same polymer sample (5.2 mg/mL in TFE; 0.024-mm path length) to confirm previously published data.[1,2] Our solution spectrum agreed with the published spectra in the overlapping region, 192–270 nm; in the region 180–192 nm our solution spectrum was qualitatively the same as our film spectrum (Figure 1). Below 180 nm our signal–noise ratio became unacceptably small. In previous studies of peptides in TFE solution[3,4] we were able to reach 165 nm; we believe the relatively high wavelength cutoff in the present study to have been caused by high absorption of the oxygen-containing side-chain chromophore.

The CD of this polymer and of poly(γ-methyl *N*-methyl-L-glutamate) above 192 nm was previously reported by Cosani et al.[2] and found to be similar to that of another N-substituted poly(amino acid), poly(*N*-methyl-L-alanine),[5,6] indicating the likelihood of a common backbone conformation for the three. Goodman et al.[6] had earlier shown the latter polymer to exist in a stable helical structure in TFE. Energy calculations[7-9] for *N*-methyl-L-alanine segments have indicated four significant energy minima in the two-dimensional ϕ,ψ potential surface, corresponding to regular helical structures. Mark and Goodman[7,8] found the most stable of these allowed conformations to be an approximately threefold right-handed helix ($n = 3.2$) with $\phi = -150°$ and $\psi = 70°$. Furthermore, Madison and Schellman[10] calculated circular dichroism spectra for the four geometries of poly(*N*-methyl-L-alanine) and found that only for the $\phi = -150°$, $\psi = 70°$ conformation did the calculated spectrum agree well with observed CD in the 192-240-nm region,[5,6] i.e., a negative n–π^* rotational strength and a pair of oppositely signed π–π^* rotational strengths, with the lower energy component being negative.

A second conformation calculated to be only slightly less stable,[7-9] with $\phi = -100°$ and $\psi = 165°$, is similar to the poly(L-proline II) conformation ($\phi = -75°$, $\psi = 145°$). However, we have previously reported the VUCD of poly(L-proline I) and poly(L-proline II) helices,[11] also N-substituted, and found that they display only negative dichroism from 140 to 200 nm. In that respect, Figure 1 reveals the positive 174-nm band in poly(γ-ethyl *N*-methyl-L-glutamate) to be an especially distinctive feature. If one estimates the glutamate side-chain chromophores to be randomly oriented in the film, with very little net dichroism, and assigns the 174-nm band to an amide backbone transition, the difference in its sign between the two polymers must be considered the result of a difference in backbone conformation. The VUCD in Figure 1 thereby helps rule out the poly(L-proline II)-like conformation and provides additional experimental evidence that poly(γ-ethyl *N*-methyl-L-glutamate) takes up the threefold right-handed helix described above. In addition, the qualitative similarity of the solid-state VUCD and the CD in solution makes it likely that the chain conformation is similar in the two cases, so that an X-ray determination of the solid-state structure will be relevant to the solution conformation.

Furthermore, Cosani et al. on the basis of their solvent-dependent study of poly(γ-ethyl *N*-methyl-L-glutamate)[12] and their recent synthesis and conformational study of poly(*N*-methyl-L-glutamic acid)[13] have rationalized the marked conformational stability observed for *N*-methyl derivatives of esters of poly(L-glutamic acid) in terms of *N*-methyl–C^{α}-methylene interactions.

Acknowledgment. This work was partially supported by NIH Grant GM 24862.

Registry No. Poly(γ-ethyl *N*-methyl-L-glutamate), 71495-59-5; (*S*)-poly[(methylimino)[1-(3-ethoxy-3-oxopropyl)-2-oxo-1,2-ethanediyl]], 71495-10-8.

References and Notes

(1) Cosani, A.; Palumbo, M.; Terbojevich, M.; Peggion, E. *Biopolymers* **1978**, *17*, 2519–2521.
(2) Cosani, A.; Palumbo, M.; Terbojevich, M.; Peggion, E. *Macromolecules* **1978**, *11*, 1041–1045.
(3) Pysh (Stevens), E. S. *Annu. Rev. Biophys. Bioeng.* **1976**, *5*, 63–75.
(4) Pysh (Stevens), E. S. In "Excited States in Organic Chemistry and Biochemistry"; Pullman, B., Pullman, A., Eds.; Reidel: Dordrecht, Holland, 1977; Vol 10, pp 409–418.
(5) Goodman, M.; Fried, M. *J. Am. Chem. Soc.* **1967**, *89*, 1264–1267.
(6) Goodman, M.; Chen, F.; Price, F. R. *Biopolymers* **1974**, *12*, 2549–2561.
(7) Mark, J. E.; Goodman, M. *J. Am. Chem. Soc.* **1967**, *89*, 1267–1268.
(8) Mark, J. E.; Goodman, M. *Biopolymers* **1967**, *5*, 809–814.
(9) Liquori, A. M.; DeSantis, P. *Biopolymers* **1967**, *5*, 815–820.
(10) Madison, V.; Schellman, J. *Biopolymers* **1972**, *11*, 1041–1076.
(11) Young, M. A.; Pysh (Stevens), E. S. *J. Am. Chem. Soc.* **1975**, *97*, 5100–5103.
(12) Cosani, A.; Terbojevich, M.; Palumbo, M.; Peggion, E.; Goodman, M. *Macromolecules* **1979**, *12*, 875–877.
(13) Cosani, A.; Terbojevich, M.; Palumbo, M.; Peggion, E.; Goodman, M. *Biopolymers* **1982**, *21*, 471–474.