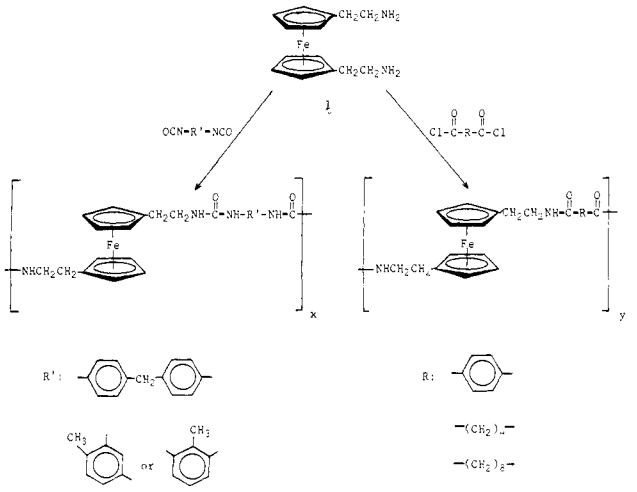
Table I. Polycondensation Reactions between 1,1′-Bis(β-aminoethyl)ferrocene (**1**) and 1,1′-Bis(β-hydroxyethyl)ferrocene (**2**) with Diacid Chlorides and Diisocyanates

monomer (M_1)	monomer (M_2)	process (base used)	% yield	intrinsic viscosity [η], dL/g[e]
1[a]	terephthaloyl chloride (CH_2Cl_2)	UI[b] (Et_3N)	72	1.50
1[a]	sebacoyl chloride (CCl_4)	UI (Et_3N)	85	0.37
1[a]	sebacoyl chloride (CCl_4)	UI (NaOH)	39	0.59
1[a]	sebacoyl chloride (CCl_4)	I[b] (Et_3N)	51	1.09
1[a]	adipoyl chloride (CCl_4)	UI (Et_3N)	47	0.53
1	terephthaloyl chloride (CH_2Cl_2)	S[b] (Et_3N)	45	0.80
2	terephthaloyl chloride (*m*-xylene, reflux)	S (pyridine)	51	0.16
2	TDI[c] (Me_2SO, 115 °C)	S	46	0.20
1[a]	TDI ($CHCl_3$)	UI	58	0.16
1	TDI ($CHCl_3$)	S	53	0.10
1	MDI[d]	S	67	*f*

[a] Monomer in aqueous phase. [b] UI, unstirred interfacial; S, solution; I, stirred interfacial. [c] TDI: tolylene 2,4-diisocyanate (80%) + 2,6 isomer (20%). [d] MDI: methylenebis(4-phenylisocyanate). [e] Determined in *m*-cresol at 32 °C. [f] Insoluble in *m*-cresol.

Scheme II



TDI, to decreased reactivity imposed by steric effects.[18]

Scanning electron microscopy X-ray analysis or EDS of the polyamide films showed qualitative collections of iron atoms on a scanned area. The distribution of these localized iron collections was fairly uniform and, as expected, was more intense for the polyamide obtained with terephthaloyl chloride than sebacoyl chloride. The polyamide obtained with adipoyl chloride was elastomeric. The polyureas were obtained as hard powders. The polyamides, in contrast to the polyesters, polyureas, and polyurethanes, showed negligible weight loss at 300 °C in a nitrogen atmosphere. The latter showed substantial weight loss at 300 °C.

The polyamides and polyureas[19] exhibited broad, intense N–H stretches around 3300 cm^{-1}. A very strong carbonyl stretching vibration was present at 1630 cm^{-1}. The amide II band was evident near 1540 cm^{-1}. In addition, sp^2 C–H stretches occurred around 3100 cm^{-1} and asymmetric and symmetric sp^3 C-H stretches at 2950 and 2860 cm^{-1}, respectively. The polyurethane showed the carbonyl absorption near 1700 cm^{-1} and C–O stretches in the vicinity of 1220 and 1280 cm^{-1}. Similar absorptions were present in the polyester. The polyamides and polyureas are thus assessed to have the structures outlined in Scheme II.

Further studies involving the polymerization behavior of **1**, **2**, and their ruthenium and osmium analogues are under way in our laboratory, including the potential for utilizing these monomers and techniques for the development of block copolymers having thermoplastic properties and for the fabrication of films for surface-modified electrodes.

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Registry No. 1, 83729-65-1; (**1**)·(terephthaloyl chloride) (copolymer), 90219-90-2; (**1**)·(terephthaloyl chloride) (SRU), 90219-97-9; (**1**)·(sebacoyl chloride) (copolymer), 90219-91-3; (**1**)·(sebacoyl chloride) (SRU), 90219-98-0; (**1**)·(adipoyl chloride) (copolymer), 90219-92-4; (**1**)·(adipoyl chloride) (SRU), 90219-99-1; (**1**)·(TDI) (copolymer), 90219-95-7; (**1**)·(TDI) (SRU), 90342-59-9; (**1**)·(MDI) (copolymer), 90219-96-8; (**1**)·(MDI) (SRU), 90220-01-2; **2**, 1272-08-8; (**2**)·(terephthaloyl chloride) (copolymer), 90219-93-5; (**2**)·(terephthaloyl chloride) (SRU), 90220-00-1; (**2**)·(TDI) (copolymer), 90219-94-6; (**2**)·(TDI) (SRU), 90342-58-8; 1,1-diacetylferrocene, 1273-94-5; ferrocene, 102-54-5; 1,1′-ferrocenedicarboxylic acid, 1293-87-4; dimethyl 1,1′-ferrocenedicarboxylate, 1273-95-6; 1,1′-ferrocenedimethanol, 1291-48-1; 1,1′-ferrocenediacetonitrile, 32677-74-0; 1,1′-ferrocenediacetic acid, 32681-19-9.

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Fourier Transform IR and NMR Studies of Hydrogen Bonding in *Helminthosporium carbonum* Toxin

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HC toxin, a metabolite of *Helminthosporium carbonum* is a host-specific phytotoxin affecting certain varieties of corn.[1-3] It

Table I. ^{1}H NMR Data for the Diacetyl Derivative of HC Toxin[a]

	L-Ala[1]	D-Ala[2]	L-AEO[3]	D-Pro[4]
δ_{N-H}[f]	7.15 (7.13)	6.35 (6.22)	6.37 (6.32)	
$\delta_{C_\alpha-H}$	4.46 (4.49)	4.56 (4.59)	4.78 (4.70)	4.70 (4.71)
$^3J_{NH-\alpha}$, Hz	10.3 (10.25)	9.92 (9.73)	10.30 (10.40)	
$\Delta\delta$/% Me_2SO-d_6[b]	−0.13	−2.55	−0.53	
$\tau_{1/2}$, h[c]	24	10.2	24	
R_{1p}, s^{-1} [d]	2.98	18.33	1.94	
R_{2p}*, s^{-1} [e]	3	24.4	3	
$\Delta\delta/\Delta t$,[g] ppb/°C	−1.7	−5.8	−2.8	

[a] Values in parenthesis refer to HC toxin. [b] Changes in chemical shift are calculated over a 40% range of Me_2SO-d_6 in $CDCl_3$ solution. [c] Values were obtained using a 2% methanol-d_4 in $CDCl_3$ solution. [d] $R_{1p} = (1/T_{1\,exp}) - (1/T_1)$; $T_{1\,exp}$ = relaxation time measured in presence of nitroxide; T_1 = relaxation time measured in absence of nitroxide. [e] $R_{2p}^* = (1/T_{2\,exp}^*) - (1/T_2^*)$; T_2^* times are expressed as $1/(\pi(\Delta\nu)_{1/2})$. [f] δ in ppm. [g] Changes in chemical shift were observed between 20 and 50 °C.

is a cyclic tetrapeptide containing two alanyl residues, one proline, and the unusual 2-amino-9,10-epoxy-8-oxodecanoic acid (AEO).[4-6] The sequence and the configuration at the α carbon of the four amino acids have been reported.[4-7] Although there has been some discrepancy[4,5] the sequence cyclo-(Ala^1-Ala^2-AEO^3-Pro^4)[7] is now generally accepted. Walton et al.[5] proposed a D configuration for the prolyl residue and L for the other three residues, a proposal inconsistent with subsequent chemical and NMR findings.[8,15] We report here a study of hydrogen bonding of the native HC toxin **1** and its diacetyl derivative **2**[6] using five different IR and NMR parameters. The assignment of the ^{1}H spectrum of **1** and **2** was accomplished by 1D and 2D NMR at 200 and 600 MHz.[9,15] The α and amide proton chemical shifts and coupling constants are in Table I.

The degree of aggregation was investigated by varying the concentration of **2** in chloroform-*d*; no chemical shift changes were detected in the concentration range 10^{-4}–10^{-2} M, suggesting that aggregation is insignificant in dilute solution. Difference FT-IR of **2**, 10^{-3} M in $CDCl_3$, showed a ratio for hydrogen-bonded (3340 cm^{-1}) to non-hydrogen (3450 cm^{-1}) N–H absorptions of 2:1, indicating two intramolecular hydrogen bonds in the peptide. A Me_2SO-d_6 titration of a 10 mM solution of **2** in chloroform-*d* showed a different dependence upon solvent composition for the three amide protons, the Ala^2-NH resonance shifts 1 ppm downfield for a 40% Me_2SO-d_6 in chloroform solution indicating exposure to the solvent:[10] in contrast the Ala^1 and AEO^3 amide proton shift dependendences indicate solvent shielding (Table I). The temperature dependence of the NH protons confirmed these conclusions. Thus, small temperature coefficients ($\Delta\delta/\Delta T$ = −1.7 and −2.8 ppb/°C) were observed for the Ala^1-NH and AEO^3-NH resonances, respectively, whereas the more accessible Ala^2-NH had $\Delta\delta/\Delta T$ = −5.8 ppb/°C.[11]

In Table I the $\tau^{1/2}$ values for proton–deuterium exchange rates are reported. A $\tau^{1/2}$ = 10 h for Ala^2-NH compared with $\tau^{1/2}$ > 24 h for the other two residues supports the observation that residues 1 and 3 have the hydrogen-bonded amides detected by FT-IR.

Finally attention was directed to the amide proton T_1's and T_2's of **2** as a function of free radical concentration. Variation of the nonselective T_1 upon addition of free radicals allows the distinction between buried and exposed to the solvent protons.[12,13] The addition of TEMPO (4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl) to a chloroform-*d* solution of **2** markedly enhanced the R_1

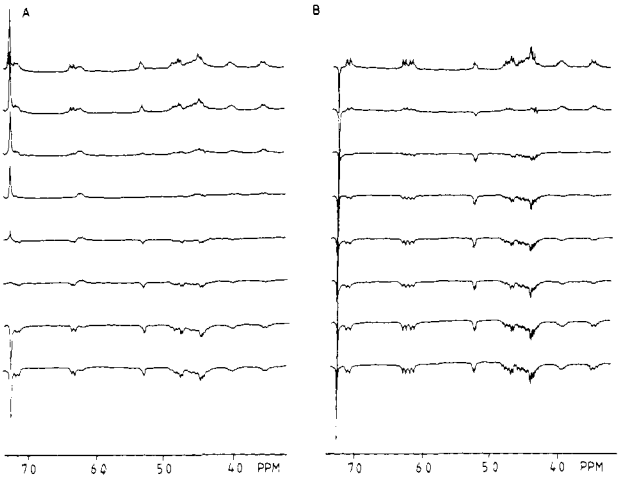
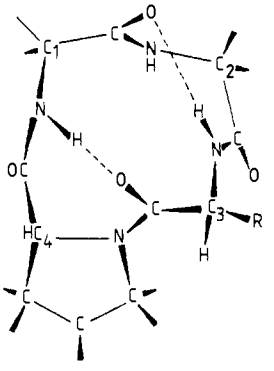


Figure 1. T_1 inversion recovery spectra of α and amide region of diacetyl HC toxin **2**: (A) **2** in $CDCl_3$ (12 mM) at 20 °C in the presence of TEMPO (20 mM), (B) **2** in $CDCl_3$ (12 mM). All sequences refer to identical values; values from top to bottom in both sections: 600, 350, 300, 200, 140, 100, 20, 5 ms.



1: R = $(CH_2)_5$-CO-CH-CH_2 (O)

2: R = $(CH_2)_5$-CO(OAc)-CH(OAc)-CH_2

Figure 2. Diagrammatic representation of proposed conformation for HC toxin and its diacetyl derivative.

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($=1/T_1$) value of Ala^2-NH pointing to its accessibility to the solvent (Figure 1). In Table I the amide relaxation rates as $R_{1p} = (1/T_{1\,exp}) - (1/T_1)$ are given. T_2 relaxation times from line widths were also investigated. As expected addition of TEMPO caused a different broadening of each of the three amide resonances—the R_2^* (24.4 s^{-1}) for Ala^2-NH is faster than R_2^* (3 s^{-1}) for residues 1 and 3. The results clearly support the proposal that Ala^1 and AEO^3 amide protons are shielded from the solvent.[12]

All the NMR data therefore unambiguously indicate the differences in the environment of Ala^2-NH proton compared with that of Ala^1-NH and AEO^3-NH. The latter two protons are solvent shielded; Ala^2-NH is instead accessible to the solvent. IR data indicated that even at low concentration two protons are hydrogen bonded. We propose therefore that Ala^1-NH and AEO^3-NH are involved in intramolecular hydrogen bonds. A similar hydrogen-bonding pattern leading to a bis-γ-turn configuration was found for other cyclic tetrapeptides.[14]

Although more detailed studies will be necessary, a conformation containing two γ turns can be also proposed for **2** (Figure 2). The derivatization of **1** to **2** yielded no significant changes in chemical shift or $^3J_{NH-\alpha}$ of α and amide protons, indicating that no conformation modification had occurred in the peptide ring (see Table I). Furthermore, the ^{13}C chemical shift for the Pro^4 C_β of **1** in chloroform solution is consistent with a γ turn involving the Pro^4 residue.[15] We therefore suggest that HC toxin also assumes the conformation of Figure 2.

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Registry No. 1, 83209-65-8; **2**, 89890-87-9.

Far-Ultraviolet Electric Linear Dichroism of Poly(α-L-glutamic acid) in the Helical and Coiled Conformations[1]

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In order to verify Moffitt's prediction that the absorption spectrum of the peptide chromophore in helical polypeptides should show a band split,[2] we initiated an electric linear dichroism (ELD) study in the far-ultraviolet region.[3] We can now report some preliminary results on reduced dichroism ($\Delta A/A$) of electric-field-oriented poly(α-L-glutamic acid), (Glu)$_n$, in helical and coiled conformations in the 230–187-nm wavelength region. On the basis of the dependence of ($\Delta A/A$) on wavelength and applied field strength, we conclude that at least three apparent component bands are involved in the isotropic spectra of the peptide chromophore of (Glu)$_n$ in the two extreme conformations and that the transition moment direction of each band makes a different angle with respect to the orientation axis of the polymer chain.

The ELD apparatus consists of an electric pulsing system and an optical system, which contains a 200-W deuterium lamp, a double-grating monochromator, and a Rochon-type magnesium fluoride polarizer. The details will be given elsewhere,[3] together with data acquisition and processing.[3-6] The sodium salt of purified (Glu)$_n$ with a degree of polymerization of 708 was dissolved in distilled water (pH 6.89). By dialysis of this stock solution against dilute HCl, a salt-free acid (Glu)$_n$ solution was prepared (pH 4.13). The reduced dichroism is given as $\Delta A/A = (A_\parallel^E - A_\perp^E)/A = (^3/_2)(3\cos^2\theta - 1)\Phi$, where $A_\parallel^E$ is the absorbance of a sample solution for incident light linearly polarized in parallel to an applied electric field, $A_\perp^E$ is the same in perpendicular to the field, A is the field-free isotropic absorbance, θ is the angle between the orientation axis of (Glu)$_n$ and the direction of a transition moment, and Φ is the orientation factor at a given field strength E.[7,8]

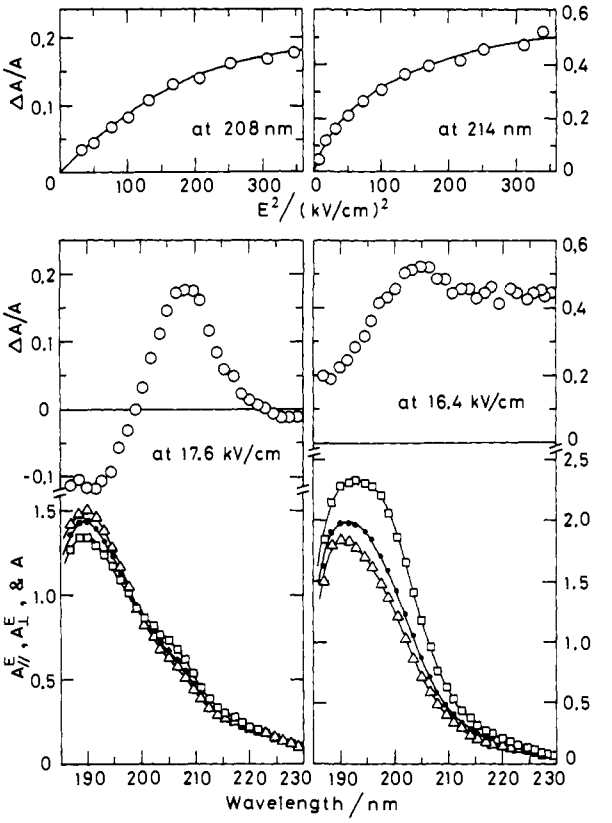

Figure 1. Dependence of reduced dichroism $\Delta A/A$ on the second power of electric field strength E^2 (top) and on wavelength (middle), and the absorption spectra (bottom) in the presence ($A_\parallel^E$ and $A_\perp^E$) and in the absence (A) of external electric field for helical (Glu)$_n$ (left halves) and coiled (Glu)$_n$ (right halves). Symbols denote experimental points (□ for $A_\parallel^E$, Δ for $A_\perp^E$, and ○ for $\Delta A/A$). The ELD signals were measured at 20 °C with "Kerr" cells, whose path lengths are 0.60 and 2.00 cm,[4,5] while the isotropic spectra (—·—) were measured on a Hitachi EPS-3T recording spectrophotometer with a pair of 0.5-cm quartz cells under nitrogen gas purge. Absorbances on the ordinate were all normalized to a path length of 0.6 cm. The residue concentrations of (Glu)$_n$ are 0.58 mM at pH 4.13 and 0.43 mM at pH 6.89. The relation $3A = A_\parallel^E + 2A_\perp^E$ was found to hold over an entire field-strength region (0–20 kV/cm) in all cases.

The dependence of $\Delta A/A$ on the square of electric field for helical and coiled (Glu)$_n$ is shown at the top of Figure 1. $\Delta A/A$ values obey the Kerr law in the low field region, but tend to saturate at high field strengths. By extrapolating $\Delta A/A$ values to infinitely high field, the saturated reduced dichroism, $(\Delta A/A)_s$,[6,8] could be estimated to be 0.280 at 208 nm for helical (Glu)$_n$ and 0.719 at 214 nm for coiled (Glu)$_n$. Hence, the degree of orientation in terms of Φ is ca. 0.61 at a field strength of 17.6 kV/cm for helical (Glu)$_n$ and ca. 0.65 at 16.4 kV/cm for coiled (Glu)$_n$. The anisotropic absorption spectra, $A_\parallel^E$ and $A_\perp^E$, were

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