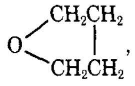
tion of Cyclic Ethers," describing the polymerization of tetrahydrofuran (1) with fluorosulfonic acid (FSO_2OH, 2) in benzene solvent over the temperature range 0–35°.[1]

These authors claim to be able to distinguish separately between 1 and 3 on the basis of ^1H nmr spectra and give assignments of the ^1H nmr chemical shifts for the H atoms of the following species coexisting in benzene solution.



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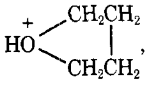

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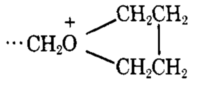


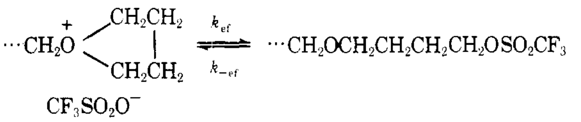
4

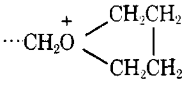
The possibility of determining 3 in the presence of an excess of 1 at room temperature seems to us to be very unlikely because the proton exchange between 1 and 3 is too fast to distinguish 1 and 3 on the nmr time scale. The chemical shifts of H bound to the α-carbon atoms in 1 and 3 cannot be observed separately and the measured chemical shift of these H atoms is a statistically weighed average of the instantaneous concentrations of 1 and 3 and the corresponding chemical shifts.

The band positions expressed in parts per million (δ) in the cited paper are probably also incorrect, since the authors have used the position of C_6H_6 solvent as the internal standard. However, due to the H^+ (solvated)-π interaction the position of C_6H_6 singlet should be dependent on the acid concentration. At the 12.5 mol % of 2 used the $\Delta\nu$ ($\nu(C_6H_6)_{obsd} - \nu(C_6H_6)_{neat}$) can be equal to several tenths of a ppm.

The error of the assignment given for 3 can also be seen on the basis of the following reasoning. The authors correctly assume the equilibrium $1 + 2 \rightleftarrows 3$ to be very rapidly established (Scheme I),[1] but in contrast to this assumption and according to the experimental data given in their Table II, the concentration of the species supposed 3 slowly within several hours increases.

According to the experimental evidence given in ref 1, there are indeed two different kinds of highly deshielded H atoms bound to the carbon atoms in the α position to the deshielding center (a positively charged oxygen atom). Since, according to our argument, one of these cannot be 3, and since it is known from our recent work, that in a similar system (with $CF_3SO_2O^-$ anion) 4 exists in equilibrium with a corresponding macroester,[2] we postulate that in reality the two different deshielded species observed by Pruckmayr and Wu are





4, FSO_2O^-

$\cdots CH_2CH_2OSO_2F$

5

Thus, we suppose that the assignment claimed for 3 corresponds in fact to 4 and the assignment attributed to 4 corresponds to 5.

In addition there are some inconsistencies within the data given in the paper under discussion. These are the results of the incorrect ^1H nmr assignments. In Figure 3 part of the ^1H nmr spectrum (220 MHz) of the polymerization mixture is given. The large triplet at δ 4.25 ppm is observed and assigned to six deshielded H atoms in 4. If this triplet were the spectrum of these H atoms in 4, then necessarily four less deshielded H atoms of 4 should also be seen. These four absorb, according to ref 1, at δ 2.19 ppm. However, there is practically no absorption at δ 2.19 ppm in Figure 3. This is in agreement with our assumption that the absorption due to the ester (5) had erroneously been taken for 4.

Our postulate is also in agreement with the value of $k_p^{\pm}$ (rate constant of 1 propagation involving the ion pairs 4) that we calculate using the experimental data given in the paper[1] and assuming that only the tertiary oxonium ions are able to propagate.[2] According to these calculations, $k_p^{\pm}$ (C_6H_6-1 mixture) = $2.6 \times 10^{-2}\ M^{-1}\ sec^{-1}$, while the k_p^{app} (apparent, including $k_p^{\pm}$ and the equilibrium constant describing the ion pair $\rightleftarrows$ ester equilibrium) is equal under the same conditions to $2.0 \times 10^{-3}\ M^{-1}\ sec^{-1}$, close to the values determined by us elsewhere for the identical monomer-solvent mixture.[2] Otherwise, if Pruckmayr and Wu's assignments were correct, the $k_p^{\pm}$ would be very much lower (by almost two orders of magnitude) than determined by us as well as by the other authors for various initiators ($k_p^{\pm}$ was found to be independent on the anion structure[2]).

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(2) K. Matyjaszewski, P. Kubisa, and S. Penczek, International Symposium on Cationic Polymerization, Rouen, Sept 1973, Paper 25.

New Method for Calculating the Conformational Entropy of a Regular Helix[1]

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The conformational entropy plays an essential role in the conformational transitions of macromolecules. In a theoretical treatment in which bond lengths and bond angles are maintained fixed, the conformational entropy of a macromolecule can be obtained from the matrix **F** of second derivatives as $-(R/2)\ \ln \det \mathbf{F}$, where the elements $f_{i,j}$ of the matrix **F** are the second derivatives of the conformational energy with respect to the independent variables q_i and q_j calculated at the minimum point.[3,4] This method was applied previously[5] (see eq 12 of ref 5 in which g is $\exp(-S_h/R)$ and $\mathbf{A}_j$ is the matrix of second derivatives of a $j$mer corresponding to $\mathbf{F}_n$ below) to calculate the conformational entropy of a regular helix; *i.e.*, the conformational entropy per repeating unit, S_h, of a regular helix was obtained as a limit, given by

$$S_h = -\lim_{n\to\infty} (R/2)\ \ln\ (\det \mathbf{F}_{n+1}/\det \mathbf{F}_n) \qquad (1)$$

where $\mathbf{F}_n$ is the matrix of second derivatives at the energy

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(1) This work was supported partially by a research grant to N. G. from the Ministry of Education of Japan, and partially by research grants to H. A. S. from the National Science Foundation (No. GB-28469X2) and from the National Institute of General Medical Sciences of the National Institutes of Health, U. S. Public Health Service (No. GM-14312). Part of this work was carried out during the summer of 1972 when N. G. and M. G. visited Cornell University.

(2) (a) Kyushu University; (b) Cornell University.

(3) N. Gō, M. Gō, and H. A. Scheraga, *Proc. Nat. Acad. Sci. U. S.*, **59**, 1030 (1968).

(4) N. Gō and H. A. Scheraga, *J. Chem. Phys.*, **51**, 4751 (1969).

(5) M. Gō, N. Gō, and H. A. Scheraga, *J. Chem. Phys.*, **52**, 2060 (1970).

Table I
Repeating Elements of the Matrix $\mathbf{F}_n$ for the Right-Handed α-Helical Conformation of Poly(L-alanine)[a,b]

	ϕ_i	ψ_i	ϕ_{i+1}	ψ_{i+1}	ϕ_{i+2}	ψ_{i+2}	ϕ_{i+3}	ψ_{i+3}	ϕ_{i+4}
ϕ_i	422.6	211.7	207.7	39.65	6.891	−2.064	−0.247	−0.176	
ψ_i		394.0	372.4	172.2	169.8	5.133	−1.192	−0.140	0.109

[a] In kcal/mol·(rad)^2, based on the data of parameter set A of ref 5. [b] Because the matrix is symmetric, only the repeating elements of the upper half are given.

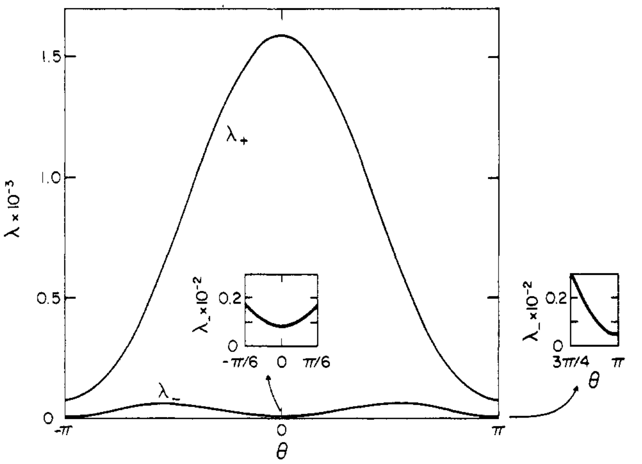

Figure 1. $\lambda_\pm$ as a function of the index θ. The behavior of λ_- near $\theta = 0$ and π, respectively, is shown in the enlarged graphs.

minimum of the helical conformation of an $n$mer. (See eq 41 of ref 4 for the problem of another conformational entropy term, $-(R/2)\ \ln \det \mathbf{G}$, and section IIA of ref 5 for the reason for its omission.) In this note, a new method (which consumes considerably less computer time) is described for calculating S_h.

As was discussed earlier,[3] the elements $f_{i,j}$ of the matrix $\mathbf{F}_n$ (with n large), which are far from the diagonal (*i.e.*, those for which $|i - j|$ is large), vanish quickly because of the helical structure of the polymer. In addition (for large n), $\mathbf{F}_n$ becomes periodic in its "interior," and the elements $f_{i,j}$ repeat; *i.e.*, $f_{i,j} \cong f_{i+k,j+k}$, where k is the number of independent dihedral angles in a repeating unit, provided that the i,j and $i+k,j+k$ elements refer to dihedral angles that are not too close to either end of the helix. Because of the end effect, the "periodicity" becomes obscure towards the ends of the helix (or at the periphery of the matrix $\mathbf{F}_n$). It is apparent from the definition of S_h in eq 1 that this quantity is determined only by the repeating elements in the interior of the matrix $\mathbf{F}_n$. An example of such repeating elements (taken from the work of ref 5) is shown in Table I for the right-handed α-helical conformation of poly(L-alanine), which contains two variable dihedral angles ϕ_i and ψ_i in the ith repeating unit. Therefore, two rows of elements repeat in the "interior" of the matrix.

Since S_h is determined only by the repeating elements in the *interior* of $\mathbf{F}_n$, it is unaffected by deviations of the elements at the periphery of $\mathbf{F}_n$ from the interior repeating values. Therefore, $\mathbf{F}_n$ of eq 1 can be replaced by a matrix $\mathbf{F}'_n$, where $\mathbf{F}'_n$ is obtained from $\mathbf{F}_n$ by replacing its nonrepeating peripheral elements by the repeating interior ones in such a way that the relation $f_{i,j} = f_{i+kl,j+kl}$ holds for an arbitrary integer l. If the value of the suffix falls outside the range between 1 and kn, then an integral multiple of kn is to be added or subtracted so that the suffix assumes a value between 1 and kn. For example, $f_{-1,1}$ should be understood as $f_{kn-1,1}$.

Now, the point is that all eigenvalues of the matrix $\mathbf{F}'_n$ can be calculated exactly and easily, so that det $\mathbf{F}'_n$ can be expressed as a product of these eigenvalues. The method is described here for the case of $k = 2$, and can be generalized easily to other cases. The mathematics is analogous to that used by Higgs[6] for the vibrational analysis of helical polymers. Each eigenvalue and its corresponding eigenvector can be characterized by an index θ. The components of an eigenvector $\mathbf{t}(\theta)$ may be taken to be of the form

$$\mathbf{t}_{2j-1}(\theta) = a \exp[i(j-1)\theta]$$

and

$$\mathbf{t}_{2j}(\theta) = b \exp[i(j-1)\theta] \tag{2}$$

where $j = 1, 2, \ldots, n$, and a and b are quantities to be determined below. When $\exp(in\theta) = 1$, *i.e.*, when

$$\theta = 2\pi m/n \quad \text{with } m = 0, 1, 2, \ldots, n-1 \tag{3}$$

the eigenvalue equation

$$\mathbf{F}'_n\mathbf{t}(\theta) = \lambda(\theta)\mathbf{t}(\theta) \tag{4}$$

reduces to an eigenvalue equation of a 2 × 2 matrix, *viz.*

$$\begin{bmatrix} 2c & e + if \\ e - if & 2d \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = \lambda(\theta) \begin{bmatrix} a \\ b \end{bmatrix} \tag{5}$$

where

$$\begin{aligned} c(\theta) &= f_{1,1}/2 + \sum_{j=1}^{\infty} f_{1,2j+1} \cos j\theta \\ d(\theta) &= f_{2,2}/2 + \sum_{j=1}^{\infty} f_{2,2j+2} \cos j\theta \\ e(\theta) &= f_{1,2} + \sum_{j=1}^{\infty} (f_{1,2j+2} + f_{2,2j+1}) \cos j\theta \\ f(\theta) &= \sum_{j=1}^{\infty} (f_{1,2j+2} - f_{2,2j+1}) \sin j\theta \end{aligned} \tag{6}$$

The eigenvalues of the 2 × 2 matrix in eq 5 are easily obtained as

$$\lambda_\pm(\theta) = [c(\theta) + d(\theta)] \pm [\{c(\theta) - d(\theta)\}^2 + \{e(\theta)\}^2 + \{f(\theta)\}^2]^{1/2} \tag{7}$$

The corresponding eigenvectors $\left[\frac{a}{b}\right]$ can be obtained easily from eq 5. Using these eigenvectors, and the eigenvalues from eq 7, we obtain

$$\det \mathbf{F}'_n = \prod_{m=0}^{n-1} \lambda_+(\theta_m)\lambda_-(\theta_m) \tag{8}$$

where θ_m is given by eq 3. Because the matrix $\mathbf{F}'_n$ is positive definite, all eigenvalues $\lambda_+(\theta_m)$ and $\lambda_-(\theta_m)$ are positive. In Figure 1, λ_+ and λ_- are plotted as a function of the index θ for the matrix $\mathbf{F}'_n$ whose elements are given in

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(6) P. W. Higgs, *Proc. Roy. Soc., Ser. A*, **220**, 472 (1953).

Table I. As $n \to \infty$, it follows from eq 8 that

$$\ln \det \mathbf{F}'_n \longrightarrow \frac{n}{2\pi}\int_{-\pi}^{\pi} \ln\,[\lambda_+(\theta)\lambda_-(\theta)]d\theta \qquad (9)$$

By substituting eq 9 into eq 1, we have

$$S_\mathrm{h} = -(R/4\pi)\int_{-\pi}^{\pi} \ln\,[\lambda_+(\theta)\lambda_-(\theta)]d\theta \qquad (10)$$

The value of S_h, computed from eq 10 for the data of Table I, is −9.42 eu, giving $g = \exp(-S_\mathrm{h}/R)$ as 116.7, which agrees well with the value of $g = 115$ (parameter set A in Table VII of ref 5) obtained previously by a direct application of eq 1. The method described here will be used in a forthcoming paper on the molecular theory of the helix-coil transition in poly(L-valine) in water.[7]

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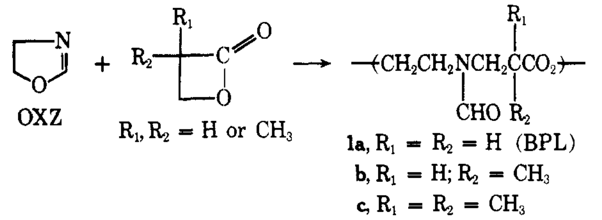
[7] M. Gō, F. Th. Hesselink, N. Gō, and H. A. Scheraga, *Macromolecules*, to be submitted.

Communications to the Editor

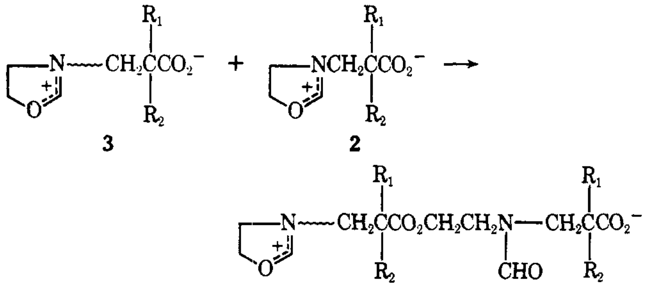
Polymerization *via* Betaine. III.[1] Alternating Copolymerization of 2-Oxazoline with Acrylic Acid Involving Proton Transfer of the Acid

In the previous papers we have reported 1:1 alternating copolymerization of 2-oxazoline (OXZ) with β-propiolactone (BPL)[2] and methyl-substituted β-propiolactones[1] to give amide-ester type copolymer 1. Copolymerization took



1a, $R_1 = R_2 = H$ (BPL)
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = R_2 = CH_3$

place without any added initiator at room temperature. For the copolymerization, a new concept of betaine propagation has been proposed in which the propagation proceeds through the reaction of macrozwitterion 3 with betaine 2 formed from OXZ and β-lactone.[1,2]



In the course of the mechanistic study on these copolymerizations we have found a novel alternating copolymerization of OXZ with acrylic acid (AA). A copolymer was obtained from OXZ and AA with a structure analogous to the 1:1 alternating copolymer from OXZ and BPL, **1a**.

An equimolar mixture of OXZ and AA (7.5 mmol each) in acetonitrile (2 ml) containing 0.04 mmol of *p*-methoxyphenol as a radical inhibitor was heated at 50-60° under nitrogen. After 28 hr the reaction mixture was poured into a large amount of diethyl ether to precipitate the copolymer. The copolymer was dried *in vacuo* to give 0.61 g (57% yield). The structure of the copolymer was examined by ir (Figure 1), nmr (Figure 2), elemental analysis, and an alkaline hydrolysis experiment.

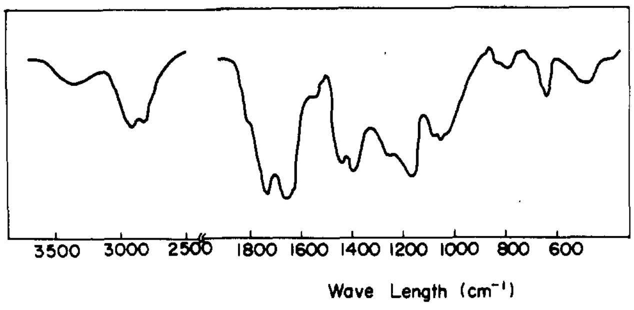


Figure 1. Infrared spectrum of OXZ-AA copolymer (KBr).

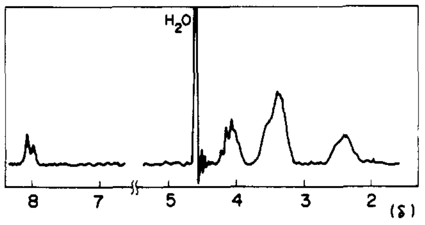


Figure 2. Nmr spectrum of OXZ-AA copolymer (in D_2O).

The ir and nmr spectra of the OXZ-AA copolymer in Figures 1 and 2, respectively, are quite similar to those of the alternating copolymer **1a** of OXZ and BPL,[2] although nmr peaks are somewhat broader probably due to incomplete solubility of the OXZ-AA copolymer in D_2O. The result of the elemental analysis shows the 1:1 composition of OXZ and AA. *Anal.* Calcd for $(C_6H_9NO_3)_n$: C, 50.34; H, 6.34; N, 9.79. Found: C, 50.32; H, 6.33; N, 9.69.

The alkaline hydrolysis of the OXZ-AA copolymer was carried out as previously reported.[2] To 0.05 g of the copolymer was added 0.5 ml of a 10% solution of NaOH in D_2O. The hydrolysis mixture was allowed to react at 100° for 3 hr and gave an equimolar mixture of the salts of *N*-(β-hydroxyethyl)-β-alanine (4) and HCO_2H, *i.e.*, the nmr spectrum of the alkaline hydrolysis mixture coincided with that of a 1:1 mixture of the salts of the authentic samples, 4 and HCO_2H. 4 was prepared by the equimolar reaction of monoethanolamine and BPL as reported,[3] mp

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[1] Part II: see T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **7**, 1 (1974).

[2] T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 354 (1972).

[3] T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert, and F. T. Fiedorek, *J. Amer. Chem. Soc.*, **73**, 3168 (1951).