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

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

The value of S_h, computed from eq 10 for the data of Table I, is −9.42 eu, giving $g = \exp(-S_h/R)$ 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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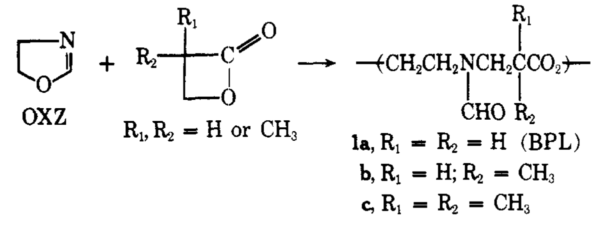
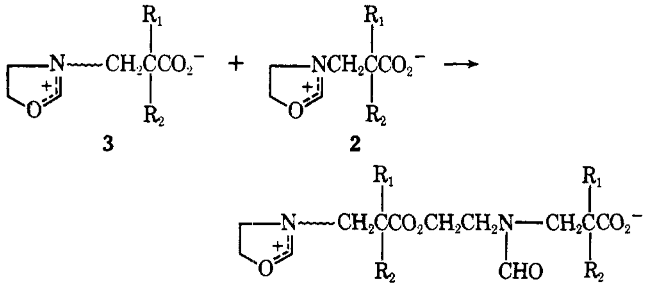
[7] M. Gō, F. Th. Hesselink, N. Gō, and H. A. Scheraga, *Macromolecules*, to be submitted.

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 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.

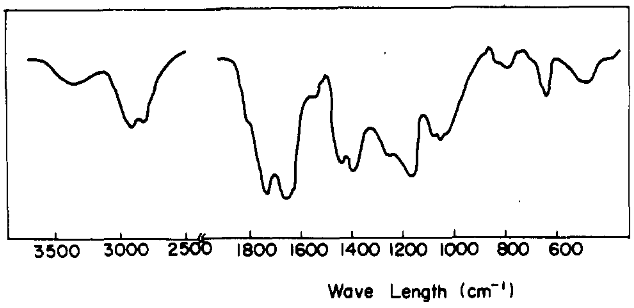


Figure 1. Infrared spectrum of OXZ-AA copolymer (KBr).

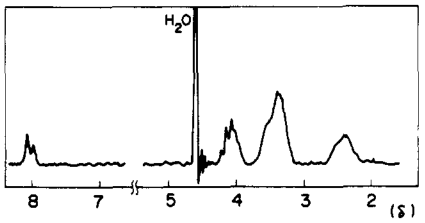


Figure 2. Nmr spectrum of OXZ-AA copolymer (in D_2O).

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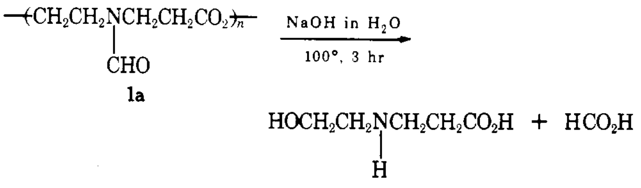
[1] Part II: see T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **7**, 1 (1974).

[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).

141-143° (lit.[3] mp 145-147°). *Anal.* Calcd for $C_5H_{11}NO_3$: C, 45.10; H, 8.33; N, 10.52. Found: C, 45.18; H, 8.31; N, 10.43.

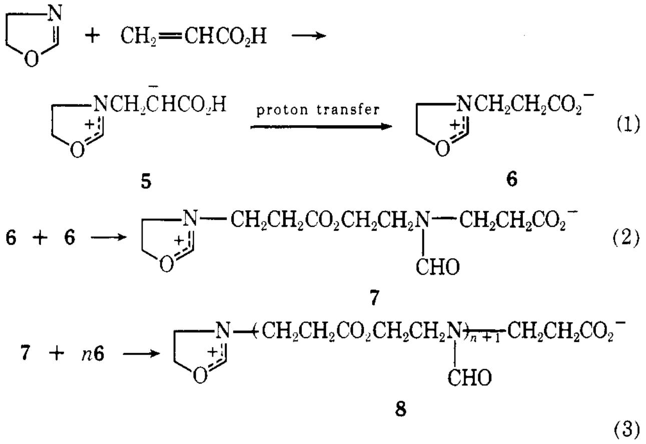


$$\mathrm{-\!(CH_2CH_2\underset{CHO}{N}CH_2CH_2CO_2\!)_n-} \xrightarrow[100°,\ 3\ \mathrm{hr}]{\mathrm{NaOH\ in\ H_2O}} \mathrm{HOCH_2CH_2\underset{H}{N}CH_2CH_2CO_2H + HCO_2H}$$

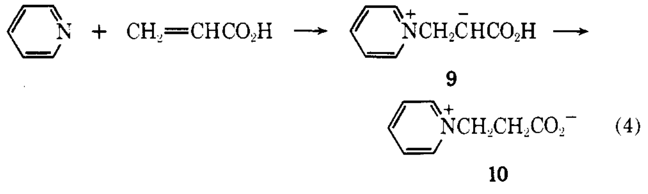
1a **4**

Based on the above findings the structure of the OXZ-AA copolymer is expressed also by **1a**. Furthermore, it should be noted that pendant carboxyl groups were not detected in the copolymer; *i.e.*, the vinyl polymerization of AA did not occur during the copolymerization. A mixture of 0.163 g of the OXZ-AA copolymer and 1.86 g of *N,N*-dimethylformamide was allowed to stir at 50°. After 30 hr, the copolymer has completely solved in dimethylformamide. The molecular weight of the copolymer was even higher than that of the OXZ-BPL copolymer. It was measured by vapor pressure osmometry in dimethylformamide at 55° and found to be 13,200. This is interestingly compared with the OXZ-BPL copolymer, *i.e.*, the molecular weight of the latter copolymer was at most 4100.[2]

The OXZ-AA copolymerization can reasonably be formulated by eq 1-3. The Michael-type adduct **5** is first formed which is followed by the proton transfer to give the betaine **6**. Once **6** is formed in the reaction system the subsequent processes should be similar to those of the OXZ-BPL copolymerization.[2] In other words the betaine **6** is a common intermediate in the 1:1 alternating copolymerizations of both OXZ-AA and OXZ-BPL systems; 2 mol of **6** forms the dimeric zwitterion **7** in which the ring-opening isomerization of OXZ is involved as shown in eq 2. Then, successive attack of **6** to **7** takes place to give the macrozwitterion **8**. Thus, the propagation proceeds through the reaction of carboxylate end of the macrozwitterion **8** with the oxazolinium of the betaine **6**.



The OXZ monomer is a base like pyridine. The formation of a betaine **10** from AA and pyridine may relevantly be mentioned here for rationalizing the betaine intermediate **6**. A mixture of 7.5 mmol each of AA and pyridine in 2 ml of acetonitrile was kept at 80° for 7 hr. After work-up a betaine **10** was isolated in 44% yield as a white crystal, mp 131-132° (lit.[3] mp 132-134°). The structure of **10** was further confirmed by nmr analysis. The nmr spectrum of **10** in D_2O showed aromatic proton signals at δ 9.0~7.8 due to the pyridinium (5 H), a triplet at δ 4.76 due to α-methylene protons (2 H) of nitrogen atom and a triplet at δ 2.94 due to α-methylene protons (2 H) of carboxylate group. The formation of **10** involves the proton transfer process of the adduct **9** (eq 4). The betaine **10** has been prepared from pyridine and BPL by Gresham *et al.*[3]



So far as we know this is the first example of the 1:1 alternating copolymerization between a cyclic monomer and a vinyl monomer.

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Hydrolysis of *p*-Nitrophenyl Acetate by a Bifunctional Nucleophilic Polymer Catalyst

The hydrolysis of phenyl esters catalyzed by imidazole-containing polymers has been studied extensively as models of esterolytic enzymes.[1] Apart from a few exceptional cases,[2] the efficiency of the imidazole catalysis is limited by the rate-determining acylation step.

The hydroxamate anion is one of the most powerful nucleophiles[3] and, therefore, its use as catalyst in the hydrolysis of phenyl esters should be quite interesting. This has been done to a limited extent in small-molecule systems,[4] and it was found that the catalytic efficiency was rather limited because of the slow decomposition of the acyl hydroxamate intermediate. It is expected from these results that high esterolytic efficiencies may be attained by combining these two complementary functions. For this purpose, we prepared a water-soluble copolymer containing the hydroxamate and imidazole functions and examined its catalytic efficiency in the hydrolysis of *p*-nitrophenyl acetate (PNPA), in comparison with that of a copolymer containing only the hydroxamate function.

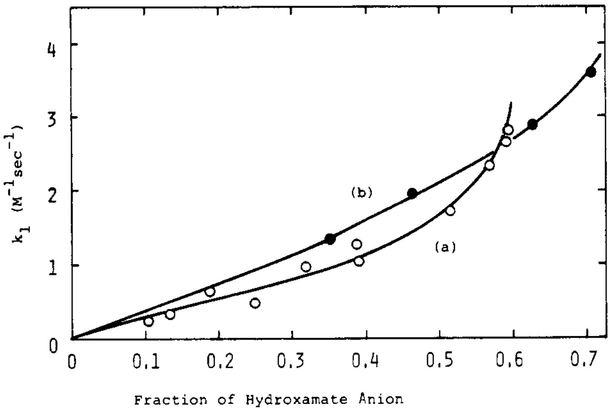

Figure 1. Acylation of hydroxamate copolymers by PNPA. Reaction condition: 30°, 0.1 *M* KCl, 28.9% (v/v) EtOH-H_2O; 0.15 *M* barbital buffer. Rate of acylation = k_1[PNPA][PHA]$_{\text{total}}$: (a) PHA-MIm-AAm copolymer, [PHA]$_{\text{total}}$ = 6.60×10^{-4} *M*, [PNPA] = 1.12×10^{-2} *M*; (b) PHA-AAm copolymer, [PHA]$_{\text{total}}$ = 5.52×10^{-4} *M*, [PNPA] = 4.02×10^{-5} *M*.

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(1) C. G. Overberger and J. C. Salamone, *Accounts Chem. Res.*, **2**, 217 (1969); H. Morawerz, *Advan. Catal.*, **20**, 341 (1969).

(2) C. G. Overberger, M. Morimoto, I. Cho, and J. C. Salamone, *J. Amer. Chem. Soc.*, **93**, 3228 (1971).

(3) J. D. Aubort and R. H. Hudson, *Chem. Commun.*, 938 (1970); M. Dessolin *et al.*, *Bull. Soc. Chim. Fr.*, 2573 (1970); *ibid.*, 2946 (1971).

(4) W. B. Gruhn and M. L. Bender, *J. Amer. Chem. Soc.*, **91**, 5883 (1969); R. Hershfield and M. L. Bender, *ibid.*, **94**, 1376 (1972).