Polymerization via Zwitterion.[1] VI.[2] A Novel Alternating Copolymerization of Acrylamide with Cyclic Imino Ethers Involving Proton Transfer of the Amide

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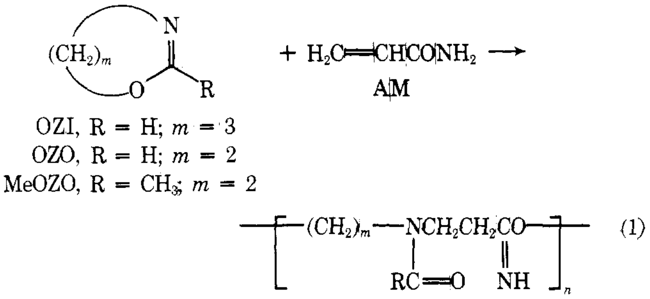
This paper describes a novel alternating copolymerization of acrylamide (AM) with cyclic imino ethers (eq 1), in which a proton-transfer process of AM is involved to produce a copolymer of the amide-imidate structure **1**. Very recently we have reported 1:1 alternating copolymerization of 2-oxazoline (OZO) with acrylic acid (AA) giving a copolymer of the amide-ester type structure **2**, which involved proton transfer of AA.[3] This provided the first example of the 1:1 alternating copolymerization between a cyclic monomer and a vinyl monomer.[3] The present reaction (eq 1), therefore, is an extension of our studies on alternating copolymerizations via zwitterions,[2-6] especially in the combination of cyclic monomers and vinyl monomers. The cyclic imino ether monomers used were 5,6-dihydro-4*H*-1,3-oxazine (OZI), 2-methyl-2-oxazoline (MeOZO), and OZO.

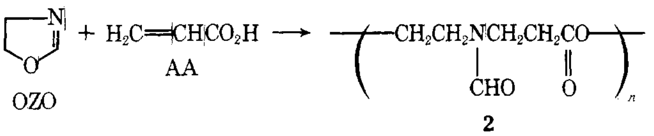


$$+\ H_2C{=}CHCONH_2 \longrightarrow \left[(CH_2)_m{-}\underset{RC=O}{N}CH_2CH_2\underset{NH}{\overset{}{C}}O \right]_n \quad (1)$$

AM

OZI, R = H; *m* = 3
OZO, R = H; *m* = 2
MeOZO, R = CH$_3$; *m* = 2

1a, R = H; *m* = 3
1b, R = H; *m* = 2
1c, R = CH$_3$; *m* = 2



$$+\ H_2C{=}CHCO_2H \longrightarrow \left(CH_2CH_2\underset{CHO}{N}CH_2CH_2\underset{\overset{\|}{O}}{C}O \right)_n$$

OZO AA **2**

In a tube under nitrogen was placed an equimolar mixture of AM and OZI (7.5 mmol each) in acetonitrile (1 ml) at room temperature. The tube was sealed and heated at 70°. After 20 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 1.16 g (quantitative yield). The structure of the copolymer was examined by ir, NMR, elemental analysis, and an alkaline hydrolysis experiment.

The ir spectrum of the copolymer (Figure 1, solid line) shows strong absorption bands at 1650 and 1585 cm^{-1}, which were assigned to $\nu_{C=O}$ and $\nu_{C=N}$, respectively. As to the structure of the copolymer unit derived from AM, there are two possibilities, *i.e.*, the amide-imidate (**1a**) and the amide-amide (**3**) structures. Figure 1 does not contain the ir bands (1680 and 1535 cm^{-1}) which are to be assigned to the secondary amide. These ir data strongly indicate the structure of **1a**. To confirm this, the copolymer was treated with dry HCl gas. Into 5 ml of a CH$_3$CN solution of the copolymer (0.20 g) dry HCl gas was introduced at room temperature until the solution no longer absorbed HCl. The copolymer–HCl salt precipitated as waxy material (0.18 g after drying). The extent of the salt formation was found by elemental analysis to be 62.5%. Anal. Calcd for $C_7H_{13}N_2O_2Cl$ (1:1 composition of **1a**:HCl): Cl, 18.40. Found: Cl, 11.50. The ir spectrum of the copolymer salt is shown in Figure 1 (dotted line). The absorption at 1585 cm^{-1} of the copolymer decreased. The structure of the copolymer–HCl salt is reasonably given by **4**. This finding supports further that the copolymer contains the imidate unit (-CH$_2$CH$_2$C(=NH)O-, **1a**) but not the amide unit (-CH$_2$CH$_2$CONH-, **3**).

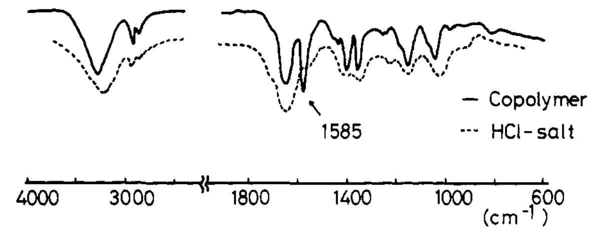


Figure 1. Ir spectra of the OZI–AM copolymer (solid line) and its HCl salt (dotted line) (NaCl).

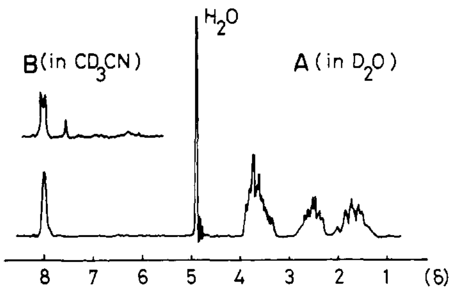
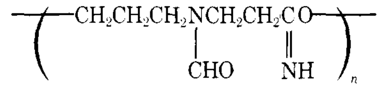
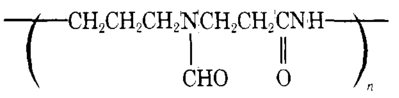


Figure 2. NMR spectra of the OZI–AM copolymer in D$_2$O (A) and in CD$_3$CN (B).



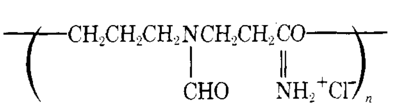
$$\left(CH_2CH_2CH_2\underset{CHO}{N}CH_2CH_2\underset{\overset{\|}{NH}}{C}O \right)_n$$

1a



$$\left(CH_2CH_2CH_2\underset{CHO}{N}CH_2CH_2\underset{\overset{\|}{O}}{C}NH \right)_n$$

3



$$\left(CH_2CH_2CH_2\underset{CHO}{N}CH_2CH_2\underset{\overset{\|}{NH_2^+Cl^-}}{C}O \right)_n$$

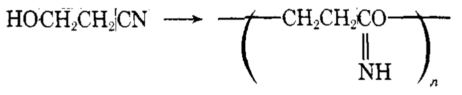
4

The NMR spectrum of the OZI–AM copolymer in D$_2$O (Figure 2A) shows a singlet at δ 8.05 due to N–CHO (1 H) and three multiplets. The multiplet at δ 3.9–3.3 is assigned to CH$_2$NCH$_2$ and OCH$_2$ (total 6 H). The δ 2.8–2.4 multiplet is assigned to CH$_2$C=N (2 H), and that centered at δ 1.88 is ascribed to CCH$_2$C (2 H). The multiplet at δ 2.8–2.4 had the same intensity as the peak centered at δ 1.88. The signal due to =NH of the copolymer was not detected in D$_2$O solvent. The NMR spectrum of the copolymer in CD$_3$CN (Figure 2B) shows a singlet at δ 7.66 and broad signals at δ 6.9 and 6.3 due to =NH (total 1 H), besides a doublet at δ 8.00 due to NCHO (1 H). This observation is quite compatible with a recently published spectrum of a polymer having the imidate structure **5**.[7] The =NH proton signal of **5** appeared at δ 7.9–7.3 as three singlets in DMSO-d_6. The elemental analysis of the copolymer supports the 1:1 compo-

Table I
Alternating Copolymerization of Cyclic Imino Ethers with AM at Various Reaction Conditions[a]

Cyclic imino ether	Solvent[b]	Temp, °C	Time, hr	Copolymer yield, %	Copolymer structure	Mol wt[c]
OZI	CH_3CN	70	20	100	**1a**	1470
OZI	DMF	50	16	36	**1a**	830
OZO	CH_3CN	70	15	100	**1b**	1320
OZO	CH_3CN	50	40	98	**1b**	1305
MeOZO	DMF	110	16	10	**1c**	650
MeOZO	DMF	120	20	32	**1c**	

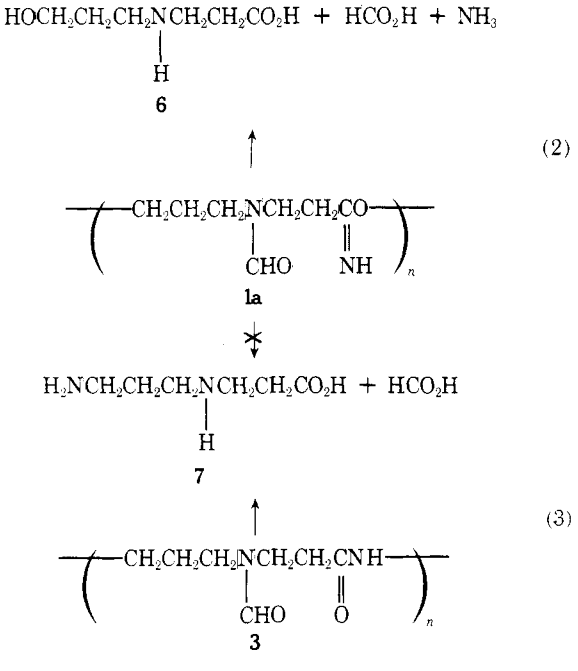
[a] The charged amount: AM = cyclic imino ether = 7.5 mmol. [b] Solvent = 1.0 ml. [c] Determined by vapor pressure osmometry.



5

sition of OZI–AM. The copolymer is very hygroscopic. Anal. Calcd for $C_7H_{12}N_2O_2(0.41 \cdot H_2O)$: C, 49.44; H, 8.20; N, 16.38. Found: C, 49.72; H, 8.23; N, 16.23.

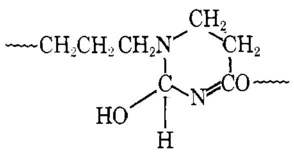
The alkaline hydrolysis of the OZI–AM copolymer was carried out as follows. To 50 mg of the copolymer was added 1.0 ml of a 10% solution of NaOH in D_2O. The reaction of the hydrolysis mixture at 90° for 10 hr gave an equimolar mixture of the sodium salts of *N*-(γ-hydroxypropyl)-β-alanine (**6**) and HCO_2H. The NMR spectrum of the reaction mixture was identical with that of a 1:1 mixture of authentic **6** and HCO_2H in D_2O–NaOH. **6** was prepared by the equimolar reaction of *n*-propanolamine with β-propiolactone according to the analogous way to *N*-(β-hydroxyethyl)-β-alanine:[3] mp 131–132°; NMR (D_2O) δ 3.68 (t, 2 H, OCH_2), 3.14 (m, 4 H, CH_2NCH_2), 2.54 (t, 2 H, CH_2CO_2), 1.90 (m, 2 H, CCH_2C). Anal. Calcd for $C_6H_{13}NO_3$: C, 48.96; H, 8.90; N, 9.52. Found: C, 48.83; H, 8.92; N, 9.28.



The absence of the salt of *N*-(γ-aminopropyl)-β-alanine (**7**) in the alkaline hydrolysis products is taken to exclude the possibility of the amide-amide structure **3**.

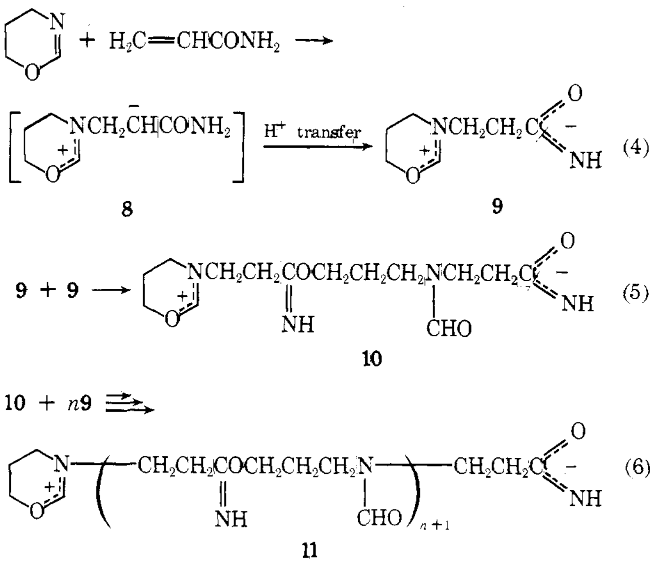
Further support for the structure **1a** of the OZI–AM copolymer was obtained by another alkaline hydrolysis experiment which is compatible with eq 2 showing the evolution of ammonia. A sample of the OZI–AM copolymer (0.344 g = 2.21 mmol of the OZI–AM unit) in 2*N* NaOH aqueous solution (9 ml) was allowed to react at 100° for 3 hr. Meantime, ammonia was evolved and led into 25.00 ml of 0.20 *N* HCl solution. In addition, 20 ml of 10 *N* NaOH was added to the mixture, which was kept at 100° for 1 hr in order to remove the dissolved ammonia from the solution mixture. The HCl solution was then back titrated with 0.20 *N* NaOH solution (Methyl Orange as an indicator). It was found that 2.03 mmol of the acid was consumed for the absorption of the evolved ammonia, which corresponds to 91.9% of the OZI–AM unit amount of the initial polymer. This finding strongly indicates that the copolymer structure is given by **1a**.

All the above findings support the amide-imidate structure **1a**. Besides **1a** the following structure **1d** might be considered, which is a cyclized form of **1a**. However, such a cyclization was taken to be negligible since any signal due to the OH group of **1d** was not detected in the NMR spectrum of the copolymer in CD_3CN.



1d

Similarly in the copolymerizations of AM with OZO and with MeOZO it was found that AM afforded the imidate unit $-CH_2CH_2C(=NH)O-$ of 1:1 alternating copolymers **1b** and **1c**. These results are given in Table I. All copolymers are soluble in water, methanol, and DMF, but insoluble in



benzene, chloroform, and other typical organic solvents. The maximum molecular weight[7] of the copolymers was 1470.

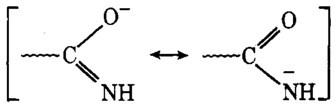
As to the scheme of the present copolymerization, a zwitterion mechanism similar to that proposed in previous studies[2–6] is plausible. The course of the OZI–AM copolymerization is formulated as eq 4–6. The first step is the formation of zwitterion **9** by the addition of OZI with AM followed by a proton-transfer process. Then, two molecules of **9** afford a dimeric zwitterion **10.** The propagation proceeds via the successive attack of **9** onto **10** to form a macrozwitterion **11.**

The present copolymerization is interestingly compared with the homopolymerization of AM by base catalysts found first by Breslow et al.[8] in which AM gave a polymer of the amide structure **12** via a hydrogen-transfer process.

$$H_2C{=}CHCONH_2 \longrightarrow \!\!-\!\!\left(\!-CH_2CH_2CONH-\right)_n\!\!-$$

12

The amide anion of **9, 10,** and **11** is an ambident anion of oxygen (**13a**) and nitrogen (**13b**). It should be noted that



13a **13b**

the regiospecific reaction took place exclusively at the oxygen anion **13a** in eq 3 and 4 to give the imidate unit.

References and Notes

(1) "Betaine" used to be employed instead of "zwitterion". Hereafter, we wish to use the terms of zwitterion and macrozwitterion according to the definition in the text in order to avoid the ambiguous terminology of "betaine".

(2) Part V: T. Saegusa, Y. Kimura, S. Sawada, and S. Kobayashi, *Macromolecules,* **7,** 956 (1974).

(3) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules,* **7,** 139 (1974).

(4) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules,* **5,** 354 (1972).

(5) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules,* **7,** 1 (1974).

(6) T. Saegusa, Y. Kimura, K. Sano, and S. Kobayashi, *Macromolecules,* **7,** 546 (1974).

(7) S. R. Sandler, *J. Polym. Sci., Polym. Chem. Ed.,* **11,** 2373 (1973).

(8) D. S. Breslow, G. E. Hule, and A. S. Mallach, *J. Am. Chem. Soc.,* **79,** 3760 (1957).

CORRECTIONS

"Liquid–Liquid Phase Separation in Multicomponent Polymer Systems. XI. Dilute and Concentrated Polymer Solutions in Equilibrium", by R. Koningsveld, W. H. Stockmayer, J. W. Kennedy, and L. A. Kleintjens, Volume 7, Number 1, January–February 1974, page 73.

The following should be added to the caption for Figure 3 on page 78:

The parameters used have the numerical values $\alpha = 0$, $\gamma = 0.3251$, $\beta_0 = 0.3832$, and $\beta_1 = 108.59K$, rather than those quoted under eq 24.

We thank Dr. R.-J. Roe for drawing our attention to this omission.

"Structural Investigation of Radiation-Induced Urea Canal Polymerization of 1,3-Butadiene", by Yozo Chatani and Shinichiro Kuwata, Volume 8, Number 1, January–February 1975, page 12.

On page 16 (line 4 from the bottom right-hand column), $CH_3CH{=}\dot{C}H_2$ should read $CH_3CH{=}CH\dot{C}H_2$.