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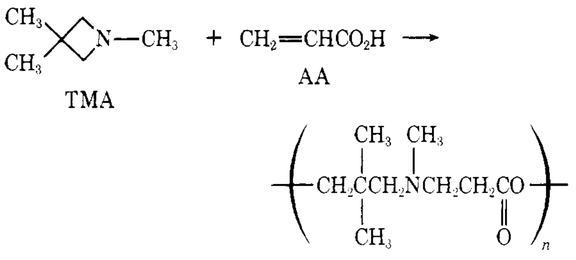
Polymerization *via* Betaine. V.[1] Alternating Copolymerization of 1,3,3-Trimethylazetidine with Acrylic Acid. A Novel Method for the Preparation of Amine-Ester Type Polymer

This communication describes an alternating copolymerization of 1,3,3-trimethylazetidine (TMA) with acrylic acid (AA) to give an amine-ester type polymer 1.



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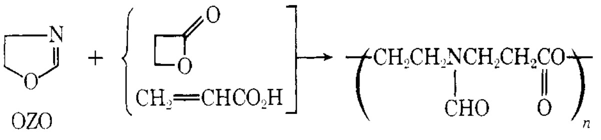
Recently, we have reported a new type of alternating copolymerizations of cyclic imino ethers, *e.g.*, 2-oxazoline (OZO) and 2-benzyliminotetrahydrofuran (BIT), with β-propiolactones (β-PL) and with AA to produce alternating copolymers of amide-ester type structures, 2 and 3, respectively (eq 2 and 3).[1-4]



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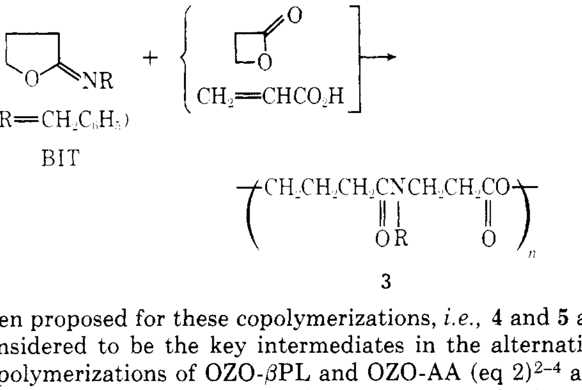

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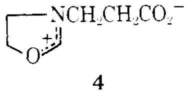
A mechanism of the "polymerization *via* betaine" has been proposed for these copolymerizations, *i.e.*, 4 and 5 are considered to be the key intermediates in the alternating copolymerizations of OZO-βPL and OZO-AA (eq 2)[2-4] and BIT-βPL and BIT-AA (eq 3),[1] respectively. In both reactions (eq 2 and 3) cyclic imino ethers of OZO and BIT serve to provide a cationic site of betaines of 4 and 5.



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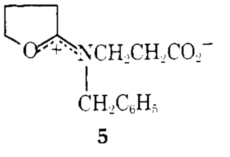

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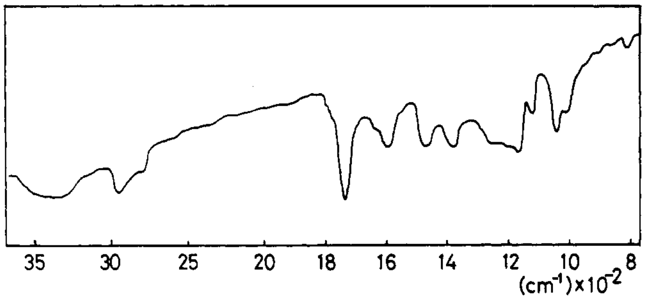


Figure 1. Ir spectrum of the TMA-AA copolymer (KBr).

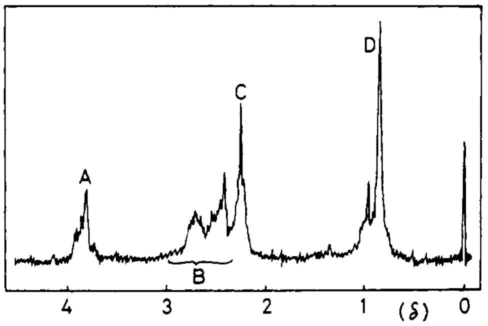


Figure 2. Nmr spectrum of the TMA-AA copolymer ($CDCl_3$).

As an extension of our studies on the copolymerization *via* betaine, we employed TMA as a comonomer providing a cationic site of the betaine components. Now, we disclose a novel type of alternating copolymerization of TMA with AA (eq 1). Cationic homopolymerization and its kinetics of TMA have recently been carried out by Schacht and Goethals.[5,6] However, the copolymerization of TMA has not been reported so far.

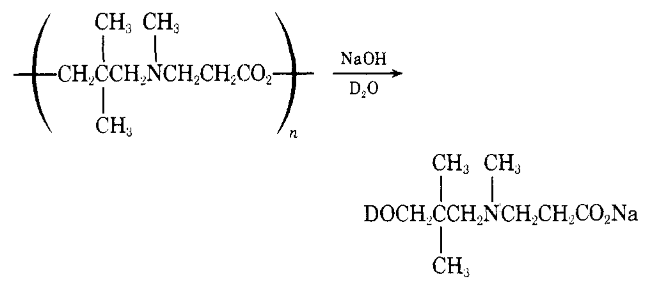
An equimolar mixture (3.3 mmol each) of TMA and AA in 1.0 ml of acetonitrile was placed in a sealed tube under nitrogen and kept at 80° for 3.5 hr. Copolymerization took place without added initiator. The reaction mixture was then poured into a large excess of diethyl ether to precipitate the polymeric material. The gummy polymer was separated by filtration, dissolved in chloroform, reprecipitated by pouring the solution into an excess amount of diethyl ether, and dried *in vacuo*. The yield was 0.51 g (89%). The structure of the copolymer was determined by nmr, ir, elemental analysis, and an alkaline hydrolysis experiment.

The ir spectrum of the copolymer (Figure 1) shows absorptions at 1735, 1170, and 1040 cm^{-1}, which indicate the presence of an ester group. Figure 2 shows the nmr spectrum of the copolymer. A signal at δ 3.8 (peak A) is ascribed to methylene protons of $-OCH_2-$. Signals at δ 3.0–2.2 (B) are due to three kinds of methylene protons of $-CH_2NCH_2CH_2CO_2-$. Signals at δ 2.2 (C) and 0.9 (D) are assigned respectively to methyl protons of NCH_3 and $C(CH_3)_2$. The relative intensity of signals A:(B + C):D was 2.0:9.0:6.0. Furthermore, signals due to neither olefinic protons nor carboxylic acid proton were observed. These spectral data strongly support that the structure of the TMA-AA copolymer is 1. The results of the elemental analysis show the 1:1 composition of TMA and AA.

Anal. Calcd for $(C_9H_{17}NO_2)_n$: C, 63.13; H, 10.00; N, 8.18. Found: C, 62.85; H, 9.95; N, 8.30.

The alkaline hydrolysis experiment further confirmed the copolymer structure 1. The copolymer (50 mg) was dissolved in 1.0 ml of a 10% solution of NaOH in D_2O and kept at 65° for 1 hr. The reaction mixture was then subjected to nmr measurement. The sole product was the sodium salt of

N-(γ-hydroxy-β,β-dimethylpropyl)-*N*-methyl-β-alanine

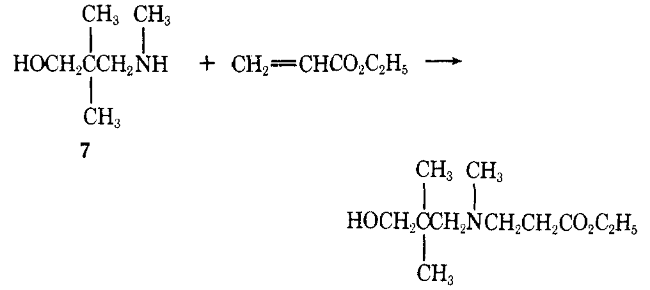


$$\left(-CH_2C(CH_3)_2CH_2N(CH_3)CH_2CH_2CO_2-\right)_n \xrightarrow[D_2O]{NaOH} DOCH_2C(CH_3)_2CH_2N(CH_3)CH_2CH_2CO_2Na$$

6

(**6**), *i.e.*, the nmr spectrum of the hydrolysis product was identical with that of sodium salt of the authentic sample of **6** in D_2O.

The authentic sample **6** was prepared as follows. The addition reaction of *N*-methyl-*N*-(γ-hydroxy-β,β-dimethylpropyl)amine (**7**) to ethyl acrylate gave **8**, bp 77–79° (0.2 mm), which is the ethyl ester of **6**. Then, **8** was subjected to alkaline hydrolysis in a NaOH solution of ethanol–H_2O at 70° to give a sodium salt of **6**, mp 102° (recrystallized from a mixed solvent of ethanol–diethyl ether).



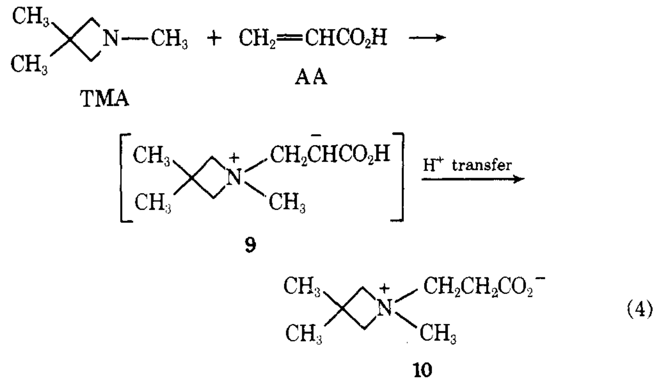
$$HOCH_2C(CH_3)_2CH_2NHCH_3 + CH_2{=}CHCO_2C_2H_5 \longrightarrow HOCH_2C(CH_3)_2CH_2N(CH_3)CH_2CH_2CO_2C_2H_5$$

7 **8**

Anal. Calcd for $C_9H_{18}O_3NNa{\cdot}(H_2O)_{0.50}$: C, 49.08; H, 8.71; N, 6.35. Found: C, 49.31; H, 9.02; N, 6.07.

The copolymer (**1**) was soluble in chloroform, acetonitrile, and methanol but insoluble in diethyl ether and water. Its molecular weight was 1350 by vapor pressure osmometry.

The above alternating copolymerization may reasonably be explained by the following scheme of reactions (eq 4–6). The addition of TMA to AA produces a transient intermediate **9**, from which the active species of betaine **10** is derived probably through the intermolecular proton transfer (eq 4).



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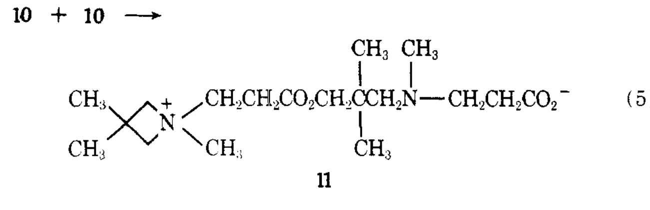

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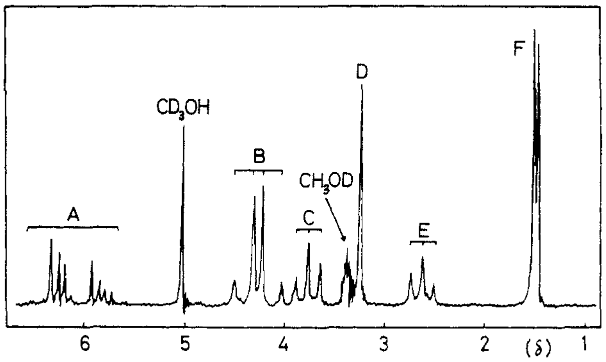
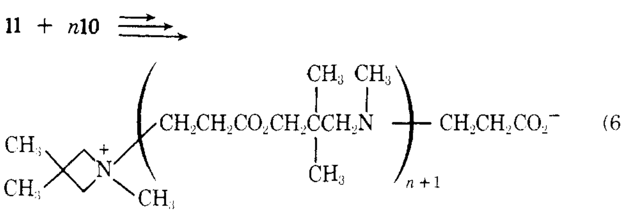


Figure 3. Nmr spectrum of the azetidinium acrylate (**13**) (CD_3OD).

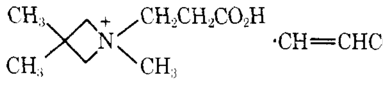


(6)

12

Besides **10**, some other salts of the combination of carboxylic acid and a nitrogen base azetidine may possibly be formed in equilibrium. Among them, **10** is responsible for the alternating copolymerization. Two molecules of **10** produce a dimeric zwitterion **11** (eq 5). Then, the propagation starts, in which **11** reacts successively with **10** to give a macrozwitterion **12** of the alternating copolymer (eq 6).

The intermediacy of **10**, especially the addition of TMA to AA to form an azetidinium group, is supported by the isolation of azetidinium acrylate **13**. An equimolar mixture of TMA and AA (2.5 mmol each) in 5 ml of diethyl ether was kept at 10° overnight to give white crystalline solid, which was isolated by filtration and dried *in vacuo*. The yield was 0.30 g (70%). The product was identified to be azetidinium acrylate (**13**), which is a 1:2 adduct of TMA and AA. The ir spectrum of **13** shows absorption bands at 3200–3400 and 1710 cm^{-1} due to the carboxyl group, 1580 and 1380 cm^{-1} due to the carboxylate anion, and 1640, 1440, 990, and 950 cm^{-1} ascribed to the vinyl group. The nmr spectrum (Figure 3) also confirms the structure **13**. A multiplet at δ 6.5–5.5 (signal A) is due to vinyl protons (3 H). An A_2B_2 type quartet centered at δ 4.25 (B) is ascribed to two ring methylene protons (4 H). Two triplets at δ 3.73 (C) and 2.60 (E) are respectively assigned to α- and β-methylene protons (2 H) of the $^+NCH_2CH_2$ group. A singlet at δ 3.20 (D) and a doublet at δ 1.46 (F) are due to *N*-methyl protons (3 H) and ring-methyl protons (6 H), respectively. The mp of **13** is 92°.

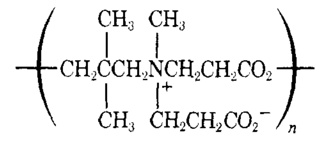


13

Anal. Calcd for $C_{12}H_{21}NO_4$: C, 59.24; H, 8.70; N, 5.76. Found: C, 58.54; H, 8.69; N, 5.72.

13 may be the most stable species among the betaines and salts derived from TMA and AA, and the transformation of **13** into **10** is quite acceptable. An equimolar mixture of **13** and TMA actually gave the 1:1 alternating copolymer of TMA and AA. A mixture of 0.40 mmol of **13** and 0.46 mmol of TMA in 0.35 ml of acetonitrile was heated at 80° for 30 hr. The copolymer was obtained in a quantitative yield (>99%), which was identified as the 1:1 alternating copolymer of TMA and AA (**1**). This finding affords an additional support to the above scheme, *i.e.*, the reaction between **13** and TMA generated **10** which was the active species of the copolymerization.

The alternating copolymer **1** has the tertiary amine group in the main chain, which may possibly form a betaine **14** through a hydrogern transfer of AA as in the case of pyridine.[3] This type of betaine formation can give rise to the



$$\left(-\mathrm{CH_2}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2}\underset{\mathrm{CH_2CH_2CO_2^-}}{\overset{\mathrm{CH_3}}{\overset{+}{\mathrm{N}}}}\mathrm{CH_2CH_2CO_2}-\right)_n$$

14

chain branching like **14**. However, quaternary ammonium species have not been detected in the alternating copolymer prepared under the present reaction conditions of the 1:1 monomer feed. The copolymer **1** is of linear structure. This is due to the fact that TMA is by far the stronger nucleophile than the tertiary amine group in the copolymer chain;[5] *i.e.*, the interaction between TMA and AA is a rapid process. In accordance with these observations, a preliminary nmr survey of the copolymerization system revealed that the formation of the quaternary ammonium species such as **10** and **13** occurred fast, which was followed by the alternating copolymerization.

The present copolymerization provides a good method to prepare the amine-ester type copolymer. Mechanistic studies as well as the alternating copolymerization of TMA with βPL are currently undertaken in our laboratory.

References and Notes

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A New Route to Optically Active Linear Poly(propylenimine)

Preparation of optically active poly(propylenimine) has been achieved first by Price, *et al.*,[1] by the ring-opening polymerization of optically active propylenimine with acid catalysts. Our recent studies have resulted in the preparation of a linear and crystalline poly(ethylenimine) by the alkaline hydrolysis of poly(*N*-formylethylenimine) which was obtained by the isomerization polymerization of 2-oxazoline.[2] This new method was applied by us to the preparation of optically active poly(propylenimine) having an unequivocal linear structure. We report now a new synthesis of optically active linear poly(propylenimine) (**2**) by the alkaline hydrolysis of poly(*N*-formylpropylenimine) (**1**) which was prepared by the isomerization polymerization of optically active 4-methyl-2-oxazoline (4-MeOZO) with a cationic initiator.

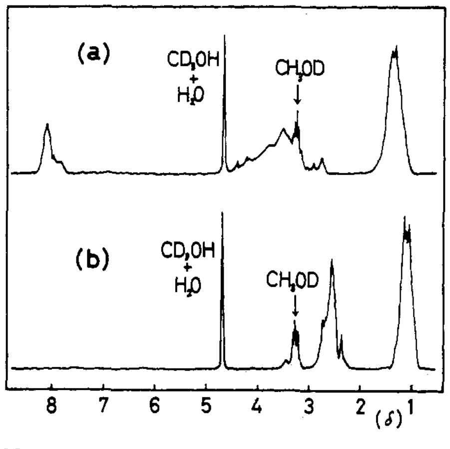
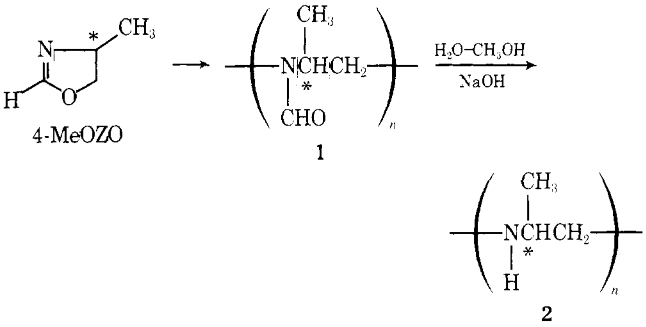
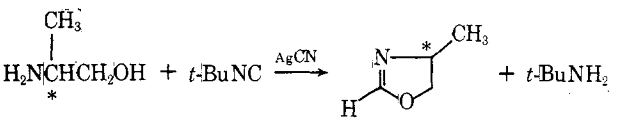


Figure 1. Nmr spectra of (a) poly(*N*-formylpropylenimine) and of (b) poly(propylenimine), both in CD_3OD.



The monomer of L-4-methyl-2-oxazoline (L-4-MeOZO) was prepared by the cyclization reaction of L-alaninol ($[\alpha]^{29}\mathrm{D}$ +21.7° (C_2H_5OH)) and *tert*-butyl isocyanide with silver catalyst, a method recently found in our laboratory.[3]



To a mixture of 15.5 mmol of L-4-MeOZO [$[\alpha]^{30}\mathrm{D}$ −148° (C_2H_5OH)] and 1.5 ml of acetonitrile was added 0.46 mmol of ethyl trifluoromethanesulfonate. The reaction mixture was allowed to react at 80° for 50 hr. The mixture was diluted with methanol, poured into a large amount of diethyl ether to precipitate a white solid, and dried *in vacuo* to give 1.20 g (91% yield) of a solid polymer melting *ca.* 160°. It was shown to be partially crystalline by X-ray diffraction spectrum. The polymer structure was established by nmr and ir spectroscopy as well as elementary analysis to be poly(*N*-formylpropylenimine) (**1**). The nmr spectrum of **1** (Figure 1a) shows a broad singlet at δ 8.3–7.8 due to *N*-formyl proton (1 H), a broad signal at δ 4.5–3.1 due to methine (1 H) and methylene (2 H) protons, and a doublet-like peak centered at δ 1.30 due to methyl protons (3 H). The ir spectrum showed a characteristic band of amide group at 1660 cm^{-1} (>NCH=O). The molecular weight of 1 was 1330 by vapor pressure osmometry.

Anal. Calcd for $C_4H_7NO(H_2O)_{0.36}$: C, 52.50; H, 8.43; N, 15.31. Found: C, 52.87; H, 8.28; N, 15.09.

Polymer **1** is quite hygroscopic. To measure the optical activity of the polymer, the polymer content of the sample solution was first determined by nmr in CD_3OD on the basis of the relative intensities of two singlets at δ 8.0 due to N–CHO and at δ 7.3 due to C_6H_6 added as an internal standard. Then, the specific rotation of **1** was determined as $[\alpha]^{25}\mathrm{D}$ +130° (CH_3OH).

The alkaline hydrolysis of **1** was carried out as follows.