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Cationic Polymerization

Cationic Polymerization of 5-Methyl-2-Oxazoline and Alkaline Hydrolysis of Product Polymer to Linear Poly(Propylenimine)

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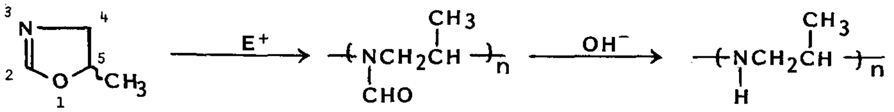
SUMMARY

A new monomer of 5-methyl-2-oxazoline(5-MeOZO) was prepared. It was found that 5-MeOZO underwent the cationic ring-opening isomerization polymerization to produce poly(*N*-formylpropylenimine) 1 of waxy or powdery materials. Alkaline hydrolysis of 1 gave linear poly(propylenimine) 2. Polymers 1 and 2 are the same as the respective polymers derived from 4-methyl-2-oxazoline.

INTRODUCTION

The ring-opening isomerization polymerization of 2-oxazolines is an attractive method to prepare poly(*N*-acylethylenimine)s having a non-branched structure (1). The cationic ring-opening polymerization and its kinetic studies of 2-methyl-2-oxazoline(2-MeOZO) have been reported(2-4). *L*-4-Methyl-2-oxazoline(4-MeOZO) was polymerized and the alkaline hydrolysis of the resulting polymer produced optically active linear poly(propylenimine)(4). The present paper reports the cationic ring-opening polymerization of a new monomer of 5-methyl-2-oxazoline(5-MeOZO) and the alkaline hydrolysis of the product polymer 1 to linear poly(propylenimine) 2.

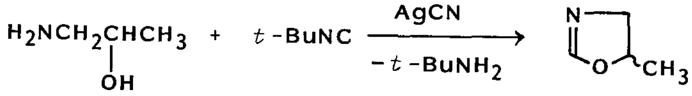


5-MeOZO 1 2

RESULTS AND DISCUSSION

Synthesis of 5-Methyl-2-oxazoline(5-MeOZO)

A new monomer of 5-MeOZO was prepared analogously to the mothod of 4-MeOZO based on the following reaction (5). The ^{1}H NMR spectrum of



5-MeOZO

5-MeOZO(bp, 104-105°C) is shown in Figure 1.

Cationic Ring-Opening Polymerization and Polymer Structure

5-MeOZO has been found to polymerize via ring-opening with cationic

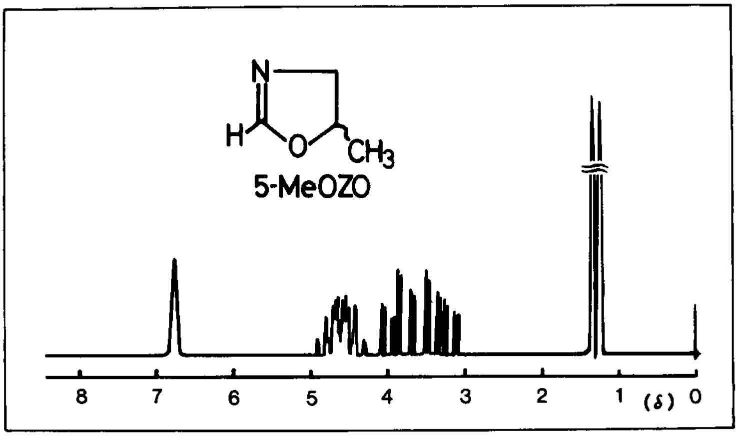


Figure 1. ^{1}H NMR spectrum of 5-MeOZO ($CDCl_3$ with Me_4Si).

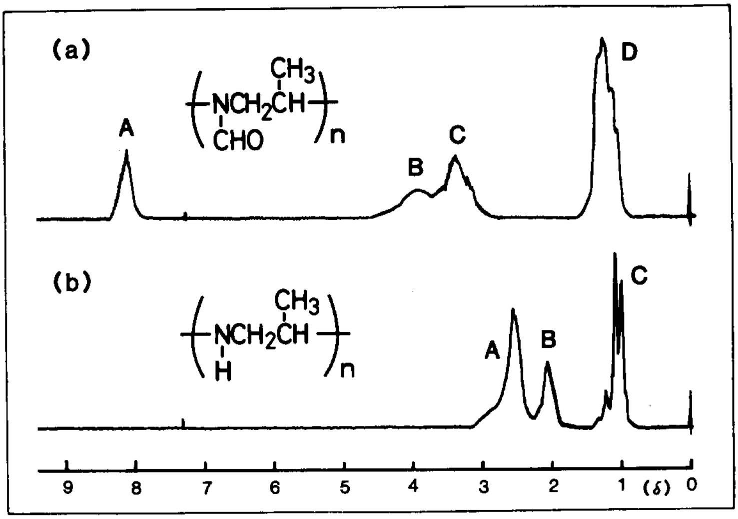


Figure 2. ^{1}H NMR spectra ($CDCl_3$ with Me_4Si) of (a) poly(*N*-formylpropylenimine) 1 and (b) poly(propylenimine) 2.

initiators. The activity of several initiators was examined (Table 1). Methyl *p*-toluenesulfonate(MeOTs), methyl iodide(MeI) and ethyl trifluoromethanesulfonate($EtOSO_2CF_3$) were moderately active. The molecular weight of the polymer was not high.

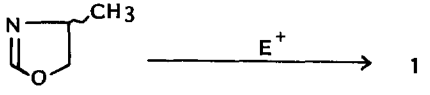
Table 1
Polymerization of 5-MeOZO by Several Cationic Initiators[a]

Initiator	Polymer Yield(%)	Mol. Wt.[b]
$BF_3 \cdot OEt_2$	10	
H_2SO_4	20	
Et_2SO_4	23	
MeOTs	42	710
MeI	30	
$EtOSO_2CF_3$	46	960

a) 5-MeOZO = 10 mmol and initiator = 0.50 mmol in 1 ml of CH_3CN at 90°C for 40 hr under nitrogen.

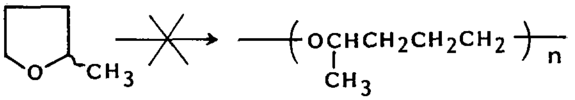
b) Determined by vapor pressure osmometry in DMF at 55°C.

Figure 2(a) shows a ^1H NMR spectrum of the polymer obtained by MeOTs initiator. Peak A at $\delta 8.1$ is assigned to *N*-formyl proton(1H). Broad peaks B centered at $\delta 3.9$ and C centered at $\delta 3.4$ are due to methine(1H) and methylene protons(2H), respectively. Peak D at $\delta 1.3$ is ascribed to methyl protons(3H). An IR characteristic band appears at 1660 cm^{-1} due to the amide carbonyl group. These results lead to the polymer structure as poly(*N*-formylpropylenimine) **1**. The NMR and IR data of **1** are very similar to those of poly(*N*-formylpropylenimine) prepared from 4-MeOZO (5), which supported the sturcture of **1**.



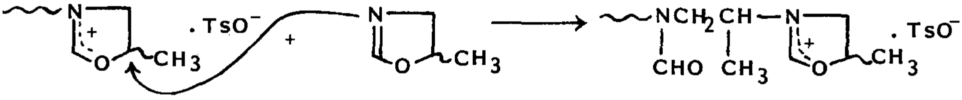
4-MeOZO

All polymers obtained in Table 1 were waxy or powdery, hygroscopic materials. Although the polymer yield was not high under the reaction conditions of Table 1, the quantitative conversion of 5-MeOZO to polymer **1** was achieved with an increased amount of initiator. This finding is interesting because a corresponding methyl substituted cyclic ether of 2-methyltetrahydrofuran does not show a ring-opening polymerizability due



to a thermodynamically unfavorable energy change from monomer to polymer(6). In the case of the 5-MeOZO polymerization the energy gain is accomplished by the conversion of an imino ether (-N=C-O) to an amide group(>N-C=O) which is more stable due to an increased resonance energy of the latter group (7).

The general scheme of propagation by MeOTs initiator is given by the following reaction (8).



Linear Poly(propylenimine) 2

An alkaline hydrolysis of 1 was carried out by heating an aqueous methanol solution of NaOH containing 1 at 100°C for 100 hr. A waxy polymer was obtained, whose ^1H NMR spectrum is shown in Figure 2(b). The structure of poly(propylenimine) 2 has been established based on the following signal assignment, i.e., signal A at $\delta 3.1$-2.3 is due to methine and methylene protons(total 3H) and a doublet-like peak C is assigned as methyl protons (3H). The polymer is very hygroscopic, and hence, peak B at $\delta 2.1$ contains overlapping signals due to protons of NH and water. A signal due to formyl proton disappeared. The ^1H NMR spectrum of 2 is again very similar to linear poly(propylenimine) prepared from the polymer of 4-MeOZO(5).

EXPERIMENTAL PROCEDURES

Materials

Solvents were purified by distillation before use. Initiators of $BF_3 \cdot OEt_2$, MeOTs and MeI were commercial reagents and distilled under nitrogen before use. $EtOSO_2CF_3$ was prepared by the reaction of Et_2SO_4 with CF_3SO_3H, bp 55-58°C/100 mmHg(9). 1-Amino-2-propanol was a commercial reagent and purified by distillation. *t*-Butyl isocyanide was prepared by the dehydration of *N*-*t*-butylformamide with $POCl_3$ in the presence of pyridine in pentane, bp 92-95°C (10).

Monomer Synthesis

5-MeOZO was prepared analogously to the method of 4-MeOZO(5). A mixture of 1-amino-2-propanol (32 ml, 0.414 mol), *t*-butyl isocyanide (50 ml, 0.495 mol) and AgCN (2.83 g, 0.021 mol) was refluxed for 4 hr. The mixture was subjected to distillation and the fraction of bp 100-105°C was collected. This fraction was further distilled by using a distillation apparatus with a spinning-band to give 5-MeOZO, bp 104-105°C. ^1H NMR ($CDCl_3$ with TMS, 60 MHz): $\delta 6.8$ (s, =CH-O-, 1 H), $\delta 4.9$-4.3 (m, C*H*(Me), 1H), $\delta 4.1$-3.1 (m, CH_2, 2 H) and $\delta 1.3$ (d with J=6.0 Hz, CH_3, 3 H).

Polymerization of 5-MeOZO

A typical run was as follows. A mixture of 10 mmol of 5-MeOZO and 0.5 mmol of MeOTs in 1 ml of CH_3CN was kept at 90°C in a seald tube under nitrogen. After 40 hr the tube was opened. The conversion of 5-MeOZO to polymer was 54% which was determined by ^1H NMR of the mixture. Solvent of CH_3CN was evaporated in vacuo. The residual waxy material was dissolved in MeOH and the MeOH solution was poured into a large amount of diethyl ether to precipitate polymeric materials. Drying the polymer in vacuo gave pale yellow solids of 1 (42% yield).

Alkaline Hydrolysis of Polymer 1 to Polymer 2

Polymer 1 (0.294 g) and NaOH (0.27 g) were placed in a sealed tube containing 1.77 ml of water and of MeOH. The tube was kept at 100°C for 100 hr. After the tube was cooled and opened, the reaction mixture was neutralized with dilute HCl solution and concentrated. The polymeric material was extracted with $CHCl_3$ and dried over Na_2SO_4. Evaporation of

$CHCl_3$ and drying the residual polymer gave pale brown polymer 2 (34% yield).

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