Double Isomerization Polymerization of 2-Amino-2-oxazolines Having Four- to Eight-Membered Cyclic Imino Substituents

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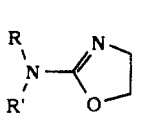
Received December 3, 1992; Revised Manuscript Received August 11, 1993•

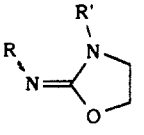
ABSTRACT: The polymerization behaviors of 2-amino-2-oxazolines having four- to eight-membered cyclic amino rings at their 2-positions, i.e., 2-(1-azetidinyl)-2-oxazoline (**1a**), 2-(1-pyrrolidinyl)-2-oxazoline (**1b**), 2-piperidino-2-oxazoline (**1c**), 2-(1-azepanyl)-2-oxazoline (**1d**), 2-(1-azocanyl)-2-oxazoline (**1e**), and 2-morpholino-2-oxazoline (**1f**), are described. Two quite different polymers were produced by the polymerization of **1** via cationic mechanisms. One was poly[(*N*-carbamoylimino)ethylene] (**2**) produced by the usual cationic ring-opening isomerization polymerization ("single isomerization polymerization") of **1** with an alkyl sulfonate initiator. The other was poly[(1,3-diazolidin-2-one-1,3-diyl)oligomethylene] (**3**) produced by a new mode of cationic ring-opening isomerization polymerization ("double isomerization polymerization") initiated by an alkyl halide, in which the isomerization of propagating species occurred during the propagation. The polymerization mechanisms were studied by the isolation of 1:1 adducts of **1** with each of the initiators, and it was proved that the nucleophilicity of the counterion derived from the initiator was the main factor which determined the polymerization pathway. The steric effect of the 2-substituent in **1** on the polymerizability is also discussed.

Introduction

A pseudourea is a compound having an N=C(OR)—N functionality, which is an isomeric form of urea. The polymerization of the family of 2-imino-1,3-oxazolidines has been investigated by Mukaiyama et al.,[1,2] but another family belonging to the pseudoureas, 2-amino-2-oxazolines, has not been investigated in polymerization chemistry.



2-amino-2-oxazolines



2-imino-1,3-oxazolidines

1

In a preceding Communication we briefly reported the synthesis and polymerization of 2-amino-2-oxazolines (**1**) and described that two quite different polymers are produced by the polymerization of **1** via cationic (electrophilic) mechanisms.[3] One is poly[(*N*-carbamoylimino)ethylene] (**2**) produced by the usual cationic ring-opening isomerization polymerization of **1** with an alkyl sulfonate initiator, methyl trifluoromethanesulfonate (triflate) (MeOTf) or methyl *p*-toluenesulfonate (tosylate) (MeOTs), in which the 2-oxazoline ring is opened as in the well-known case of 2-alkyl-, 2-aryl-, or 2-alkoxy-2-oxazoline.[4,5] The other is poly[(1,3-diazolidin-2-one-1,3-diyl)oligomethylene] (**3**) produced by a new mode of cationic ring-opening isomerization polymerization initiated by an alkyl halide, methyl iodide or benzyl chloride or bromide (Scheme I). In the latter polymerization, the isomerization of propagating species occurs during the propagation. Thus, the 2-oxazoline ring in the monomer rearranges to a five-membered cyclic urea unit, and the cyclic imine moiety of the monomer suffers ring-opening.

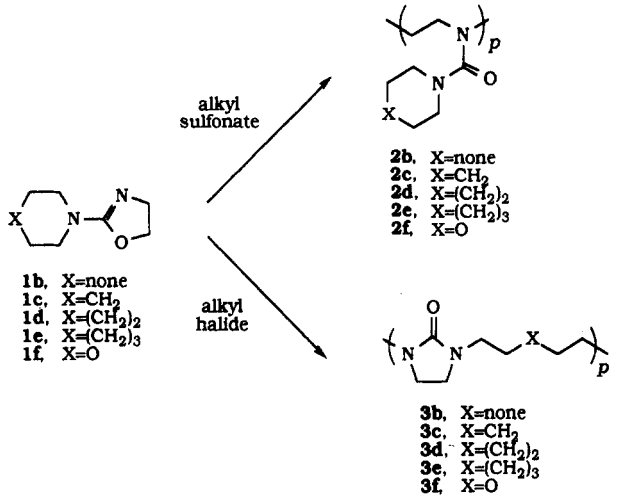
Polymerization of a dual-functional monomer sometimes yields two polymers of different structure depending on the type of initiator, i.e., cationic, radical, or anionic. For example, the polymerization of acrylic acid with a radical initiator yields a vinyl-propagated polymer, while that with an anionic initiator gives poly(β-propiolactone) via the proton transfer mechanism.[6] However, none of the monofunctional monomers, as far as we know, has been known to yield two different types of polymers, selectively, by the choice of initiator among the same type until now.

Although both modes of polymerization of **1** belong to the same category of isomerization ring-opening polymerization, hereafter, the second mode of polymerization involving the opening of the cyclic imine ring is called "double isomerization polymerization (DIP)", meaning "the *isomerization polymerization* accompanying the *isomerization* of propagating species", to distinguish it from the first mode of polymerization. On the other hand, the first mode of polymerization is called "single isomerization ring-opening polymerization (SIP)". In the preceding Communication we reported that a series of 2-amino-2-oxazolines, i.e., 2-(1-pyrrolidinyl)-2-oxazoline (**1b**), 2-piperidino-2-oxazoline (**1c**), and 2-(1-azepanyl)-

• Abstract published in *Advance ACS Abstracts*, October 1, 1993.

0024-9297/93/2226-7116$04.00/0

Scheme I



2-oxazoline (**1d**) caused DIP. These monomers bear five- to seven-membered cyclic imino groups at their 2-positions. In the present paper we describe the polymerization behaviors of the above three monomers as well as 2-(1-azetidinyl)-2-oxazoline (**1a**) having a four-membered cyclic imino function, 2-(1-azocanyl)-2-oxazoline (**1e**) having an eight-membered ring, and 2-morpholino-2-oxazoline (**1f**). Moreover, the present study deals with the isolation and identification of intermediate species in both polymerization systems to clarify the polymerization mechanisms.

Experimental Section

Materials. 2-Ethoxy-2-oxazoline was prepared as described in the previous paper.[5] Azetizine was prepared as described in the literature.[7] Other reagents and solvents were commercially available ones, which were dried by conventional methods and distilled under nitrogen. The solvents were stored over 3-Å molecular sieves after distillation.

Measurements. ^{1}H NMR spectra were recorded on a 60-MHz Hitachi R-600, a 90-MHz JEOL JNM-FX90Q, or a 400-MHz JEOL JNM-JX-400 NMR spectrometer. ^{13}C NMR spectra were recorded on a Hitachi R-900 NMR spectrometer operated at 22.6 MHz. FT-IR spectra were obtained on a Perkin-Elmer 1600 infrared spectrometer. High-resolution mass spectra were measured with a JEOL MS-DX 300, and GC–MS measurements were carried out on a Shimadzu GC–MS QP2000. GPC analysis was performed with a Tosoh HLC 8020 system using a Shodex AC803 column in chloroform. Number-average molecular weights of the samples were measured by a vapor pressure osmometer (Corona Model 117) in chloroform at 35 °C. TGA thermograms were obtained on a Shimadzu TG-30 under nitrogen at a heating rate of 15 °C/min.

General Procedure for the Preparation of Cyclic Pseudourea. In a 200-mL two-necked flask equipped with a reflux condenser and a magnetic stirrer bar were placed 13.0 mL of 2-ethoxy-2-oxazoline (0.12 mol), 0.13 mol of the cyclic imine, and 100 mL of benzene. To the mixture was added 230 mg of *p*-toluenesulfonic acid (1.2 mmol), and the mixture was heated to reflux. The heating was continued until the GLC analysis of the mixture showed the almost complete consumption of 2-ethoxy-2-oxazoline. After evaporation of the solvent, the residual product 1 was purified further by distillation under reduced pressure.

1a: colorless liquid; ^{1}H NMR ($CDCl_3$) δ 2.24 (quintet, $CH_2CH_2CH_2$, 2 H), 3.7–3.9 (m, NCH_2 of oxazoline ring, 2 H), 3.98 (t, CH_2N of azetidinyl group, 4 H), 4.2–4.4 (m, OCH_2, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.1 ($CH_2CH_2CH_2$), 51.0 (C_4), 53.3 (CH_2N of azetidinyl group), 68.6 (C_5), 163.1 (C=N); IR (neat) 2930, 2880 (ν_{CH}), 1660 ($\nu_{C=N}$), 1485, 1285, 1145, 985, 930 cm^{-1}; mass spectrum *m/e* 126 (M^+), 125, 68, 56; exact mass found, *m/e* 126.0792 (calcd for $C_6H_{10}N_2O$, *m/e* 126.0793).

1b: waxy solid; mp 31–32 °C; ^{1}H NMR ($CDCl_3$) δ 1.88 (m, $CH_2CH_2CH_2$, 4 H), 3.41 (m, CH_2N of pyrrolidinyl group, 4 H), 3.80 (m, NCH_2 of oxazoline ring, 2 H), 4.30 (m, OCH_2, 2 H); IR (neat) 2960, 2860 (ν_{CH}), 1655 ($\nu_{C=N}$), 1435, 1283, 1073, 938, 710 cm^{-1}; mass spectrum *m/e* 140 (M^+), 112, 98, 70; exact mass found, *m/e* 140.0951 (calcd for $C_7H_{12}N_2O$, *m/e* 140.0950).

1c: colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.3–1.8 (m, $NCH_2CH_2CH_2CH_2$, 6 H), 3.1–3.5 (m, NCH_2 of piperidino ring, 4 H), 3.6-3.9 (m, NCH_2 of oxazoline ring, 2 H), 4.0–4.4 (m, OCH_2, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.3 (4-position of piperidino group), 25.4 (3- and 5-positions of piperidino group), 46.6 (2- and 6-positions of piperidino group), 52.8 (C_4), 68.1 (C_5), 162.4 (C=N); IR (neat) 2930, 2855 (ν_{CH}), 1660 ($\nu_{C=N}$), 1430, 1298, 1260, 1035, 935, 878 cm^{-1}; exact mass found, *m/e* 154.1100 (calcd for $C_8H_{14}N_2O$, *m/e* 154.1106).

1d: colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.3–1.8 (m, $NCH_2CH_2CH_2CH_2$, 8 H), 3.2–3.6 (m, NCH_2 of azepanyl group, 4 H), 3.6-3.9 (m, NCH_2 of oxazoline ring, 2 H), 4.0–4.4 (m, OCH_2, 2 H); exact mass found, *m/e* 168.1264 (calcd for $C_9H_{16}N_2O$, *m/e* 168.1263).

1e: colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.5–1.8 (m, $NCCH_2CH_2CH_2CH_2$, 10 H), 3.38 (t, NCH_2 of azocanyl group, 4 H), 3.7–3.9 (m, NCH_2 of oxazoline ring, 2 H), 4.2–4.4 (m, OCH_2, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.0, 26.9 (5-position of azocanyl ring), 27.0, 48.9 (2-positions of azocanyl ring), 52.9 (4-position of oxazoline ring), 68.1 (5-position of oxazoline ring), 162.1 (C=O); exact mass found, *m/e* 182.1413 (calcd for $C_{10}H_{18}N_2O$, *m/e* 182.1419).

1f was isolated by drying the reaction mixture and purified by recrystallization from dichloromethane. White solid; mp 97–99 °C; ^{1}H NMR ($CDCl_3$) δ 3.48 (t, NCH_2 of morpholine ring, 4 H), 3.64 (t, OCH_2 of morpholine ring, 4 H), 3.70 (m, NCH_2 of oxazoline ring, 2 H), 4.30 (m, OCH_2 of oxazoline ring, 2 H); IR (neat) 2968, 2855, 1650, 1435, 1278, 1240, 1118, 1070, 935, 873, 710 cm^{-1}; exact mass found, *m/e* 156.0902 (calcd for $C_7H_{12}N_2O_2$, *m/e* 156.0899).

Typical Procedure for the Ring-Opening Isomerization Polymerization of Cyclic Pseudoureas. In a test tube equipped with a magnetic stirrer bar and a three-way stopcock were placed 0.520 g (3.71 mmol) of **1b** and 2.5 mL of benzonitrile under nitrogen. To the solution was added 69.6 mg (0.374 mmol) of methyl tosylate with stirring. The tube was sealed and allowed to react at 105 °C for 15 h. The produced polymer **2b** was isolated by precipitation from diethyl ether, purified further by repeated reprecipitation from dichloromethane to diethyl ether, and dried in vacuo. The yield was 0.504 g (97%). **2b**: white powder; ^{1}H NMR ($CDCl_3$) δ 1.81 ($NCH_2CH_2CH_2CH_2$, 4 H), 3.32 (NCH_2, 8 H); ^{13}C NMR ($CDCl_3$) δ 25.8 ($NCH_2CH_2CH_2CH_2$), 47.3 (NCH_2 of main chain), 48.3 (NCH_2 of pyrrolidinyl group), 160.9 (C=O); IR (film) 2976, 2870, 1622 ($\nu_{C=O}$), 1456, 1418, 749 cm^{-1}.

2a: ^{1}H NMR ($CDCl_3$) δ 2.0–2.4 ($NCH_2CH_2CH_2$, 2 H), 3.0–3.5 (NCH_2 of azetidinyl ring, 4 H), 3.8–4.3 (NCH_2 of main chain, 4 H); ^{13}C NMR ($CDCl_3$) δ 16.1 ($NCH_2CH_2CH_2$), 46.3 (NCH_2 of main chain), 51.4 (NCH_2 of azetidinyl group), 162.3 (C=O); IR (film) 3000, 2880, 1620 ($\nu_{C=O}$), 1425, 1220, 755 cm^{-1}.

2c: ^{1}H NMR ($CDCl_3$) 1.55 ($NCH_2CH_2CH_2CH_2CH_2$, 6 H), 3.10 (m, NCH_2CH_2N, 4 H), 3.27 ($NCH_2CH_2CH_2CH_2CH_2N$, 4 H); δ ^{13}C NMR ($CDCl_3$) δ 25.5 (4-position of piperidino group), 26.6 (3- and 5-positions of piperidino group), 46.7 (NCH_2 of main chain), 48.4 (2- and 6-positions of piperidino group), 162.9 (C=O); IR (film) 2937, 2854, 1636 ($\nu_{C=O}$), 1419, 753 cm^{-1}.

2d: ^{1}H NMR (PhCN) δ 1.3–2.0 ($NCH_2CH_2CH_2CH_2$, 8 H), 3.1–3.8 ($NCH_2CH_2CH_2CH_2$, 8 H); ^{13}C NMR ($CDCl_3$) δ 27.9 (4- and 5-positions of hexamethleneiminyl group), 28.8 (3- and 6-positions of hexamethyleneiminyl group), 47.7 and 48.6 (NCH_2), 162.7 (C=O); IR (film) 2928, 2856, 1628 ($\nu_{C=O}$), 1417, 1263, 754 cm^{-1}.

2e: ^{1}H NMR ($CDCl_3$) δ 1.2–2.0 ($NCCH_2CH_2CH_2CH_2CH_2$, 10 H), 2.9–3.7 ($NCH_2CH_2CH_2CH_2$, 8 H); ^{13}C NMR ($CDCl_3$) δ 24.8, 25.5–27.0, 47.4–49.2 ($NCH_2CH_2CH_2CH_2$), 163.6 (C=O); IR (film) 2930, 2855, 1640 ($\nu_{C=O}$), 1443, 1275, 1152, 758 cm^{-1}.

2f: ^{1}H NMR ($CDCl_3$) 3.2–3.5 (m, NCH_2CO, 4 H), 3.5–3.9 (m, OCH_2 and NCH_2CH_2N, 8 H); ^{13}C NMR ($CDCl_3$) δ 46.8 (NCCN), 47.9 (NCCO), 66.6 (OCH_2), 162.7 (C=O); IR (KBr) 2985, 2847, 1640 ($\nu_{C=O}$), 1423, 1250, 1118, 672 cm^{-1}.

Typical Procedure for the Double Isomerization Polymerization of Cyclic Pseudoureas. In a test tube equipped with a magnetic stirrer bar and a three-way stopcock were placed 2.436 g (17.4 mmol) of **1b** and 5 mL of benzonitrile under nitrogen. To the solution was added 61.9 mg (0.362 mmol) of benzyl bromide with stirring. The tube was sealed and allowed to react at 100 °C for 100 h. The mixture was homogeneous through the reaction. The polymeric product precipitated out from the solution when the tube was kept at room temperature. The white powdery

polymer **3b** was isolated by filtration, purified further by repeated reprecipitation from chloroform to diethyl ether, and dried in vacuo. The yield was 2.361 g (95%). **3b**: ^{1}H NMR ($CDCl_3$) δ 1.51 ($NCH_2CH_2CH_2CH_2$, 4 H), 3.18 (NCH_2CH_2N, 4 H), 3.28 ($NCH_2CH_2CH_2$, 4 H); ^{13}C NMR ($CDCl_3$) δ 24.3 ($NCH_2CH_2CH_2$), 41.8 and 43.0 (NCH_2), 159.5 (C=O); IR (film) 2933, 2864, 1676 ($\nu_{C=O}$), 1497, 1449, 759 cm^{-1}.

The polymers of **1a** initiated by alkyl halides consisted of **2a** and **3a** units: ^{1}H NMR ($CDCl_3$) δ 1.5–1.9 ($CH_2CH_2CH_2$ of **3a** unit), 2.0–2.4 ($CH_2CH_2CH_2$ of **2a** unit), 3.0–3.5 ($CH_2CH_2CH_2$), 3.8–4.3 (NCH_2CH_2N); ^{13}C NMR ($CDCl_3$) δ 15.8 ($CH_2CH_2CH_2$ of **2a** unit), 25.9 ($CH_2CH_2CH_2$ of **3a** unit), 41.9 ($CH_2CH_2CH_2$ of **3a** unit), 42.1–42.9 (NCH_2CH_2N of **3a** unit), 45.1–45.6 (NCH_2CH_2N of **2a** unit), 51.2 (NCH_2 of azetidinyl ring), 161.1 (C=O of **3a** unit), 162.2 (C=O of **2a** unit); IR (film) 2990, 1685 ($\nu_{C=O}$), 1620, 1492, 1435, 1220, 755 cm^{-1}.

3c: ^{1}H NMR ($CDCl_3$) δ 1.3–1.4 ($NCH_2CH_2CH_2$, 2 H), 1.5–1.6 ($NCH_2CH_2CH_2$, 4 H), 3.1–3.2 (NCH_2 of main chain, 4 H), 3.2–3.4 (NCH_2 of diazolidinone ring, 4 h); ^{13}C NMR δ 23.8 ($NCH_2CH_2CH_2$), 27.7 ($NCH_2CH_2CH_2$), 43.2 (NCH_2 of pentamethylene unit), 44.4 (NCH_2 of diazolidinone ring), 159.9 (CO); IR (film) 2929, 2858, 1684 ($\nu_{C=O}$), 1496, 1448, 1369, 1261 cm^{-1}.

3d: ^{1}H NMR (PhCN) δ 1.1–1.7 ($NCCH_2CH_2$, 8 H), 3.0–3.5 (NCH_2, 8 H); ^{13}C NMR ($CDCl_3$) δ 26.3 ($NCH_2CH_2CH_2$), 27.6 ($NCH_2CH_2CH_2$), 42.5 (NCH_2 of main chain), 43.9 (NCH_2 of diazolidinone ring), 158.2 (C=O); IR (film) 2930, 2858, 1684 ($\nu_{C=O}$), 1496, 1448, 1260, 754 cm^{-1}.

3e: ^{1}H NMR ($CDCl_3$) δ 1.2–1.8 ($NCCH_2CH_2CH_2$, 10 H), 2.9–3.4 (NCH_2, 8 H); ^{13}C NMR ($CDCl_3$) δ 26.7 ($NCH_2CH_2CH_2$), 27.6 ($NCH_2CH_2CH_2$), 29.1 ($NCH_2CH_2CH_2CH_2$), 42.8 (NCH_2 of main chain), 44.2 (NCH_2 of diazolidinone ring), 161.4 (C=O); IR (film) 2930, 2855, 1680 ($\nu_{C=O}$), 1485, 1452, 1260, 758 cm^{-1}.

3f: ^{1}H NMR ($CDCl_3$) δ 3.4 (broad triplet, NCH_2CO, 4 H), 3.5 (s, NCH_2CH_2N, 4 H), 3.7 (broad triplet, OCH_2, 4 H); ^{13}C NMR δ 44.6 (NCH_2), 69.9 (OCH_2), 159.9 (C=O); IR (KBr) 2990, 1685, 1495, 1269, 1120, 668 cm^{-1}.

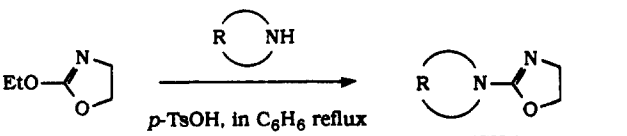
Isolation of 3-Methyl-2-(1-pyrrolidinyl)-2-oxazolinium *p*-Toluenesulfonate (4a). All operations were carried out under nitrogen. To an ice-cooled solution of methyl *p*-toluenesulfonate (0.81 g (4.35 mmol)) in 0.63 mL of nitromethane was added 0.31 g (2.21 mmol) of **1a** dropwise with vigorous stirring. After mixing at 35 °C for 1 h, the solvent was removed in vacuo. The crude salt was purified by recrystallization from a mixture of methylene chloride and diethyl ether. **4a**: white crystals; 88% yield; mp 47–48 °c (under nitrogen); ^{1}H NMR ($C_6D_5NO_2$) δ 1.66 (m, $C(CH_2)_2C$, 4 H), 2.11 (s, CH_3Ph, 3 H), 3.18 (s, NCH_3, 3 H), 3.45 (m, CH_2CCCH_2, 4 H), 3.95 (m, CH_2N, 2 H), 4.55 (m, OCH_2, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.8 (CH_3Ph), 25.0 ($NCH_2CH_2CH_2$), 33.9 (NCH_3), 49.0 ($NCH_2CH_2CH_2CH_2$), 52.1 (NCH_2CH_2O), 67.4 (OCH_2), 124.0, 126.7, 137.4, 143.1 (aromatic carbons), 156.4 (C=N); IR (CH_2Cl_2) 3049, 2984, 1683, 1522, 1201 cm^{-1}.

Isolation of 3-Methyl-2-(1-pyrrolidinyl)-2-oxazolinium Iodide (4b). To an ice-cooled solution of emthyl iodide (5.76 g (40.6 mmol)) in dry nitromethane was added 1.07 g (7.64 mmol) of **1a** dropwise with vigorous stirring under nitrogen. The reaction mixture was allowed to stand at room temperature, and isolation of **4b** was carried out in a similar manner as above. **4b**: 86% yield; orange needles; mp 55 °C; ^{1}H NMR ($CDCl_3$) δ 2.03 (m, $C(CH_2)_2C$, 4 H), 3.47 (s, CH_3N, 3 H), 3.84 (m, CH_2CCCH_2, 4 H), 4.32 (m, CH_2N, 2 H), 4.83 (m, CH_2O, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.0 ($NCH_2CH_2CH_2$), 34.9 (NCH_3), 49.3 ($NCH_2CH_2CH_2CH_2$), 52.7 (NCH_2CH_2O), 67.2 (OCH_2), 157.3 (C=N); IR (KBr) 2955, 1683 ($\nu_{C=O}$), 1519, 1458, 1294 cm^{-1}.

Isolation of 3-Methyl-1-azonia-3-azaspiro[4.4]nonan-2-one Iodide (6b). All operations were carried out under nitrogen. In $C_6D_5NO_2$, **4b** was heated at 80 °C for 10 min. During the cooling at −20 °C, **6b** was crystallized from the mixture, which was collected by filtration as pale yellow needles. **6b**: mp 132 °C; ^{13}C NMR ($CDCl_3$) δ 23.6 (*COCC*), 32.6 (CH_3N), 44.1 ($CH_3NCH_2CH_2N$), 54.2 ($CH_3NCH_2CH_2N$), 62.2 (*COCC*), 151.4 (C=O); IR (CH_2Cl_2) 3039, 2959, 1813 ($\nu_{C=O}$), 1494, 1450, 1431, 1410, 1105 cm^{-1}.

Isolation of 1,3,3-Trimethyl-1,3-diazolidin-2-on-1-ium Triflate (8). All operations were carried out under nitrogen. To a solution of 1,3-dimethyl-1,3-diazolidin-2-one (1.00 g, 8.76 mmol) in 10 mL of chloroform was added 1.29 mL (11.4 mmol) of MeOTf with stirring. The mixture was allowed to reflux for 3 h. When the mixture was cooled to room temperature, it separated into two layers. To the mixture was added 10 mL of diethyl ether, and the upper layer was decanted off. The crude liquid product was washed three times with 10 mL of diethyl ether and kept at −20 °C overnight to induce crystallization. The resulting solidified product was washed twice with diethyl ether again and dried in vacuo. The yield was 1.89 g (78%). **8**: white crystals; mp 107.1–108.2 °C; ^{1}H NMR (CD_3NO_2) δ 3.11 (s, 3 H, NCH_3), 3.33 (s, 6 H, $N^+(CH_3)_2$), 2.90 (t, 3 H, NCH_2), 4.02 (t, 3 H, N^+CH_2); ^{13}C NMR (CD_3NO_2) δ 30.7 (NCH_3), 41.9 (s, 6 H, NCH_2), 48.5 ($N^+(CH_3)_2$), 55.0 (N^+CH_2), 119.2 (q, CF_3, $|J|_{CF}$ = 318 Hz), 151.6 (C=O); IR (CH_3NO_2) 1820 (C=O), 1275, 1227, 1158 cm^{-1}.

Scheme II



1a, R=$(CH_2)_3$
1b, R=$(CH_2)_4$
1c, R=$(CH_2)_5$
1d, R=$(CH_2)_6$
1e, R=$(CH_2)_7$
1f, R=$(CH_2)_2O(CH_2)_2$

Table I. Preparation of Cyclic Pseudoureas[a]

starting amine	time, h	product	yield, %	bp, °C/Torr	pK_a[b]
azetidine	9	1a	78	44/11	9.5
pyrrolidine	1	1b	69	83/5	9.7
piperidine	2	1c	70	76/2.6	9.3
azepane	1	1d	82	68/0.5	9.6
azocane	2	1e	59	99/2.1	9.6
morpholine	2	1f	82	97–99 (mp)	8.1

[a] 2-Ethoxy-2-oxazoline was treated with 1.1 equiv of cyclic amine and 1 mol % of *p*-toluenesulfonic acid monohydrate in benzene under reflux. [b] In water at 25 °C.

Results and Discussion

Preparation of Cyclic Pseudoureas. Six aminooxazolines **1a–f** were prepared by the condensation reactions of 2-ethoxy-2-oxazoline with the corresponding cyclic imines catalyzed by *p*-toluenesulfonic acid in benzene (Scheme II).[8] The preparation of **1a** required a longer time for the completion of reaction due to the low boiling point of azetidine (61–62 °C). The yields of **1** shown in Table I are values after the purification by distillation under reduced pressure, which are generally good. A similar acid-catalyzed reaction of 2-ethoxy-2-oxazoline with aziridine did not yield the expected 2-(1-aziridinyl)-2-oxazoline but gave the polymer of ethylenimine.[9]

All these compounds are basic as common amines are and their pK_a values are higher than those for 2-alkyl- and 2-alkoxy-2-oxazolines, indicating the electron-donating effect of the 2-dialkylamino substituent: the pK_a values of **1** are around 9 as indicated in Table I, while those of 2-methyl- and 2-isopropoxy-2-oxazolines are 5.5 and 5.4, respectively.

Polymerization of 2-(1-Pyrrolidinyl)-2-oxazoline (1b). The results of the ring-opening polymerizations of **1b** with sulfonate esters and alkyl halides as cationic initiators are summarized in Table II.

The polymerization with MeOTs ([M]/[I] = 10.7) proceeded smoothly at 80 °C in benzonitrile and gave a polymer quantitatively (run 1 in Table II). The structure of the polymer was poly{[*N*-(1-pyrrolidinyl)carbonylimino]-ethylene} (**2b**), which was identified from IR and ^{1}H and ^{13}C NMR spectroscopies (vide infra). Acetonitrile and dichloromethane were also good solvents for the polymerization of **1b** (runs 2 and 3), but the polymer yields in these runs were lower than that in benzonitrile. No polymerization of **1b** occurred in a protic solvent, such as methanol. Therefore, benzonitrile was chosen as solvent

Table II. Single and Double Isomerization Polymerizations of 2-(1-Pyrrolidinyl)-2-oxazoline (1b)

run no.	initiator	[M]/[I]	solvent	temp, °C	time, h	polymer: unit ratio 2b:3b	yield, %	M_n[a]	M_w/M_n[a]	M_n[b]	M_n[c]	$M_{n,theor}$[d]
1	MeOTs	10.7	PhCN	80	24	1:0	100	730	1.15	1700	1600	1500
2	MeOTs	10.2	CD_3CN	80	19	1:0	89	750	1.19			1460
3	MeOTs	12.2	CD_2Cl_2	80	64	1:0	89	670	1.48			1740
4	MeOTs	49.8	PhCN	105	15	1:0	97	3000	1.52	2500		6980
5	MeOTs	99.2	PhCN	105	15	1:0	87	5500	1.49	4300	16000	13900
6	MeOTf	9.8	PhCN	80	24	1:0	97	800	1.11	1400	1300	1370
7	$PhCH_2Br$	9.5	PhCN	80	47	0:1	93	2100	1.32			1330
8	$PhCH_2Br$	48.0	PhCN	100	100	0:1	95	8300	1.32	5700	6800	6730
9	$PhCH_2Cl$	9.8	PhCN	140	30	0:1	93	2000	1.23	1900	1800	1370
10	MeI	9.9	PhCN	80	16	0.17:0.83	97	1100	1.36	2000	1900	1390
11	MeI	47.3	PhCN	100	168	0.15:0.85	74	3600	1.80	3200		6630

[a] Determined by GPC with polystyrene standards. [b] Determined by VPO in chloroform at 35 °C. [c] Determined from the integral ratio of the peaks ascribed to NCH_3 (or NCC_6H_5 for run nos. 7–9) and NCH_2 in the ^1H NMR spectrum on the assumption that each polymer molecule has one initiator-derived alkyl group. [d] Theoretical molecular weight calculated from the feed ratio of monomer to initiator.

in the following experiments. The polymerization of **1b** with MeOTf also yielded **2b** (run 6). The produced polymer had a slightly narrower molecular weight distribution than that prepared with MeOTs under similar conditions, reflecting a higher rate of initiation in this system, but no significant structural difference was observed between the resulting polymers.

The polymerization of **1b** with ca. 10 mol % of benzyl bromide also smoothly proceeded at 80 °C and gave a polymer in a high yield (run 7). Interestingly, the structure of the resulting polymer was completely different from that of **2b**. The polymer obtained with benzyl bromide was poly[(1,3-diazolidin-2-one-1,3-diyl)tetramethylene] (**3b**) consisting of a five-membered ethyleneurea ring and tetramethylene moiety. The polymerization of **1b** with benzyl chloride also gave **3b**, although a higher temperature, 140 °C, was required for the polymerization due to the poorer reactivity of the propagating species (vide infra).

The structural difference between **2b** and **3b** was most clearly characterized by IR spectroscopy since the C=O carbonyl stretching frequency of a five-membered cyclic urea was higher than that of a linear or six-membered cyclic urea having similar substituents. The C=O stretching band of **3b** appears at 1676 cm^{-1}, whereas that of **2b** appears at 1622 cm^{-1}.[10] The comparison of these frequencies with those of noncyclic and five- and six-membered ureas, e.g., *N,N,N',N'*-tetramethylurea (TMU) (1640 cm^{-1}), 1,3-dimethyl-1,3-diazolidin-2-one (DMD) (1700 cm^{-1}), and 1,3-dimethylperhydro-1,3-diazin-2-one (1640 cm^{-1}), shows the presence of the five-membered 1,3-diazolidin-2-one ring in **3b**.[11]

In the 400-MHz ^1H NMR spectra of **2b** and **3b**, the peak ascribed to the β-methylene protons of the tetramethylene unit in **3b** appears at δ 1.51 while that of the pyrrolidinyl ring in **2b** is observed at δ 1.81.[10] The latter value is in good accordance with the chemical shifts for the β-methylene protons of the pyrrolidine ring in *N*-acylpyrrolidines (ca. δ 1.9).[12] This fact also supports the presence of the pyrrolidine ring in **2b** and its absence in **3b**.

Figure 1 shows the 22.6-MHz ^{13}C NMR spectra of **2b** (prepared in run 6) and **3b** (run 9) in $CDCl_3$. The peaks at δ 25.8 (c), 47.3 (a), 48.3 (b), and 160.9 (d) in Figure 1a are ascribed to the carbons of the repeating unit of **2b**, and the small peak at δ 38.1 is due to the N-CH_3 carbon at the initiating end. In Figure 1b the peaks at δ 24.3 (c'), 41.8 (a' or b'), 43.0 (b' or a'), and 159.5 (d') are ascribed to the carbons of the **3b** repeating unit, and the small peaks at δ 29.4, 48.5, and ca. 126.4–136.5 are respectively ascribed to $ClCH_2$, $PhCH_2$, and aromatic carbons at the polymer ends. Although the difference in the chemical shifts of the peaks is relatively small, it is obvious that these two polymers have uniform structures and they are quite different from each other.

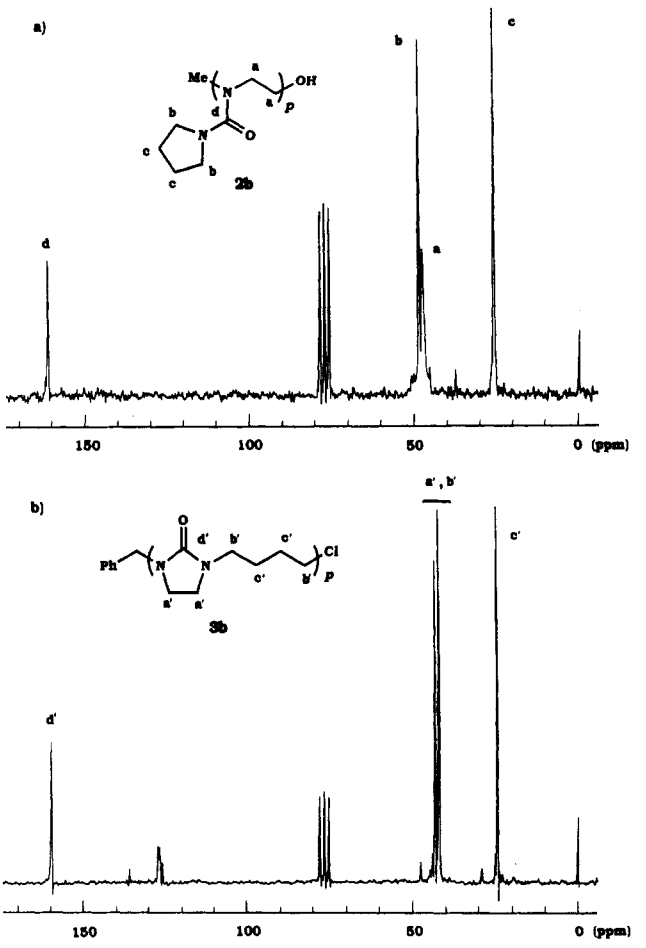


Figure 1. 22.6-MHz ^{13}C NMR spectra of **2b** (a) and **3b** (b) (in $CDCl_3$/TMS).

With methyl iodide initiator, the polymerization of **1b** afforded a polymer consisting of both the [*N*-(1-pyrrolidinyl)carbonylimino]ethylene unit (**2b** unit) as the main component and the (1,3-diazolidin-2-one-1,3-diyl)tetramethylene unit (**3b** unit). The content of the **2b** unit in the polymer (**2b**/**3b**) varied a little according to the feed ratio and was 0.15–0.17, which was determined by ^1H NMR spectroscopy.

Polymers **2b** and **3b** show somewhat different solubilities and thermal properties from each other. Polymer **2b** is a crystalline yellow material with a melting point of 223 °C and is very soluble in halogenated hydrocarbons such as dichloromethane and chloroform. On the other hand, **3b** is a slightly hygroscopic, yellow semicrystalline material with a melting point of 163 °C. Their solubilities are summarized in Table III. Although TMU is one of the representative aprotic polar solvents and is miscible with

Table III. Solubilities of 2b and 3b at Room Temperature[a]

	H_2O	MeOH	MeCN	DMF	$MeNO_2$	PhCN	Me_2CO	THF	CH_2Cl_2	$CHCl_3$	CCl_4	Et_2O	C_6H_6
2b	±	+	–	–	–	–[c]	–	–	++	++	–	–	–
3b	–	++	–	–	–[b]	–[c]	–	–	++	++	–	–	–

[a] ++, very soluble; +, soluble; ±, partly soluble, –, insoluble. [b] Soluble at 60 °C. [c] Soluble at 80 °C.

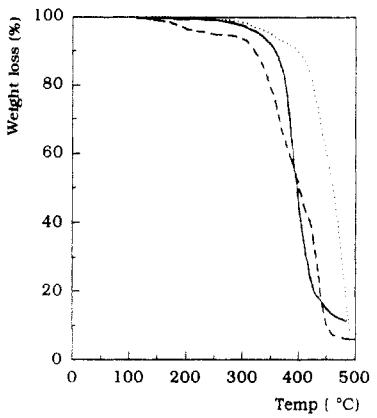


Figure 2. TGA thermograms of **2b** (—), **2b/3b** (– – –), and **3b** (· · ·) (under nitrogen at a heating rate of 15 °C/min).

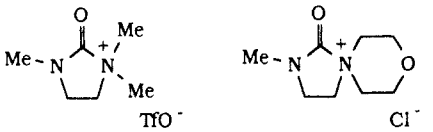
almost all solvents from water to hexane, its polymer homologues, **2b** and **3b**, show poorer solubilities, especially to aprotic polar solvents including TMU. Probably, this is due to their highly crystalline nature.

Figure 2 shows the TGA thermograms of **2b**, **3b**, and **2b/3b** (prepared with methyl iodide) measured under nitrogen. Polymers **2b** and **3b** are stable above their melting points, and **3b** is the most stable among them.

The number-average molecular weights (M_n) of the polymers were estimated from GPC and VPO. The integral ratio of the peak ascribed to *N*-CH_3 (or *N*-CPh) to others in the ^{1}H NMR spectrum was also used for the calculation of M_n on the assumption that each polymer molecule has one initiator-derived end group. These values as well as those calculated from the feed ratio of monomer to initiator ($M_{n,theor}$) are summarized in Table II. The M_n values determined from ^{1}H NMR generally agree with the corresponding $M_{n,theor}$ values, indicating a good initiator efficiency. On the other hand, the disagreement between the M_n values from VPO and the $M_{n,theor}$ values in the runs of high [M]/[I] ratio (runs 4, 5, and 11) suggests the occurrence of chain transfer. As for **2b/3b**, the much broader molecular weight distribution may be partly ascribed to its mixed structure.

Preparation and Isomerization of 1:1 Adducts of 1a with Initiators. To investigate the mechanism of this peculiar polymerization, 1:1 adducts of **1b** with MeOTs and with methyl iodide were prepared (Scheme III). The reaction of **1b** with an excess of methyl tosylate yielded thermally stable 3-methyl-2-pyrrolidino-2-oxazolinium tosylate (**4a**) as colorless crystals. An analogous oxazolinium salt having an iodide counteranion, **4b**, could also be isolated as orange needles by the reaction of **1b** with methyl iodide under a similar condition. This salt **4b** is thermally unstable: when **4b** was dissolved in benzonitrile and heated to 80 °C, ca. 60% of **4b** isomerized into two new species (**6b** and **7b**; vide infra) after 10 min. This is in contrast to the fact that **4a** remained unchanged after heating at 80 °C for 8 h. By cooling this mixture, **6b** was deposited as pale yellow needles. The structure of **6b** was identified from ^{1}H and ^{13}C NMR and IR spectroscopies as an ionic spiro compound having an *N*-quarternary alkylated urea group, 3-methyl-1-azonia-3-azaspiro[4.4]-nonan-2-one iodide.

To confirm the structure of **6b**, its model compound was prepared by the methylation of 1,3-dimethyl-1,3-diazolidin-2-one (DMD). It was reported that the alkylation of urea with a strong alkylating reagent yielded two compounds, *O*-alkylated and *N*-alkylated salts, and the latter was more crystalline than the former.[13] By cooling a chloroform solution of DMD with 2 equiv of MeOTf, an *N*-methylated salt of DMD, 1,3,3-trimethyl-1,3-diazolidin-2-on-1-ium triflate (**8**) could be isolated as white crystals in 78% yield.



8 **9**

In Figure 3 the ^{13}C NMR spectrum of **6b** is compared with that of **8**. The peaks ascribed to the 1,3-diazolidin-2-one ring carbons appear at δ 44.1 (b), 54.2 (a), and 151.4 (c) in Figure 3a. These chemical shifts agree well with those of the corresponding peaks of **8**, δ 43.5 (b′), 56.4 (a′), and 152.6 (c′) in Figure 3b. The upfield shift of the carbonyl peaks of **6b** and **8** in comparison with DMD (δ 161.3) is explained by the electron-withdrawing effect of the adjacent ammonium group. The comparison of the ^{1}H NMR spectroscopic data of **6b** and **8**, which are shown in Figure 4 and given in the Experimental Section, also supports the structural analogy between these compounds.

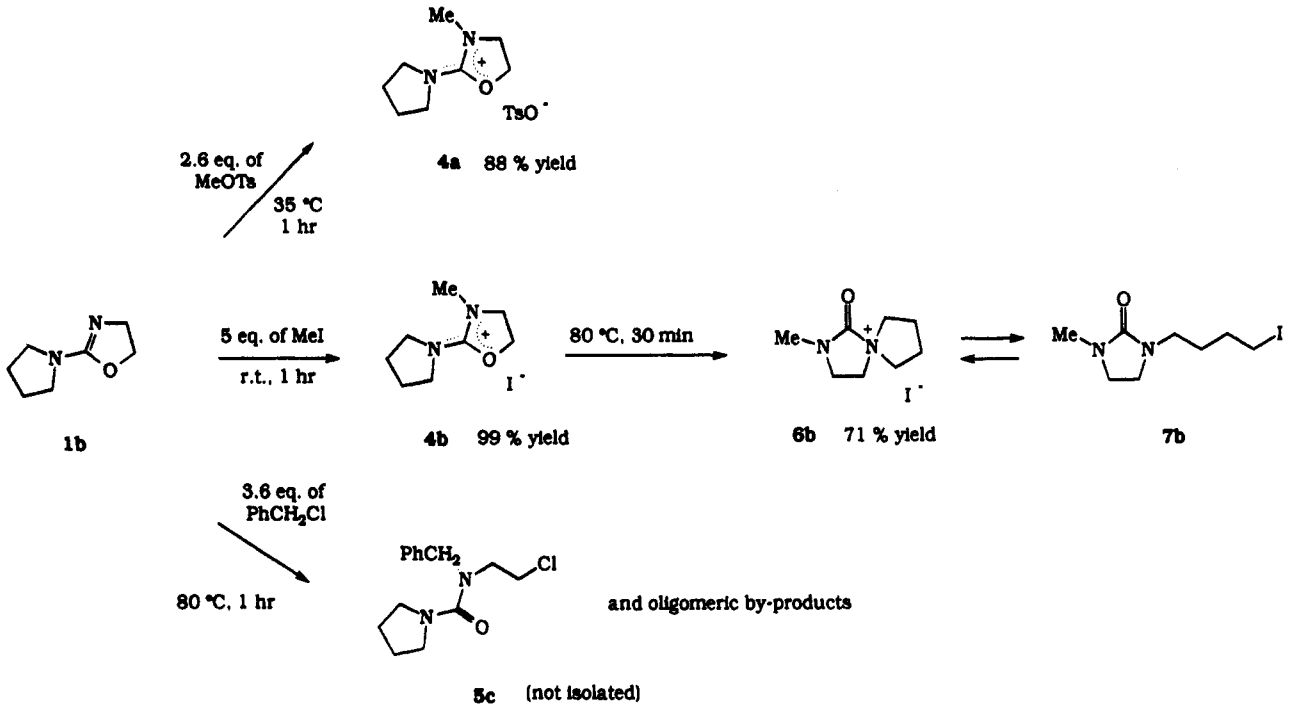
The frequencies of the carbonyl stretching bands of **6b** and **8** in their IR spectra were also quite similar, 1813 cm^{-1} for **6b** and 1820 cm^{-1} for **8**, again indicating the attachment of the electron-withdrawing substituent on the carbonyl group. An analogous ionic spiro compound **9** has already been prepared by the reaction of *N*-ethyl-2-aminoethanol and 1-(chloroformyl)morpholine, whose carbonyl stretching band has been reported to appear at 1800 cm^{-1}.[14]

When the isolated **6b** was dissolved again in nitrobenzene-d_5 and heated at 80 °C, it was converted slowly to a covalent type species **7b** and no isomerization of **6b** back to **4b** was observed. The conversion from **6b** to **7b** was not completed, but an equilibrium between them was found (Scheme IV).

Figure 4 shows the ^{1}H NMR spectrum of an equilibrated mixture of **6b** with **7b**. The signals ascribed to the α-methylene protons of the pyrrolidinium ring of **6b** appear at δ 3.78 and 4.12, while the two α-methylene carbons of the pyrrolidinium ring give a single peak in its ^{13}C NMR spectrum at δ 61.9. These facts strongly support the rigid spiro-ammonium structure of **6b** because the splitting of the peaks in the ^{1}H NMR spectrum should be due to the shielding and deshielding effects of the carbonyl group: the two α-methylene protons located near the carbonyl group suffer the shielding effect due to the carbonyl π-electrons, and the peak ascribed to them appears at δ 3.78. The protons of the opposite side, in return, suffer the deshielding effect, and the peak ascribed to them appears at δ 4.12. A similar effect is also observed for the β-methylene protons to a lesser extent (δ 2.28 and 2.39). The equilibrium constant between **7b** and **6b** ([**7b**]/[**6b**]) at 35 °C was determined as 0.59 from the spectrum.

The 1:1 adduct between **1b** and benzyl chloride could not be isolated since the poorer electrophilicity of benzyl chloride required a higher temperature (80 °C) for the alkylation, which resulted in the formation of an oligomeric

Scheme III



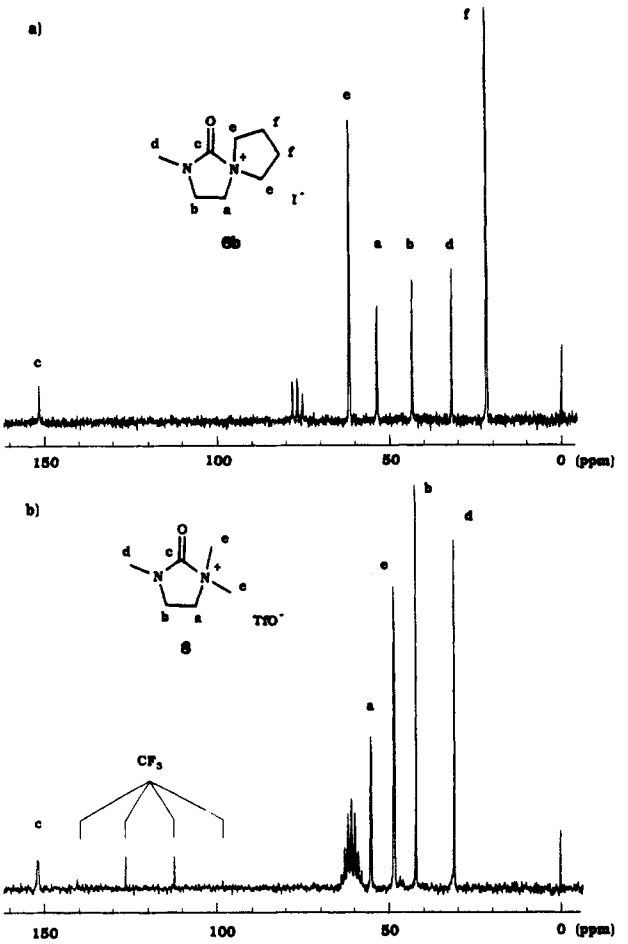


Figure 3. 22.6-MHz ^{13}C NMR spectra of **6b** (a) and **8** (b) (in $CDCl_3$/TMS).

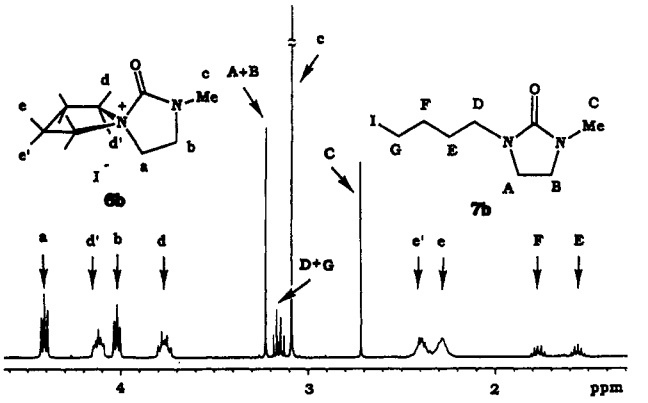
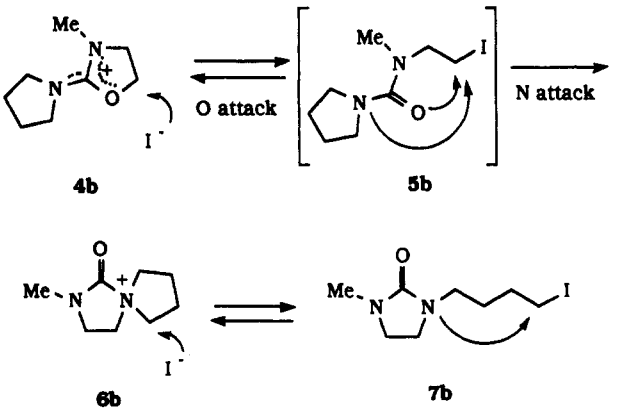


Figure 4. 400-MHz ^1H NMR spectrum of an equilibrated mixture of **6b** and **7b** (in $C_6D_5NO_2$/TMS, at 35 °C).

Scheme IV



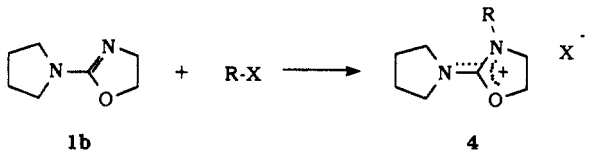
byproduct. However, the absence of ionic species in the resulting mixture was confirmed from ^1H NMR spectroscopy and, instead, the formation of covalent species, **5c** and **7c**, was suggested.

The isomerization from **4** to **6**, i.e., from an *O*-alkylated salt of urea to an *N*-alkylated one, is quite new not only in polymerization chemistry but also in organic chemistry.[15] However, an analogous isomerization of a kinetically preferred product to a thermodynamically favored one is known for the alkylation of a urethane.[16]

Polymerization Mechanism. Considering the above experimental results, the polymerization mechanisms of the present SIP and DIP are explained as follows. In all the present systems an oxazolinium salt species **4**, an *O*-alkylated salt of urea, is first formed by the reaction of the monomer with each of the initiators (Scheme V). With the sulfonate initiator, the nucleophilicity of the counteranion of **4**, tosylate or triflate, is so weak that **4** exists stably in the system and directly concerns the further

Scheme V

Initiation



1b 4

propagation. Hence, the propagation via the oxazolinium species secures the SIP process. However, when the counterion of the salt is sufficiently nucleophilic as in the case of halides, it catalyzes the rearrangement of the *O*-alkylated salt **4** to the *N*-alkylated salt **6** according to Scheme IV. First, the counteranion attacks the 5-position of **4** to give a covalent-type alkyl halide species **5** as an intermediate. This covalent species **5** is thermodynamically unfavorable when X = I or, perhaps, Br. Therefore, a major part of **5b** goes back to the oxazolinium salt **4b** by a nucleophilic attack of the oxygen atom. The existence of an equilibrium between **4b** and **5b** was not detected from the ^{1}H NMR measurement of **5b**, although a similar equilibrium has already been observed between an ionic oxazolinium salt and a covalent alkyl halide species.[17]

A minor part of **5b** converts to the *N*-alkylated salt of urea, **6b**, by the attack of the nitrogen atom. The resulting compound **6b** is considered to be more thermodynamically favorable than the corresponding *O*-alkylated salt, **4b**, because the C=O bond is generally stronger than the C=N bond. This salt **6b** is sufficiently electrophilic to suffer the attack of the counteranion or the monomer. Although **6b** possesses two electrophilic reaction sites, i.e., the α-positions of the pyrrolidinium ring and the α-methylene carbon of the diazolidinone ring, the attack of the counteranion exclusively occurs at the pyrrolidinium ring, and the covalent ethyleneurea species **7b** is generated selectively.

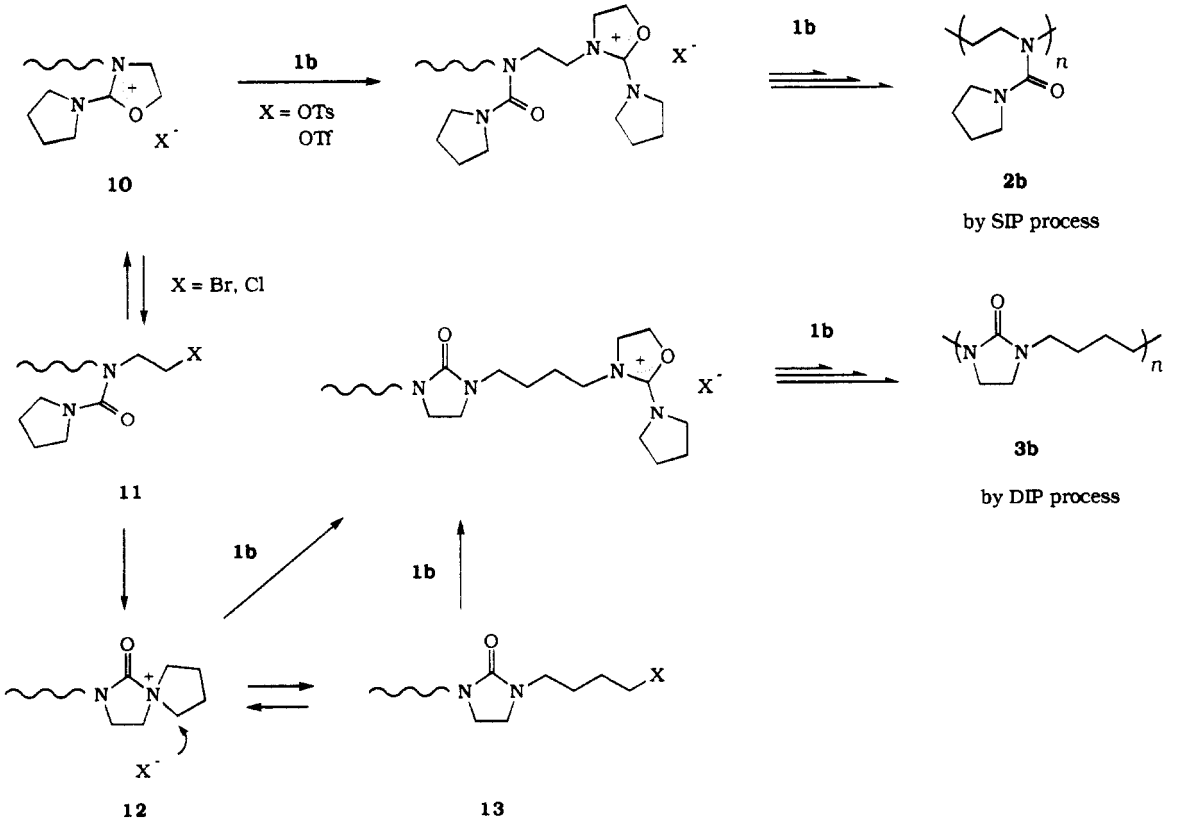
With benzyl chloride as the initiator, the formation of the corresponding covalent-type species **5c** is preferable since the chloride ion is more nucleophilic than the iodide ion in organic solvents and, moreover, its leaving ability is poor.[18] By the nucleophilic attack of the nitrogen atom, **5c** is isomerized to **6c**, which is also unstable and immediately converts to **7c**.

The propagating species in the DIP are considered to have analogous structures to the above 1:1 adducts, **4**–**7**. Each of them can react with the monomer to undergo the propagation. If the isomerization from the 4-like oxazolinium-type species, **10**, to the 6-like spiro-ammonium-type species, **12**, is fast enough, the propagation exclusively occurs via **12** or the 7-like covalent species, **13**, as in the case of the benzyl chloride or bromide initiator. Since alkyl chloride is less electrophilic than alkyl bromide, the DIP with benzyl chloride requires more severe conditions than for the DIP with benzyl bromide. With methyl iodide initiator, the propagation via **10** cannot be negligible because of the relatively low nucleophilicity and the high leaving ability of iodide anion, which results in the contamination of **2a** unit in the polymer.

Polymerization of 1c–f. The polymerizations of **1c–e** having six- to eight-membered cyclic imine rings also gave two types of polymers **2** and **3**. With MeOTs or MeOTf initiator, the polymerization of **1c–e** respectively gave poly{[*N*-(1-piperidinyl)carbonylimino]ethylene} (**2c**), poly{[*N*-(1-azepanyl)carbonylimino]ethylene} (**2d**), and poly{[*N*-(1-azocanyl)carbonylimino]ethylene} (**2e**) (Table IV). In these cases the yields of polymer were generally poor or, otherwise, the polymerization required more severe conditions than in the polymerization of **1b** due to the poorer nucleophilicities of these monomers: the α-hydrogens of the six- to eight-membered rings in these monomers will sterically disturb the nucleophilic attack of the nitrogen atom (vide infra).

Scheme VI

Propagation



10 11 12 13

Table IV. Single Isomerization Ring-Opening Polymerization of 1c–f[a]

run no.	monomer	initiator	[M]/[I]	temp, °C	time, h	polymer structure	polymer yield, %	polymer M_n[b]	polymer M_w/M_n[b]	polymer $M_{n,theor}$
1	1c	MeOTs	9.1	80	24	2c	39	520	1.32	580
2	1c	MeOTs	11.7	100	170	2c	44	880	1.26	790
3	1c	MeOTf	49.3	110	160	2c	76	1300	1.45	5810
4	1c	MeOTf	97.1	150	200	2c	44	3300	1.69	6620
5	1d	MeOTs	10.7	80	50	2d	60	1690	1.25	1110
6	1d	MeOTf	9.5	80	20	2d	90	1580	1.03	1470
7	1e	MeOTf	10.3	100	40	2e	77	2600	1.17	1480
8	1f	MeOTs	9.4	80	24	2f	86	470	1.30	1290
9	1f	MeOTs	36.7	100	200	2f	70	1200	1.52	4040
10	1f	MeOTf	50.7	120	50	2f	87	2100	1.57	6920

[a] In benzonitrile. [b] Determined by GPC with polystyrene standards.

Table V. Double Isomerization Polymerization of 1c–f[a]

run no.	monomer	initiator	[M]/[I]	temp, °C	time, h	polymer structure	polymer yield, %	polymer M_n[b]	polymer M_w/M_n[b]	polymer $M_{n,theor}$
1	1c	MeI	9.7	120	48	3c	99	2100	1.41	1620
2	1c	MeI	99.8	120	200	3c	27	1700	1.57	4300
3	1c	$PhCH_2Br$	94.5	150	200	3c	92	5200	1.66	13600
4	1d	MeI	9.5	80	40	3d	91	3440	1.22	1600
5	1e	$PhCH_2Br$	10.2	100	40	3e	88	3000	1.31	1670
6	1e	$PhCH_2Br$	53.4	100	40	3e	41	4900	1.48	4020
7	1e	MeI	9.5	100	40	3e	88	2900	1.30	1550
8	1e	MeI	51.4	100	40	3e	75	6100	1.55	7050
9	1f	MeI	10.1	120	120	3f	84	2000	1.48	1470

[a] In benzonitrile. [b] Determined by GPC with polystyrene standards.

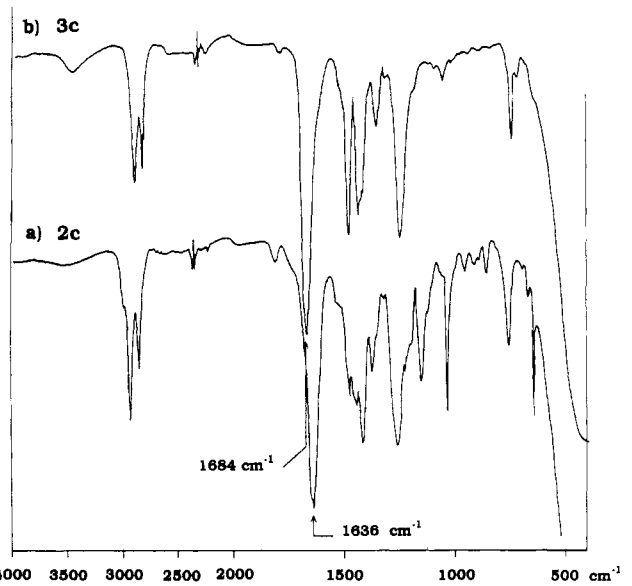


Figure 5. FT-IR spectra of 2c (a) and 3c (b).

The polymerization of 2-morpholino-2-oxazoline (**1f**) with the sulfonate initiator similarly gave a polymer of poly{[*N*-morpholino)carbonylimino]ethylene} (**2f**). The presence of the ether-type oxygen did not significantly influence the type of polymerization; nevertheless, it significantly decreases the basicity and, supposedly, nucleophilicity of 1.

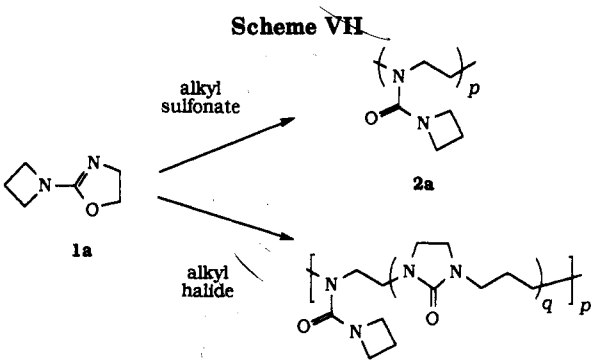
The polymerizations of these monomers **1c–f** with methyl iodide or benzyl bromide produced polymers of pure main-chain type, poly[(1,3-diazolidin-2-one-1,3-diyl)-oligomethylene]s (**3c–e**) and poly[oxyethylene(1,3-diazolidin-2-one-1,3-diyl)ethylene] (**3f**) (Table V). No contamination of **2** unit in the polymers was confirmed from IR and ^1H and ^{13}C NMR spectroscopies even in the runs with methyl iodide. For example, the carbonyl stretching band of **2c** appears at 1636 cm^{-1} while that of **3c** is observed at 1684 cm^{-1} in their IR spectra, which are shown in Figure 5. The comparison of these spectra clearly shows the homogeneous structure of **3c**. The frequencies of the carbonyl stretching band for these polymers are summarized in Table VI.

Table VI. Carbonyl Stretching Band Frequencies of Polymers 2 and 3

monomer	$\nu_{C=O}$, cm^{-1} 2	$\nu_{C=O}$, cm^{-1} 3
1a	1620 and 1685[a]	1685
1b	1622	1676
1c	1636	1684
1d	1628	1684
1e	1640	1680
1f	1640	1685

[a] Pure **2a** could not be prepared, but a polymer consisting of both units (**2a/3a**) was obtained.

Scheme VII



Polymerization of 1a. Among the 2-amino-2-oxazolines, the DIP of 2-(1-azetidinyl)-2-oxazoline (**1a**) did not proceed in the complete form. The SIP of **1a** with MeOTf proceeded smoothly at 80 °C and gave poly{[*N*-(1-azetidinyl)carbonylimino]ethylene} (**2a**) almost quantitatively in a similar manner. However, the polymerization of **1a** with benzyl bromide did not yield pure poly[(1,3-diazolidin-2-one-1,3-diyl)trimethylene] (**3a**) but produced a polymer consisting of both [*N*-(1-azetidinyl)carbonylimino]ethylene and (1,3-diazolidin-2-one-1,3-diyl)trimethylene units (**2a/3a**) whose ratio was determined from ^1H NMR spectroscopy (Scheme VII). The 90-MHz ^1H NMR spectrum of **2a/3a** is compared with that of **2a** in

Table VII. Polymerization of 2-(1-Azetidinyl)-2-oxazoline (1a)[a]

run no.	initiator	[M]/[I]	time, h	polymer: unit ratio 2a:3a	polymer: yield, %	polymer: M_n[b]	polymer: M_w/M_n[b]	$M_{n,theor}$
1	MeOTf	18.4	40	1:0	99	2400	1.52	2330
2	MeOTf	97.4	200	1:0	98	9600	1.75	12100
3	$PhCH_2Br$	19.7	40	0.23:0.77	99	2600	1.33	2630
4	$PhCH_2Br$	49.4	40	0.23:0.77	96	4700	1.53	6210
5	MeI	20.7	40	0.40:0.60	75	1900	1.37	2100

[a] In benzonitrile at 80 °C. [b] Determined by GPC with polystyrene standards.

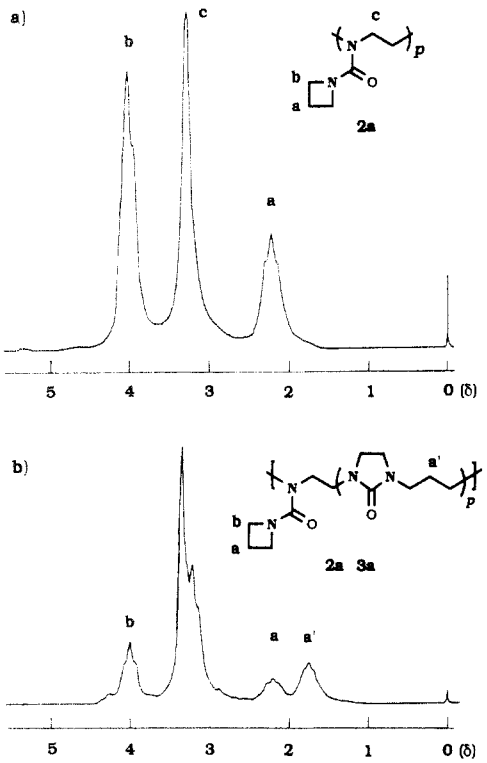


Figure 6. 90-MHz ^1H NMR spectra of 2a (a) and 2a/3a (b).

Figure 6. The peak at ca. δ 1.7 is ascribed to the β-protons of the trimethylene group in the 3a unit (a'), while the peak at ca. δ 2.2 is ascribed to the β-protons of the azetidine ring in the 2a unit (a). The unit ratio of 2a/3a was estimated from the integral ratio of these peaks. The peak at ca. δ 4.0 is due to the α-protons of the azetidine ring in the 2a unit (b). The mixed structure of 2a/3a was also confirmed form ^{13}C NMR and IR spectroscopies (see Experimental Section). The results of the polymerization of 1a are summarized in Table VII.

The polymerization mechanism for 1a, 1c, and 1d is considered to be intrinsically similar to that of 1b. But, as described above, the structure of the polymer of 1 with alkyl halide initiator strongly depends on the ring size of the cyclic imine unit in the monomer. It will be caused by the difference of the monomer nucleophilicity. The protons located at the α-position of the cyclic imine moiety in 1 sterically prevent the nucleophilic attack of the monomer, unless the small-membered ring structure keeps the α-methylene protons away from the imino nitrogen in the oxazoline ring as in the case of 1a and, to a lesser extent, in the case of 1b. The diverging point of the DIP from the SIP is the attack of the halide anion on the oxazolinium cation. In the 1a/benzyl bromide system, the nucleophilic attack of the bromide anion on the oxazolinium ion competes with the attack of 1a, which results in the contamination of 2a unit in the polymer. On the other hand, in the DIP of 1c and 1d, these monomers are supposed to be less nucleophilic than 1b and, hence, no attack of 1c and 1d on the oxazolinium ion proceeds even with the iodide counterion.

The difference among the required conditions for the polymerizations of 1 suggests the order of monomer nucleophilicity: The polymerization of 1c with benzyl bromide required 150 °C for the complete conversion while the polymerization of 1a with benzyl bromide proceeded readily even at 80 °C.

The present DIP has already been successfully applied to a bifunctional monomer, 1,4-bis(2-oxazolin-2-yl)piperazine, which yields a linear polyurea, poly[(1,3-diazolidin-2-one-1,3-diyl)ethylene].[19] Through these works, we could prepare the novel series of polymers of 1,3-diazolidin-2-one (ethyleneurea) connected by ethylene to heptamethylene bridges. These polymers may be considered as polymeric homologues of TMU or DMD and are expected to produce a new type of polyamines by hydrolysis. The DIP of six-membered cyclic pseudoureas also proceeded, which will be reported in a following paper.[20]

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