Polymer Journal, Vol. 27, No. 5, pp 469—480 (1995)

Preparation and Double Isomerization Polymerization of Substituted Cyclic Pseudoureas

Masatoshi MIYAMOTO,† Masakazu SHIMAKURA,* Satoshi SHIMODA,* and Kiyoshi HASEGAWA*

Department of Polymer Science and Engineering, Faculty of Textile Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan
** Department of Chemical and Biochemical Engineering, Faculty of Engineering, Toyama University, Gofuku, Toyama 930, Japan*

(Received June 9, 1994)

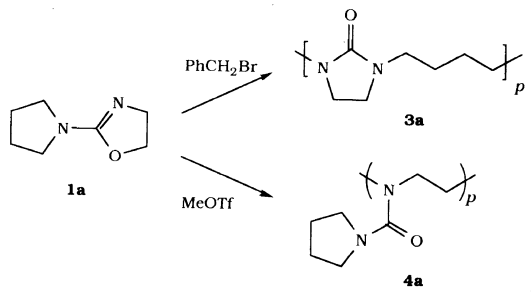
ABSTRACT: Four cyclic pseudoureas, 2-(2-isoindolinyl)-2-oxazoline (**1e**), 2-(1,2,3,4-tetrahydroisoquinolin-2-yl)-2-oxazoline (**1f**), 2-(1-indolinyl)-2-oxazoline (**1g**) and, 2-(1,3,3-trimethyl-6-azabicyclo[3.2.1]oct-6-yl)-2-oxazoline (**1i**) were newly prepared. The polymerization of these monomers with methyl trifluoromethanesulfonate gave poly[(*N*-carbamoylimino)ethylene]s (**4**), pendant-type polyureas. On the other hand, the double isomerization polymerization of **1e—g** with methyl iodide yielded main-chain-type polyureas, poly(1,3-diazolidin-2-one-1,3-diylalkylene)s (**3**). The polymerization of **1i** with alkyl halides, however, did not produce **3i**, but produced a polymer consisting of both **4i** (the main component) and **3i** units.

KEY WORDS Double Isomerization Polymerization / Cyclic Pseudoureas / 2-(2-Isoindolinyl)-2-oxazoline / Aromatic Polyureas /

The polymerization behavior of cyclic pseudoureas (**1**) is unique and interesting: although they have only one functional group, they give two quite different polymers from each other *via* cationic mechanisms.[1-4] For example, the polymerization of 2-(1-pyrrolidinyl)-2-oxazoline (**1a**) with benzyl bromide gives poly{(1,3-diazolidin-2-one-1,3-diyl)tetramethylene} (**3a**), which has urea groups in the main-chain, whereas that with methyl trifluoromethanesulfonate (triflate) (MeOTf) gives poly[{*N*-(1-pyrrolidinylcarbonyl)imino}ethylene] (**4a**), which has pendant urea groups.

. The formation of **3a** is due to the new mode of cationic ring-opening isomerization polymerization, "double isomerization polymerization" (DIP). Although it is well known that the polymerization of 2-oxazoline with either an alkyl halide or a sulfonate gives a **4a**-like polyamide, this DIP is unique to cyclic pseudoureas.[5] The propagation in the DIP process accompanies isomerization reactions of propagating species catalyzed by the halide anion.

In previous papers it has been clarified that completely different two types of polymers can be prepared from a series of cyclic pseudoureas



Scheme 1.

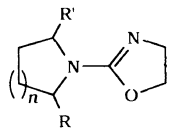
† To whom correspondence should be addressed.

having 5 to 8-membered simple cyclic imino ring as the 2-substituent of 2-oxazoline ring, *i.e.*, **1a**, 2-(1-piperidinyl)-2-oxazoline (**1b**) and their homologues.[1,2]

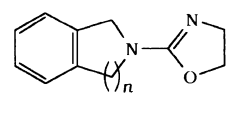
In the present paper we first describe the preparation of three types of substituted cyclic pseudoureas by the reactions of 2-ethoxy-2-oxazoline with a variety of cyclic imines: one is the monomer having a methyl substituent on the imino ring, 2-(2-methylpiperidin-1-yl)-2-oxazoline (**1c**), the second type has a phenylene group fused to the imino ring, *i.e.*, 2-(2-isoindolinyl)-2-oxazoline (**1e**), 2-(1,2,3,4-tetrahydroisoquinolin-2-yl)-2-oxazoline (**1f**), or 2-(1-indolinyl)-2-oxazoline (**1g**), and the third is the derivative of a bicyclic imine, 2-(1,3,3-trimethyl-6-azabicyclo[3.2.1]oct-6-yl)-2-oxazoline (**1i**).

Among these monomers **1c** could not be isolated as the pure form, but was obtained as the minor component of the mixture with 1-{2-(*N*-ethoxycarbonyl)aminoethyl}-2-methylpiperidine (**2c**). The examination on the preparation of 2-(2,6-dimethylpiperidin-1-yl)-2-oxazoline (**1d**) and 2-(1,2,3,4-tetrahydroquinolin-2-yl)-2-oxazoline (**1h**) by the reactions of 2-ethoxy-2-oxazoline with the corresponding imines failed, which produced urethane-type products.

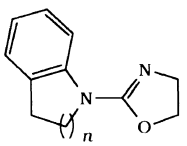
The two modes of cationic polymerizations of the monomers **1e—g** and **1i** were examined further to investigate the influence of these substituents.



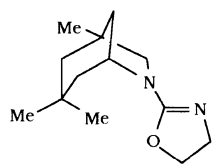
1a; R=R'=H, *n*=1
1b; R=R'=H, *n*=2
1c; R=Me, R'=H, *n*=2
1d; R=R'=Me, *n*=2



1e; *n*=1
1f; *n*=2



1g; *n*=1
1h; *n*=2



1i

EXPERIMENTAL

Materials

2-Ethoxy-2-oxazoline was prepared by the reaction of 2-oxazolidone with triethyloxonium tetrafluoroborate as described in the previous paper.[2] Isoindoline was prepared according to the literature.[6] 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-24B or a 90 MHz JEOL JNM-FX90Q NMR spectrometer. ^{13}C NMR spectra were recorded on a JEOL JNM-FX90Q NMR spectrometer operated at 22.6 MHz. IR spectra were obtained on a Jasco IR-810 infrared spectrometer. High resolution mass spectra were measured with a JEOL JMS-D300. GPC analysis was performed with a Shodex 880 system using a Shodex AC803 column in chloroform. GLC analysis was performed with a Shimadzu GC-8A system using a Silicone OV-1 column (3 m). Number-average molecular weights of the samples were measured by a vapor pressure osmometer (Corona Model 114) in chloroform at 35°C.

Typical Procedure for the Preparation of **1**

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 monohydrate (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 was purified further by distillation under reduced pressure. The reaction conditions as well as the yields and the

boiling (or melting) points of the products are summarized in Table I.

1e was prepared from isoindoline as white needles. ^{1}H NMR ($CDCl_3$): 3.7—3.9 (m, NCH_2, 2H), 4.3—4.5 (m, OCH_2, 2H), 4.73 (s, NCH_2Ar, 4H), 7.23 (br s, Ar, 4H). ^{13}C NMR ($CDCl_3$): 53.1 (NCH_2CH_2), 53.3 (NCH_2Ar), 68.7 (OCH_2), 122.5, 127.2, and 137.1 (Ar), 160.5 (C=N). IR (KBr): 3010 (ν_{C-H}), 1655 ($\nu_{C=N}$), 1590, 1445, 760 (δ_{C-H}) cm^{-1}. Mass: *m/z* 188 (M^+), 160, 144, 118, 90. Exact mass: *m/z* 188.0953 (calcd for $C_{11}H_{12}N_2O$, *m/z* 188.0950).

1f was prepared from 1,2,3,4-tetrahydroisoquinoline as transparent liquid. ^{1}H NMR ($CDCl_3$): 2.87 (t, J=6.3 Hz, $ArCH_2CH_2$, 2H), 3.65 (t, J=6.2 Hz, NCH_2CH_2Ar, 2H), 3.7—3.9 (m, NCH_2CH_2O, 2H), 4.2—4.4 (m, OCH_2, 2H), 4.6 (s, NCH_2Ar, 2H), 7.1 (br s, Ar, 4H). ^{13}C NMR ($CDCl_3$): 28.6 ($ArCH_2CH_2$), 43.1 (NCH_2CH_2Ar), 47.4 (NCH_2Ar), 52.9 (NCH_2CH_2O), 68.4 (OCH_2), 126.2, 126.3, 126.4, 128.7, 133.4, and 134.4 (Ar), 162.0 (C=N). IR (neat): 3045, 3005, 2895, 2850, 1650 ($\nu_{C=N}$), 1580, 1424, 1298, 1232, 990, 930, 750 (γ_{C-H}) cm^{-1}. Mass: *m/z* 202 (M^+), 187, 132, 104. Exact mass: *m/z* 202.1106 (calcd for $C_{12}H_{14}N_2O$, *m/z* 202.1106).

1g was prepared from indoline as transparent liquid. ^{1}H NMR ($CDCl_3$): 3.12 (t, J=8.5 Hz, NCH_2CH_2Ar, 2H), 3.8—4.1 (m, NCH_2, 4H), 4.3—4.5 (m, OCH_2, 2H), 6.8—7.7 (Ar). ^{13}C NMR ($CDCl_3$): 27.8 (NCH_2CH_2), 49.0 (NCH_2CH_2), 52.9 (NCH_2), 68.2 (OCH_2), 113.5, 121.4, 124.6, 127.4, 130.6, 143.3 (Ar), 158.3 (C=N). IR (KBr): 3070, 2900, 2860 (ν_{C-H}), 1660 ($\nu_{C=N}$), 1595, 1495 ($\nu_{C=C}$), 1430, 1010, 750 (γ_{C-H}) cm^{-1}. Mass: *m/z* 188 (M^+), 118, 91, 70. Exact mass: *m/z* 188.0949 (calcd for $C_{11}H_{12}N_3O$, *m/z* 188.0950).

1i was prepared from 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane as transparent liquid. ^{1}H NMR ($CDCl_3$): 0.9—1.2 (m, CH_3, 9H), 1.3—2.2 (m, CCH_2C, 6H), 3.2—3.4 (m, NCH_2CH, 2H), 3.7—3.9 (m, NCH_2, 2H), 4.2—4.4 (m, OCH_2 and CH, 3H). ^{13}C NMR ($CDCl_3$): 24.9, 29.9 ($C(CH_3)_2$), 31.5, 36.5, 39.4 (CCH_3), 42.4 ($C(CH_3)CH_2C(CH_3)_2$), 44.2 ($(CH_3)_2CCH_2CH$), 51.9 ($CHCH_2CH$), 53.0 (NCH_2), 56.8 (NCH), 57.4 (NCH_2CCH_3), 68.2 (OCH_2), 167.3 (C=N). IR (neat): 2945, 2860, 1660 ($\nu_{C=N}$), 1435, 1068, 940 cm^{-1}. Mass: *m/z* 222 (M^+), 166, 151, 99, 87. Exact mass: *m/z* 222.1732 (calcd for $C_{13}H_{22}N_2O$, *m/z*= 222.1732).

The reaction of 2-methylpiperidine with 2-ethoxy-2-oxazoline at 120°C and the subsequent workup gave a mixture (1:9 from GLC) of **1c** and **2c**, each of which was identified by GC-MS. Other spectroscopic data could be obtained only for the major product, **2c**.

1c. IR (a mixture with **2c**, neat): 1665 ($\nu_{C=N}$) cm^{-1}. Mass: *m/z* 168 (M^+), 153, 113, 99, 97.

2c. ^{1}H NMR ($CDCl_3$): 1.03 (d, J=6.0 Hz, $CHCH_3$, 3H), 1.26 (t, J=7.0 Hz, CH_2CH_3, 3H), 1.4—1.7 (m, $CCH_2CH_2CH_2C$, 6H), 2.0—2.4 (m, $CHNCH_2CC$, 3H), 2.7—2.9 (m, $CONCH_2CH_2$, 2H), 3.1—3.3 (m, $CONCH_2$, 2H), 4.09 (q, J=7.0 Hz, OCH_2, 2H), 5.1 (br s, NH, 1H). IR (neat), 3330 (ν_{N-H}), 2935 (ν_{C-H}), 1705 ($\nu_{C=O}$), 1535, 1260, 1140, 1038 cm^{-1}. Mass: *m/z* 214 (M^+), 214, 199, 169, 153, 113, 84.

The reactions of 2,6-dimethylpiperidine and 1,2,3,4-tetrahydroquinoline with 2-ethoxy-2-oxazoline exclusively gave urethanes.

1-{2-(*N*-Ethoxycarbonyl)aminoethyl}-2,6-dimethylpiperidine (**2d**) from 2,6-dimethylpiperidine. ^{1}H NMR ($CDCl_3$): 1.15 (d, J=6.3 Hz, $CHCH_3$, 6H), 1.24 (t, J=7.0 Hz, CH_2CH_3, 3H), 1.4—1.7 (m, $CCH_2CH_2CH_2C$, 6H), 2.3—2.5 (m, NCH, 2H), 2.6—2.8 (m, $CONCH_2CH_2$, 2H), 3.0—3.3 (m, $CONCH_2$, 2H), 4.06 (q, J=7.0 Hz, OCH_2, 2H), 5.0 (br s, NH, 1H). IR (neat): 3330 (ν_{N-H}), 2925 (ν_{C-H}), 1710 ($\nu_{C=O}$), 1535, 1250, 1140, 1038, 945 cm^{-1}. Mass: *m/z* 228 (M^+), 213, 167, 126, 113, 58.

1-{2-(*N*-Ethoxycarbonyl)aminoethyl}-1,2,3,4-tetrahydroquinoline (**2h**) from 1,2,3,4-tetrahydroquinoline. ^{1}H NMR ($CDCl_3$): 1.25 (t, J=7.0 Hz, CH_3, 3H), 1.9—2.4 (m, $ArCH_2CH_2$, 4H), 2.9 (t, J=6.3 Hz, $ArNCH_2$,

4H), 3.3—3.5 (m, $CONCH_2CH_2O$, 4H), 6.5—7.2 (m, Ar, 4H).

Typical Procedure for the Double Isomerization Polymerization of **1**

In a test tube equipped with a magnetic stirrer bar and a three-way stopcock were placed 0.565 g (3.00 mmol) of **1e** and 2 ml of benzonitrile under nitrogen. To the solution was added 21.1 mg (0.149 mmol) of methyl iodide with stirring. The tube was sealed and allowed to react at 100°C for 40 h. The produced polymer, poly[1,3-diazolidin-2-one-1,3-diylmethylene-1,2-phenylene-methylene] (**3e**) was isolated by precipitation from an equivolume mixture of diethyl ether with hexane, purified further by repeated reprecipitation from dichloromethane to the diethyl ether-hexane mixture, and dried *in vacuo*. The yield was 0.525 g (93%).

3e. IR (film): 3020, 2860, 1690 ($\nu_{C=O}$), 1495, 1450, 1240, 1220, 760, 670 cm^{-1}. ^1H NMR (DMSO-d_6) 3.0—3.2 (4H, NCH_2CH_2), 4.3—4.5 (4H, NCH_2Ar), 7.1—7.3 (4H, Ar). ^{13}C NMR (DMSO-d_6): 41.9 (NCCN), 44.6 (NCAr), 127.2, 128.3, and 135.5 (respectively the 4, 3, and 1 positions of Ar), 160.0 (CO).

Poly[1,3-diazolidin-2-one-1,3-diylmethylene-1,2-phenylene-ethylene] (**3f**). IR (film): 3015, 2860, 1690 ($\nu_{C=O}$), 1492, 1218, 750, 665 cm^{-1}. ^1H NMR ($CDCl_3$): 2.7—3.0 (2H, CH_2Ar), 3.1—3.8 (6H, NCH_2CH_2), 4.3—4.6 (2H, NCH_2Ar), 7.1—7.5 (4H, Ar). ^{13}C NMR: 30.7—31.5 (ArCC), 42.6, 43.3, 45.4, and 46.4 (CNCO), 126.2—126.6, 127.8, 129.1—139.5, 130.3, 135.1, and 137.9 (aromatic carbons), 160.6 (CO).

Poly[1,3-diazolidin-2-one-1,3-diyl-1,2-phenylene-ethylene] (**3g**). IR (film): 3020, 2870, 1695 ($\nu_{C=O}$), 1600, 1485, 1220, 750 cm^{-1}. ^1H NMR: 2.7—3.0 (2H, $ArCH_2$), 3.2—3.8 (6H, NCH_2), 6.7—7.9 (4H, Ar).

Ring-Opening Isomerization Polymerization of **1**

The polymerization was carried out by using methyl triflate according to a similar procedure to that described above.

Poly[{*N*-(1-isoindolinyl)carbonylimino}ethylene] (**4e**). IR (film): 3020, 2870, 1630 ($\nu_{C=O}$), 1420, 1220, 760 cm^{-1}. ^1H NMR (DMSO-d_6): 3.1—3.5 (NCH_2CH_2N), 4.4—4.8 (NCH_2Ar), 6.8—7.4 (Ar).

Poly[{*N*-(1,2,3,4-tetrahydroisoquinolin-2-yl)carbonylimino}ethylene] (**4f**). IR (film): 3010, 1638 ($\nu_{C=O}$), 1420, 1218, 750, 668 cm^{-1}. ^1H NMR ($CDCl_3$): 2.5—2.9 (2H, CH_2Ar), 3.0—3.7 (6H, NCH_2CH_2), 4.0—4.4 (2H, NCH_2Ar), 6.8—7.2 (4H, Ar). ^{13}C NMR ($CDCl_3$): 38—39 (ArCC), 41—44, 45—50, 126—129, 133.6, and 134.4 (aromatic carbons), 164.0 (CO).

Poly[{*N*-(1-indolinyl)carbonylimino}ethylene] (**4g**). IR (film): 3010, 2950, 1650 ($\nu_{C=O}$), 1602, 1480, 1415, 1220, 750 cm^{-1}. ^1H NMR ($CDCl_3$): 2.6—2.9 (2H, CH_2Ar), 3.2—3.5 (4H, NCH_2CH_2N), 3.5—3.9 (2H, NCH_2CH_2Ar), 6.6—7.8 (4H, Ar).

Poly{(*N*-(1,3,3-trimethyl-6-azabicyclo-[3.2.1]oct-6-yl)carbonylimino}ethylene] (**4i**). IR (neat): 2948, 2860, 1630 ($\nu_{C=O}$), 1415, 800, 638 cm^{-1}. ^1H NMR ($CDCl_3$): 0.9—1.1 (9H, CH_3), 1.2—1.8 (6H, CCH_2C), 3.0—3.4 (6H, CH_2N), 4.0—4.3 (1H, CH).

RESULTS AND DISCUSSION

Preparation of **1**

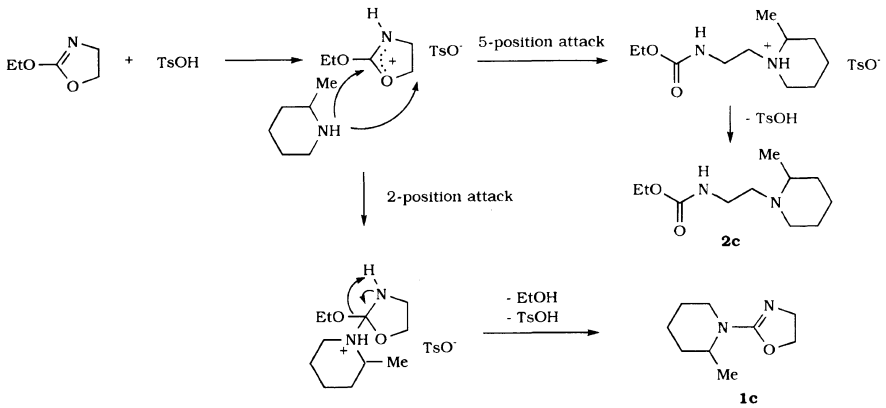
In a previous paper we described that cyclic pseudoureas can easily be prepared by the condensation reactions of unsubstituted cyclic imines with 2-ethoxy-2-oxazoline.[2] The condensation readily proceeded in refluxing benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid. However, the present work revealed that the presence of the substituent on the cyclic imine strongly influenced on this condensation.

As described in the previous paper, the condensation of pyrrolidine or piperidine with 2-ethoxy-2-oxazoline completed within 2 h in refluxing benzene (Table I).[2] When a sterically

Table I. Preparation of cyclic pseudoureas[a]

Amine	Solvent	Temp	Time	Product	Yield	bp[b]	mp
		°C	h		%	°C mmHg^{-1}	°C
Pyrrolidine	Benzene	Reflux	1	**1a**[c]	69	83/5.0	32
Piperidine	Benzene	Reflux	2	**1b**[c]	70	76/2.6	
2-Methylpiperidine	Mesitylene	120	16	**2c**[d]	12	~100/1.0	
2,6-Dimethylpiperidine	Mesitylene	Reflux	23	**2d**	5	110/1.0	
Isoindoline	Benzene	Reflux	1	**1e**	70		124.9—126.2
1,2,3,4-Tetrahydro-isoquinoline	Benzene	Reflux	3	**1f**	67	131/0.8	
Indoline	Benzene	Reflux	10	**1g**	28	142/2.3	67.1—68.0
1,2,3,4-Tetrahydro-quinoline	Benzene	Reflux	66	**2h**	20	74/1.5	
1,3,3-Trimethyl-6-aza-bicyclo[3.2.1]octane	Benzene	Reflux	6	**1i**	30	120/4.0	

[a] With 1% of *p*-toluenesulfonic acid. [b] Distilled with a Kügel-röhr. [c] From ref 2. [d] Obtained as a mixture with **1c** (10 mol%).



Scheme 2.

hindered imine, 2-methylpiperidine, was employed, the condensation with 2-ethoxy-2-oxazoline required a severer condition: no reaction proceeded in refluxing benzene and the slow consumption of the starting materials was observed at 120°C in mesitylene. Vacuum distillation using a Kügel-röhr gave a mixture of two products, and the spectroscopic analyses showed that they were 2-(2-methylpiperidin-1-yl)-2-oxazoline (**1c**) and a urethane, 1-{2-(*N*-ethoxycarbonyl)aminoethyl}-2-methylpiperidine (**2c**), whose yields were 1.3 and 11.7%, respectively.

The formation of urethane is explained as follows (Scheme 2). In this acid-catalyzed condensation, the protonated species of 2-ethoxy-2-oxazoline, 2-ethoxy-2-oxazolinium *p*-toluenesulfonate, is considered to be the key compound. The attack of the imine to the 2-position of the oxazolinium ion and the subsequent elimination of ethanol yield **1c**. However, this route is unfavorable in the present case due to the steric interaction between the two substrates and, instead, the 5-position attack of the imine occurs relatively slowly, which results in the formation of **2c**.

The introduction of one more methyl group to the other adjacent carbon to the nitrogen

atom in the piperidine ring completely prohibited the 2-attack: the reaction of 2,6-dimethylpiperidine with 2-ethoxy-2-oxazoline gave 1-{2-(*N*-ethoxycarbonyl)aminoethyl}-2,6-dimethylpiperidine **2d** as the only product. In this case the condensation did not proceed even at 120°C, but occurred slowly in refluxing mesitylene (bp 180°C).

As for aniline-type cyclic imines, a similar steric effect of substituent was observed. When 1,2,3,4-tetrahydroquinoline was employed for the condensation, a urethane-type product **2h** was selectively produced. On the other hand, 2-(1-indolinyl)-2-oxazoline **1g** could be prepared successfully from indoline and 2-ethoxy-2-oxazoline, although the preparation required a longer reaction time than that for **1a** or **1b**. Obviously, the five-membered structure of indoline reduces the steric crowdedness around the nitrogen atom.

The condensations of 2-ethoxy-2-oxazoline with non-aniline-type aromatic imines, isoindoline and 1,2,3,4-tetrahydroisoquinoline, proceeded smoothly in refluxing benzene, completed within 3 h, and selectively yielded cyclic pseudoureas, 2-(2-isoindolinyl)-2-oxazoline (**1e**) and 2-(1,2,3,4-tetrahydroisoquinolin-2-yl)-2-oxazoline (**1f**), respectively.

When a bicyclic amine having a methylene bridge at the α-position of the nitrogen, 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane was employed for the reaction, the condensation proceeded relatively easily and 2-(1,3,3-trimethyl-6-azabicyclo[3.2.1]oct-6-yl)-2-oxazoline (**1i**) was obtained in 30% yield. In this case the 5-membered bicyclic structure of this imine is also considered to reduce the steric hindrance around the nitrogen atom.

Thus, five cyclic pseudoureas were newly prepared. The polymerization of these monomers except **1c** was examined further.

Polymerization of **1e**

Table II shows the results for the two types of the cationic polymerizations of **1e**. The polymerization of **1e** with methyl iodide proceeded smoothly at 100°C in benzonitrile or dimethyl formamide (DMF) and yielded a polymeric product in a high yield. The system was homogeneous during the polymerization. The resulting polymer was pale brown solid and soluble in dichloromethane, chloroform, dimethyl sulfoxide (DMSO), and the solvents for the polymerization.

The polymerization of **1e** with methyl triflate in DMF or nitrobenzene also proceeded smoothly at 100°C. However, the polymerization systems became heterogeneous. When benzonitrile was chosen as the solvent the system gelled during the polymerization. In DMF the produce polymer was precipitated out from the reaction medium according to the progress of the reaction. The resulting polymer was white powder and insoluble in di-

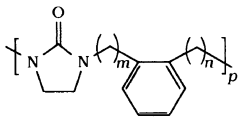
Table II. Polymerization of **1e**

Initiator	Solvent[d]	[M]/[I]	Temp / °C	Time / h	Polymer				
					Structure	Yield / %	M_n[a] (VPO)	M_n[b] (GPC)	M_w/M_n[b] (GPC)
MeI	PhCN	20.2	100	40	**3e**	93	2500	1100	1.35
MeI	DMF	15.8	100	40	**3e**	94	5100	4100	1.47
MeI	DMF	96.4	120	200	**3e**	98	8300	7700	1.37
MeOTf	PhCN	20.3	100	40	**4e**	93	—	1500[c]	1.49[c]
MeOTf	DMF	18.9	100	40	**4e**	53	4000[c]	1500[c]	1.51[c]
MeOTf	DMF	97.4	120	200	**4e**	59	—	1500[c]	1.44[c]

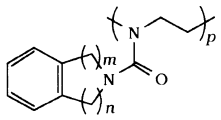
[a] Determined by VPO. [b] Determined by GPC with polystyrene standards. [c] Molecular weights of $CHCl_3$ soluble parts. [d] DMF, dimethyl sulfoxide.

chloromethane, DMF, methanol, acetone, diethyl ether, and hexane and partly soluble in chloroform or DMSO: the values of the molecular weight shown in Table II were those for the chloroform soluble parts. This different solubility indicates that both polymers are completely different in structure from each other.

The structure of the product prepared with methyl iodide was identified as poly[1,3-diazolidin-2-one-1,3-diylmethylene-1,2-phenylene-methylene] (**3e**) from the IR and ^{1}H NMR spectroscopies, while that with methyl triflate was poly[{N-(1-isoindolinyl)carbonyl-imino}ethylene] (**4e**).



3e; m=n=1
3f; m=1, n=2
3g; m=0, n=2



4e; m=n=1
4f; m=1, n=2
4g; m=0, n=2

The structural difference between them was most clearly indicated by the IR spectroscopy since the C=O carbonyl stretching frequency of a 5-membered cyclic urea was higher than that of its linear homologue.[7] Figure 1 shows the IR spectra of **3e** (Figure 1a) and **4e** (Figure 1b). The C=O stretching band of **3e** appears at 1690 cm^{-1}, whereas that of **4e** appears at 1630 cm^{-1}.

In the 90-MHz ^{1}H NMR spectra of **3e** and **4e** (Figure 2), the peak ascribed to the methylene protons of the ethyleneurea ring in **3e** appears at δ 3.1 while that of the main chain methylenes of **4e** is observed at δ 3.3, which also supports the structural difference between **3e** and **4e**.

The polymerization mechanism for **1a** was investigated in the preceding paper, which is also applicable to the polymerization of **1e** (Schemes 3 and 4).[2,3] The initially formed propagating species in both polymerizations are oxazolinium salts, 3-methyl-2-(2-isoindoli-

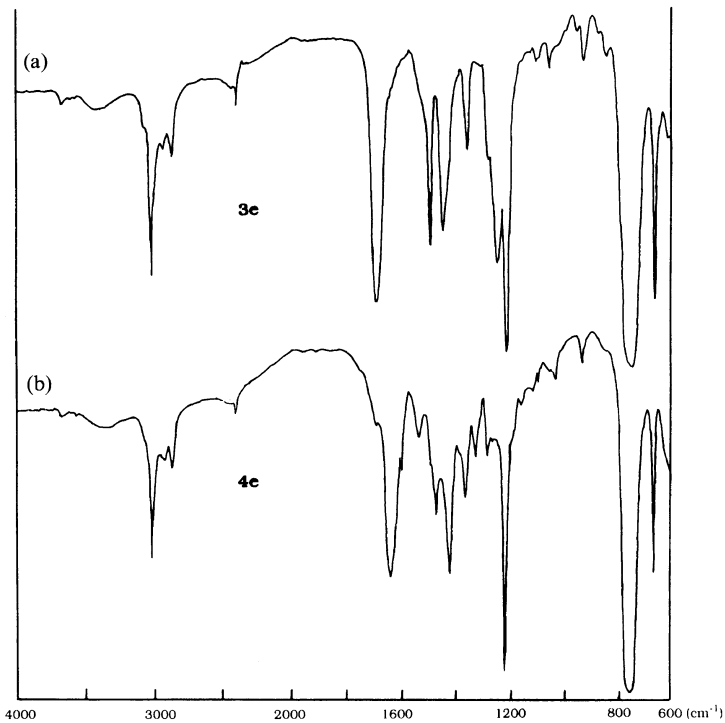


Figure 1. IR spectra of **3e** (a) and **4e** (b).

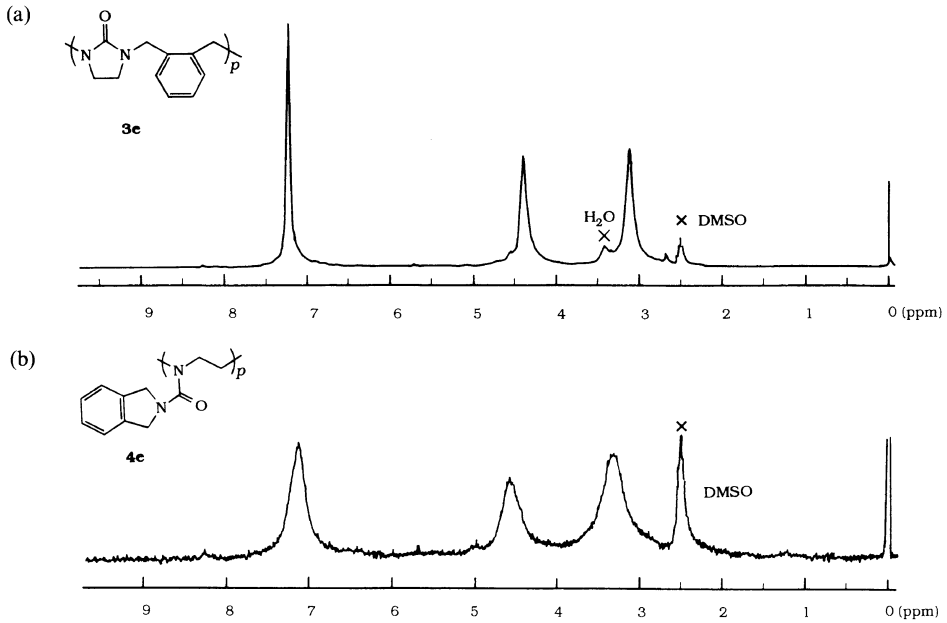
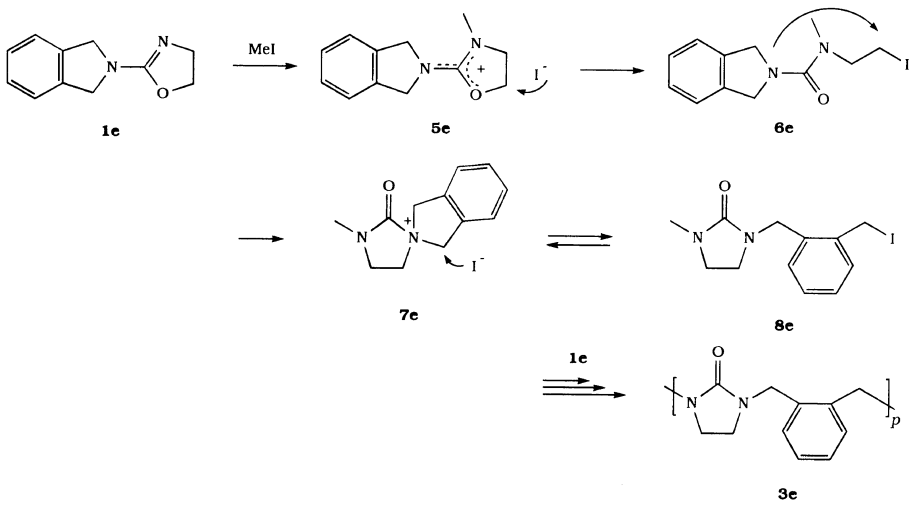
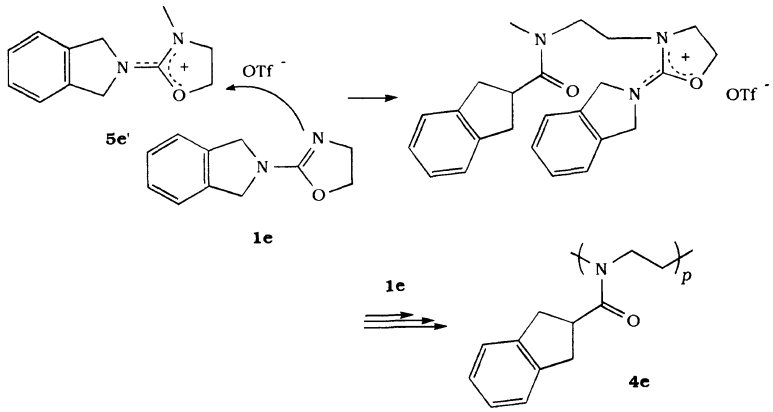


Figure2. 90 MHz ^{1}H NMR spectra of **3e** (a) and **4e** (b) (in DMSO-d_6).



Scheme 3.

nyl)-2-oxazolinium iodide (**5e**) and triflate (**5e'**). In the DIP, the counteranion of **5e**, the iodide anion, is nucleophilic and it catalyzes the isomerization of **5e** to a covalent species **8e** *via* a spiro-ammonium species **7e**. Namely, the counter anion attacks the 5-position of **5e** to give a covalent type alkyl halide species **6e**, which isomerizes further to **7e**. This ionic species **7e** is electrophilic enough to accept the attack of the counter anion and it isomerizes again to another covalent species **8e**. The propagation from **7e** or **8e** results in the formation of the **3e** unit (the main-chain-type unit) (Scheme 3).



Scheme 4.

With methyl triflate initiator, on the other hand, the oxazolinium species **5e'** is stable due to the poor nucleophilicity of counteranion and directly concerns the propagation, which generates the **4e** unit (the pendant-type unit) (Scheme 4).

It is noteworthy that **1e** has a greater tendency to the DIP than that of **1a**: when **1a** was employed as the monomer, the polymerization with methyl iodide did not produce the pure main-chain-type polymer, but gave a polymer consisting of both main-chain and pendant type units, while that with benzyl bromide or chloride gave the pure main-chain-type polymer. It is due to the poorer nucleophilicity of the iodide anion in organic media.[2] In the present case, however, the electrophilic sites of **5e** are the benzyl carbons and they readily accept the attack of the iodide anion, which leads to the selective formation of **3e**.

Polymerization of **1f** *and* **1g**

The polymerization of **1f** with either methyl iodide or methyl triflate in benzonitrile proceeded homogeneously. The polymerization with methyl iodide gave a main-chain-type polyurea, **3f**, whereas that with methyl triflate gave a pendant type one, **4f**, in a similar manner. The yield of **3f** was quantitative and its molecular weight increased as increasing the monomer to initiator ratio, although its number-average molecular weight determined by VPO was generally lower than the value calculated from the feed ratio.

Since the spiro-ammonium-type cationic propagating species possesses two reaction sites, two structures were possible for the **3f** unit, which were hardly distinguished from each other (Scheme 5). The relatively complicated ^{13}C NMR spectrum of **3f** suggested the existence of both the two units in **3f**, although the exact assignment of the peaks could not be achieved.

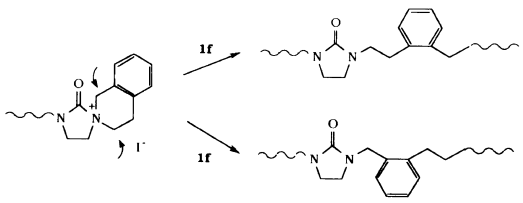
The yield of **4f** was generally lower than that of **3f** prepared under the same condition and depended on the feed ratio, which suggests a lower rate of polymerization. The yield increased to 95% when the polymerization was carried out at 120°C for 100 h. The chain transfer seems to occur frequently in the isomerization ring-opening polymerization of **1f** as far as judging from the molecular weight.

The polymerization of **1g** also proceeded in a similar manner and **3g** and **4g** were obtained by the polymerizations with methyl iodide and triflate, respectively. The yields of **3g** were not so high, nevertheless the DIP of **1g** required a severer condition, at 120°C for 100 h, than those for **1e** and **1f**. This low reactivity of **1g** to the DIP will be due to the lack of the reactive benzyl-type methylene group in its structure.

Table III. Polymerization of **1f** and **1g**[a]

Monomer	Initiator	[M]/[I]	Temp / °C	Time / h	Polymer				
					Structure	Yield / %	M_n[a] (VPO)	M_n[b] (GPC)	M_w/M_n[b] (GPC)
1f	MeI	21.2	100	40	**3f**	99	3800	4100	1.42
1f	MeI	53.3	100	40	**3f**	100	6900	5700	1.45
1f	MeI	109	100	40	**3f**	100	11000	6800	1.42
1f	MeOTf	21.5	100	40	**4f**	92	2200	2400	1.43
1f	MeOTf	48.2	100	40	**4f**	91	3500	2300	1.99
1f	MeOTf	97.6	100	40	**4f**	46	2800	1500	1.81
1f	MeOTf	96.0	120	100	**4f**	95	4000	3100	1.74
1g	MeI	19.0	120	100	**3g**	87	2600	1100	1.38
1g	MeI	49.1	120	100	**3g**	86	1700	900	1.36
1g	MeI	101	120	100	**3g**	77	1700	580	1.40
1g	MeOTf	20.3	100	40	**4g**	100	2800	940	1.32
1g	MeOTf	47.6	100	40	**4g**	99	3500	2200	1.38
1g	MeOTf	102	100	40	**4g**	96	4200	3000	1.58

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



Scheme 5.

Polymerization of **1i**

The polymers prepared from **1**, *e.g.*, **3a** or **4a**, can be considered as the polymeric homologue of urea-type organic solvents, *i.e.*, *N*,*N*′-dimethylethyleneurea and *N*,*N*,*N*′,*N*′-tetramethylurea (TMU). The latter is miscible in any proportion not only with water but with all common solvents, even aliphatic hydrocarbons such as hexane.[8] However, the solubility of either **3a** or **4a** was rather limited, perhaps, due to their high crystallinity.

The polymerization of **1i** with methyl triflate gave a viscous liquid polymer (Table IV). It was soluble in water and in most common organic solvents, even hexane. This high solubility is not a surprise when one considers the above high miscibility of TMU. Therefore, this polymer could not be isolated by reprecipitation. After the polymerization, the solvent—acetonitrile was used due to its low boiling point—and the remaining monomer was evaporated and the resulting crude polymer was directly subjected to the spectroscopic and GPC analyses. The IR spectroscopy showed the structure of the polymer was pendant type, **4i**.

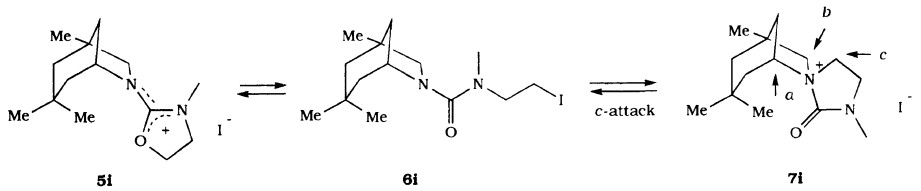
The polymerization of **1i** with methyl iodide did not produce the main-chain-type polymer **3i**, but gave a polymer consisting of both main-chain-type and pendant-type units (the main component, >90%), whose composition was roughly estimated from the IR spectroscopy. Neither benzyl bromide nor chloride could produce the main-chain-type polymer and the composition of the produced polymer was independent of the kind of halide ion derived from the initiator. These results indicated that the polymer structure is not determined by the step from **5i** to **6i**, since if the attack of monomer competes to that of the counter anion, the pendant unit content must be reduced as the counter anion changes from I to Br and, then, Cl (Scheme 6).

The formation of the pendant-type unit is

Table IV. Cationic isomerization polymerization of **1i**[a]

Initiator	[M]/[I]	Polymer			
		Yield	Unit type[c]	M_n[b]	M_w/M_n[b]
			%		
MeOTf	20	100	Pendant	1500	1.26
MeI	16	100	Pendant Rich	920	1.57
$PhCH_2Br$	19	91	Pendant Rich	1400	1.22
$PhCH_2Cl$	9.3	50	Pendant Rich	780	1.23

[a] The polymerization was carried out in acetonitrile at 100°C for 24 h. [b] Determined by GPC with polystyrene standards. [c] Estimated by IR.



5i **6i** **7i**

Scheme 6.

explained as follows. The first formed oxazolinium species changes into a spiroammonium species **7i** by the halide-catalyzed isomerization. This compound possesses three reaction sites, which is indicated in Scheme 6. In the DIP the halide ion or the monomer attacks the "a" or "b" position, which results in the formation of the main-chain-type unit. However, in the present case, the "a" position is secondary and the "b" position is covered by the methyl and methylene substituents attached to the adjacent position. Therefore, the monomer is forced to attack the remaining "c" position, which produces the pendant type unit.

The polymer prepared with the alkyl halide had a similar solubility to the pure **4i**. It is soluble from hexane to water, although the solubility to hexane was not so high. When the polymer was fractionated from hexane, the molecular weight of the hexane-insoluble part (25% recovery, $M_n=660$) was lower than that before the treatment (1400). It indicates that the high solubility of the polymer is not due to its relatively low molecular weight.

These results show the polymerization of cyclic pseudourea is sensitive to its substituent and the introduction of substituent to the α-position of cyclic imino ring strongly reduces the tendency to the DIP.

By these experiments the polymers having different solubility were prepared. The examination on the physical property of these polymers is now in progress.

REFERENCES

1. M. Miyamoto, K. Aoi, S. Yamaga, and T. Saegusa, *Macromolecules*, **25**, 5111 (1992).
2. M. Miyamoto, M. Shimakura, K. Tsutsui, K. Hasegawa, K. Aoi, S. Yamaga, and T. Saegusa, *Macromolecules*, **26**, 7716 (1993).
3. M. Miyamoto, M. Morimoto, and T. Saegusa, *Polym. J.*, **25**, 1133 (1993).
4. M. Miyamoto, H. Amii, K. Aoi, and T. Saegusa, *Macromolecules*, **26**, 1474 (1993).
5. For the polymerization of 2-alkyl- and 2-aryl-2-oxazolines, for example, see: (a) S. Kobayashi and T. Saegusa, "Ring-Opening Polymerization," Vol. 2, Elsevier Applied Science Publishers, New York, 1985, Chapter 11. b) S. Kobayashi, *Prog. Polym. Sci.*, **15**, 751 (1990).
6. J. Bornstein, J. E. Shields, and A. P. Boisselle,

"Organic Synthesis," Coll. Vol. 5, John Wiley & Sons, New York, 1973, p 406.
7. K. Nakanishi, "Infrared Absorption Spectroscopy-Practical," Holden-Day, San Francisco and Nankodo Company Ltd., Tokyo, 1962, Chapter 2.
8. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, John Wiley & Sons, New York, N.Y., 1967.