Double Isomerization Polymerization of Bispseudoureas: A New Cyclopolymerization

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Introduction

Monomers having two or more polymerizable functional groups, divinylbenzene as the most common example, are often used as cross-linking agents. If two polymerizable groups are properly arranged, cyclopolymerization proceeds. Cyclopolymerization of vinyl monomers is well known, but that of ring-opening monomers is rare.[1] In the present paper we describe the preparation of linear polymers, polyureas, from bifunctional monomers having two cyclic pseudourea groups (**1**) via a novel mode of polymerization, "double isomerization polymerization" (Scheme I).

Recently, we reported that the polymerization of cyclic pseudoureas **4** initiated by alkyl halides yields poly(1,3-diazolidin-2-on-1,3-diyloligomethylene)s **5** (Scheme II).[2] For example, the cationic polymerization of 2-piperidino-2-oxazoline (**4a**) with benzyl bromide produces poly(1,3-diazolidin-2-on-1,3-diylpentamethylene) (**5a**). This polymerization was named "double isomerization polymerization" (DIP) to distinguish it from the other type of ring-opening polymerization of **4** to produce poly[(*N*-carbamoyl)iminoethylene]s (**6**). This DIP is a unique and unknown type of polymerization since it proceeds accompanying the isomerization of propagating species.

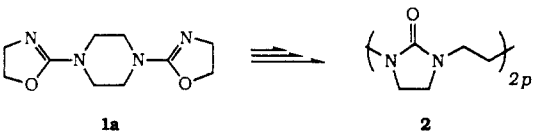
Two bispseudoureas, bis(2-oxazolin-2-yl)piperazine (**1a**) and bis(2-oxazolin-2-yl)homopiperazine (**1b**), were newly synthesized and their DIP was carried out, which yielded linear polymers containing cyclic urea units. Each monomer **1** has three rings, one cyclic diimino ring and two oxazoline rings. During the DIP of **1**, all three rings open and two cyclic urea rings are newly formed.

Experimental Section

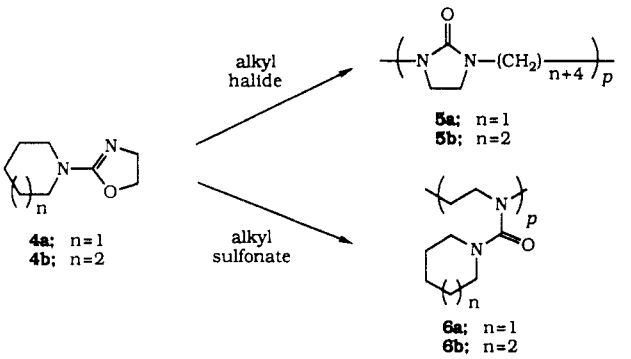
Materials. 2-Ethoxy-2-oxazoline was prepared as described in the previous paper.[3] Other reagents and solvents were commercially available and were dried by the conventional methods and distilled under nitrogen. The solvents were stored over 3Å molecular sieves after distillation.

Measurements. ^{1}H NMR spectra were recorded on a 60-MHz Hitachi R-600 or 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 Toso HLC 8020 system using a Shodex AC803 column in chloroform. Number-average molecular weights of the samples were measured with a vapor pressure osmometer (Corona Model 117) in chloroform at 40 °C. DSC analysis was carried out on a SEIKO SSC-5000.

Scheme I



Scheme II



Procedure for the Preparation of 1a. In a two-necked flask equipped with a reflux condenser and a magnetic stirrer bar were placed 20 g of 2-ethoxy-2-oxazoline (0.173 mmol), 6.35 g of piperazine, and 150 mL of benzene. To the mixture was added a catalytic amount of *p*-toluenesulfonic acid, and the mixture was heated to reflux. The consumption of 2-ethoxy-2-oxazoline was traced by GLC, and the almost complete conversion of 2-ethoxy-2-oxazoline was attained after 4 h. After evaporation of the solvent, the resulting white residue was dissolved in dichloromethane, washed with aqueous K_2CO_3, and dried over anhydrous K_2CO_3. After filtration, hexane was added to the filtrate to precipitate the product, **1a**, which was further purified by recrystallization from dichloromethane. The yield after recrystallization was 9.30 g (56%): colorless needles, mp 209.2 °C (DSC); ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.4 (s, NCH_2CH_2N, 4 H), 3.6–3.9 (m, NCH_2CH_2O, 4 H), 4.2–4.5 (m, OCH_2, 4 H); ^{13}C NMR ($CDCl_3$) δ 45.1 (NCH_2CH_2N), 52.7 (NCH_2CH_2O), 68.3 (OCH_2); IR (NaCl) 2987 (ν_{C-H}), 2869 (ν_{C-H}), 1655 ($\nu_{C=N}$), 1432, 1288, 1247, 1091, 933, 714 cm^{-1}; mass spectrum *m/e* 224 (M^+), 113, 99, 87, 55; exact mass found: *m/e* 224.12532 (calcd for $C_{10}H_{16}N_4O_2$: *m/e* 224.12731).

1b was prepared by a similar procedure, but purified by distillation: white crystalline solid, 46% yield, mp 51.0 °C (DSC), bp 210 °C/2.0 Torr; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.8 (q, $NCH_2CH_2CH_2N$, 2 H), 3.4 (t, $NCH_2CH_2CH_2N$, 4 H), 3.5 (s, NCH_2CH_2N, 4 H), 3.5–3.8 (m, NCH_2CH_2O, 4 H), 4.1–4.4 (m, OCH_2, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.5 ($NCH_2CH_2CH_2N$), 47.5 ($NCH_2CH_2CH_2N$), 49.6 (NCH_2CH_2N), 53.1 (NCH_2CH_2O), 68.3 (OCH_2); IR (NaCl) 2958 (ν_{C-H}), 1645 ($\nu_{C=N}$), 1484, 1436, 1305, 931, 716 cm^{-1}; mass spectrum *m/e* 238 (M^+), 169, 152, 139, 125, 113, 99, 87; exact mass found: *m/e* 238.14116 (calcd for $C_{11}H_{18}N_4O_2$: *m/e* 238.14296).

Typical Procedure for the Double Isomerization Polymerization of Bispseudoureas. In a test tube equipped with a magnetic stirrer bar and a three-way stopcock were placed 0.493 g (2.20 mmol) of **1a** and 10 mL of benzonitrile under nitrogen. To the solution was added 46.0 mg (0.269 mmol) of benzyl bromide with stirring. The tube was sealed and allowed to react at 150 °C for 100 h. The produced polymer **2b** was isolated by precipitation from an equivolume mixture of diethyl ether with hexane as an orange crystalline solid, which was purified further by repeated reprecipitation from dichloromethane to an ether–hexane mixture and dried in vacuo. The yield was 0.40 g (81%).

Results and Discussion

Preparation of Cyclic Bispseudoureas. The bisoxazolines **1a** and **1b** were newly prepared in moderate yields

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Table I
Double Isomerization Polymerization of Bispseudoureas 1[a]

						polymer				
									DP	
1	initiator	$[M]_0/[I]_0$	temp, °C	time, h	yield, %	structure	M_n[b]	M_w/M_n[c]	obs[b]	theor[d]
1a	MeI	10.3	100	200	53	2	1500	1.29	6.6	5.5
1a	$PhCH_2Br$	8.3	100	110	24	2	600	1.24	2.6	2.0
1a	$PhCH_2Br$	9.0	120	50	83	2	2000	1.12	9.1	7.5
1a	$PhCH_2Br$	9.1	150	50	81	2	2000	1.23	8.8	7.4
1a	$PhCH_2Br$	50.3	150	100	58	2	6700	1.33	30	29
1b	$PhCH_2Br$	9.7	100	40	89	3	1600	1.20	6.3	8.6
1b	$PhCH_2Br$	45.0	150	100	89	3	9000	1.28	38	40

[a] In benzonitrile. Typically, $[M]_0$ = 0.22 mol/L. [b] Determined by VPO in chloroform at 35 °C. [c] Determined by GPC with polystyrene calibration. [d] Theoretical molecular weight calculated from the feed ratio combined with the polymer yield.

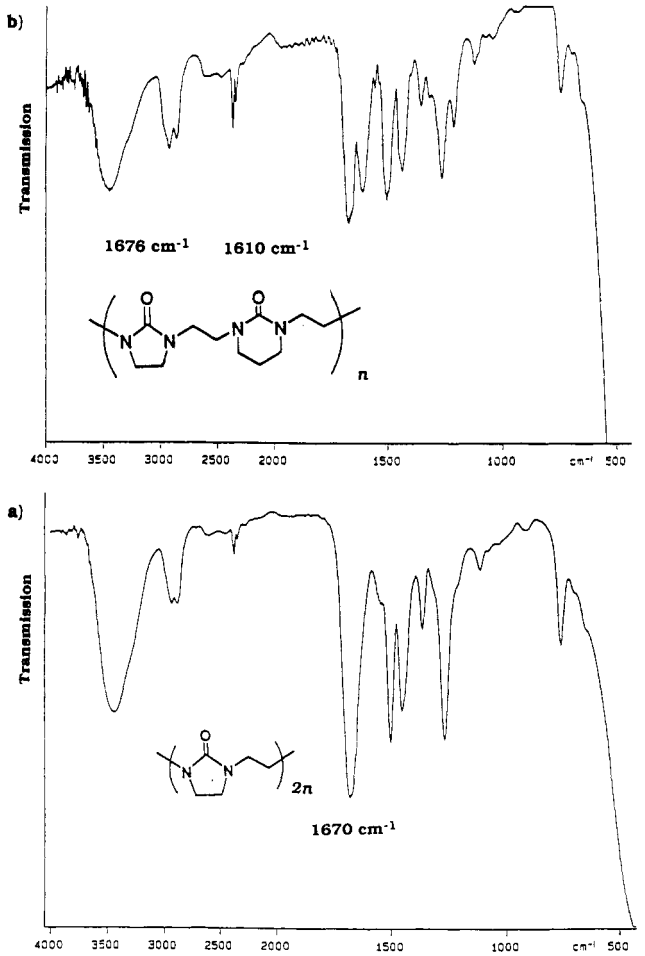
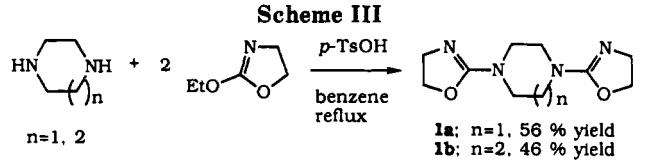


Figure 1. FT-IR spectra of 2 (a) and 3 (b).

Scheme III



by the condensation reactions of 2-ethoxy-2-oxazoline with the corresponding cyclic diimine catalyzed by *p*-toluenesulfonic acid in benzene (Scheme III). The monomers are white needles and were purified by recrystallization (for **1a**) or distillation (for **1b**).

Double Isomerization Polymerization of Bis(2-oxazolin-2-yl)piperazine (1a). When the monomer was heated with an alkyl halide, methyl iodide or benzyl bromide, the DIP of **1a** proceeded. Benzonitrile was chosen as solvent since the DIP of **4** gave the best results in this solvent.[2] The results are summarized in Table I. The polymerization of **1a** was examined at 100 °C and above, but the highest monomer conversion was attained at 120 °C and above. The resulting polymer **2** is highly crystalline and soluble in benzonitrile only above 60 °C. Therefore, **2** precipitated out from the polymerization mixture as brown needles when the reaction mixture was kept at room temperature after the heating. It was soluble in water, methanol, dichloromethane, and chloroform but insoluble in DMF, acetonitrile, acetone, THF, diethyl ether, carbon tetrachloride, and hydrocarbons. It is soluble in nitromethane at 60 °C.

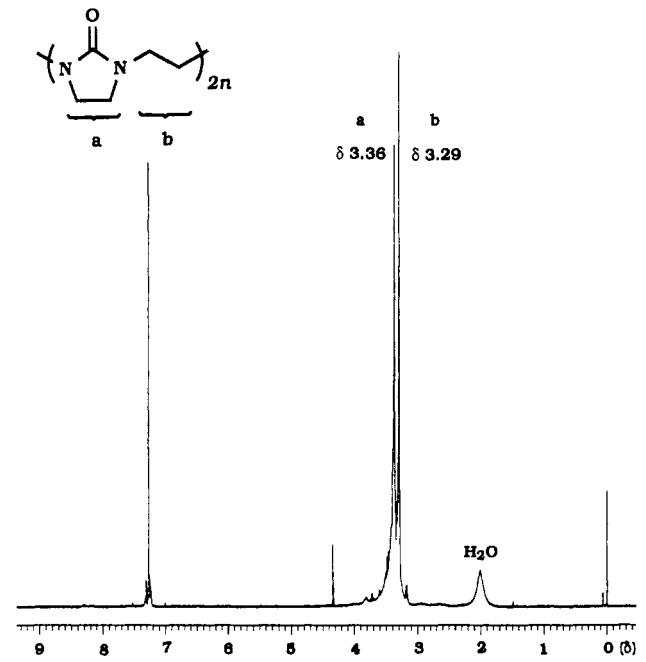


Figure 2. 400-MHz ^1H NMR spectrum of 2 ($CDCl_3$/TMS).

The structure of the resulting polymer was determined from IR and ^1H and ^{13}C NMR spectroscopies. Figure 1a shows the IR spectrum of **2**, in which only one carbonyl stretching band appeared at 1670 cm^{-1}. The absence of the absorbance ascribed to the C=N stretching band of pseudourea at 1655 cm^{-1} suggests that both pseudourea moieties in **1a** react in the polymerization. The position of the carbonyl stretching band in Figure 1a coincides well with that for **5a** (at 1676 cm^{-1}) and is higher than those for linear and six-membered cyclic ureas, indicating the presence of a five-membered cyclic urea unit, the 1,3-diaozolidin-2-one unit, in the polymer.

In the ^1H NMR spectrum of **2** (Figure 2), only two main peaks are observed at δ 3.29 and 3.36, indicating a simple and regulated structure of **2**. The peaks around δ 7.3 and at δ 4.35 are ascribed to the benzyl group at the initiating end. The peak assignments were carried out taking into consideration the assignments for poly(**1b**) (vide infra).

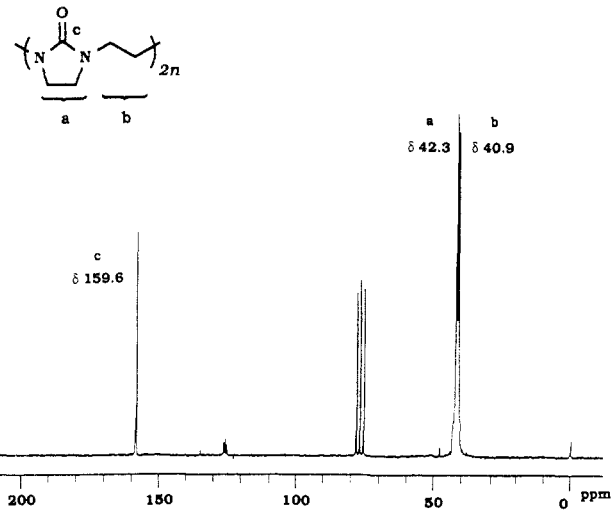


Figure 3. 22.6-MHz ^{13}C NMR spectrum of 2 ($CDCl_3$/TMS).

The ^{13}C NMR spectrum of 2 is shown in Figure 3. The spectrum is again very simple and three major peaks are observed at δ 40.9, 42.3, and 159.6. The second and third peaks are reasonably ascribed to the methylene and carbonyl peaks of the 1,3-dioazolidin-2-one unit, respectively. The corresponding peaks in the spectrum of **5a** appeared at δ 41.8 and 159.5.[4] No peak ascribed to the pendant oxazoline ring or the carbamoyliminoethylene chain by the simple ring-opening polymerization of the oxazoline ring is observed in either NMR spectrum. From these results the polymer structure of 2 was identified as poly(1,3-diazolidin-2-on-1,3-diylethylene).

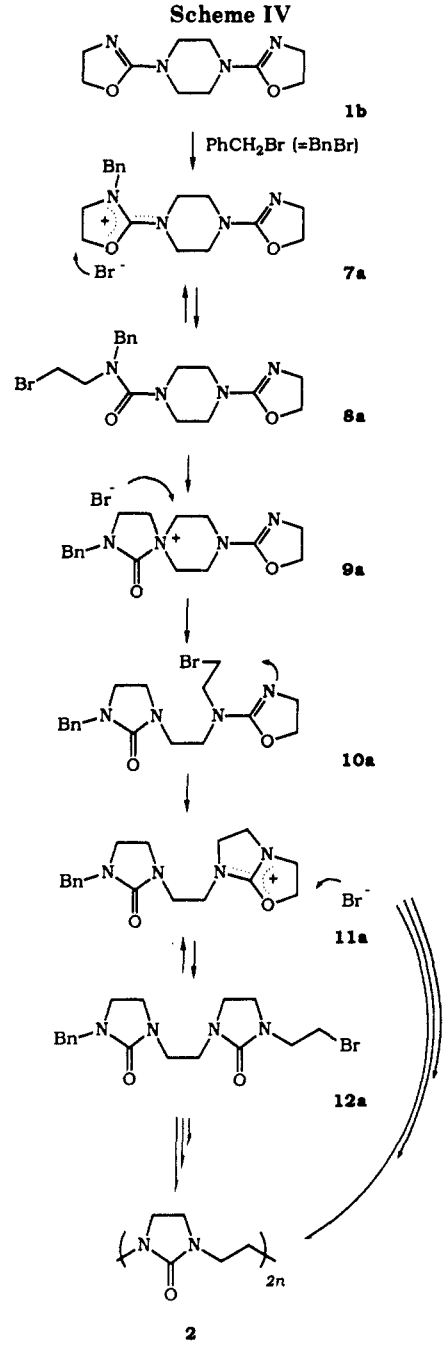
The observed molecular weights of 2 determined from VPO are summarized in Table I, which agreed well with the corresponding calculated ones on the basis of the feed ratio combined with the monomer conversion. The observed values agreed with those determined by GPC with polystyrene calibration. The molecular weight distribution of 2 is generally narrower than that of 5 having an analogous molecular weight.

Polymerization Mechanism for 1a. It is very unusual that the polymerization of a bifunctional monomer of a cyclic rigid structure gives linear polymer, 2. However, we expected the formation of linear polymer for **1a**. The polymerization mechanism of **1a** to yield 2 is supposed to be very complicated and, thus, we have not yet confirmed it from experimental evidence. However, it can be elucidated reasonably on the analogy of that for the DIP of **4** as well as with the consideration of the mechanism for cyclic imino ethers.[2,5]

The presumed mechanism is illustrated in Scheme IV. By reaction of **1a** with the initiator, benzyl bromide for example, an oxazolinium salt species, **7a**, is formed. The counteranion of this salt, bromide, then attacks the 5-position of **7a** to give a covalent-type alkyl bromide species **8a** as an intermediate. This covalent species **8a** converts to an ionic spiro compound, **9a**, by the attack of the nitrogen atom. The resulting compound **9a** of the N-alkylated urea structure is considered to be more thermodynamically favorable than the corresponding O-alkylated salt, **7a**, because the C=O bond is generally stronger than the C=N bond. This salt **9a** is electrophilic enough to suffer the attack of the counteranion or the monomer. The attack of the counteranion on the piperazinium ring forms a covalent ethyleneurea species **10a**.

Although we have no experimental evidence to support these isomerizations from **7a** to **10a**, the existence of similar intermediates corresponding to **7a**, **9a**, and **10a** was confirmed in the DIP of **4a** with methyl iodide.[2]

Scheme IV

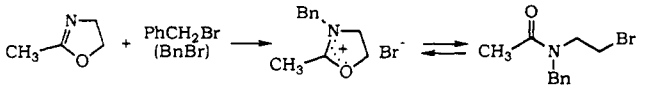


When **10a** is once formed, the other oxazoline moiety of **10a** enters the reaction: the nitrogen atom of the oxazoline moiety attacks the methylene carbon adjacent to bromide to produce a bicyclic oxazolinium species, **11a**. The attack of bromide on the 5-position of the oxazolinium ring will yield a covalent species **12a**. Then both **11a** and **12a** can propagate by the attack of monomer. Presumably, an equilibrium will exist between them. We have no data showing which is the real propagating species. Perhaps it depends on the relative nucleophilicity of the counterion derived from the initiator to monomer as in the well known cases of cyclic imino ethers.[5,6]

The route from **10a** to **12a** has not been supported by experimental results but is highly likely since a similar reaction pathway is known: the propagating species for the polymerization of 2-methyl-2-oxazoline with benzyl bromide are of both ionic and covalent species in equilibrium (Scheme V).[7]

The attack of monomer on **11a** or **12a** yields another **7a**-like oxazolinium species. If the consequent isomer-

Scheme V



izations from the **7a**-like propagating species to a **12a**-like species occur rapidly enough, the resulting polymer is linear. The attack of monomer on a **9a**-like propagating species will form an oxazoline pendant group, which will cause branching and cross-linking. However, intramolecular attack of bromide anion predominantly occurs. The attack of monomer on a **10a**-like propagating species will also form an oxazoline pendant group. However, the intramolecular cyclization forming the five-membered ring predominates.

The double isomerization polymerization of cyclic pseudoureas proceeds exclusively with alkyl halide initiators. On the other hand, the polymerization of **4** with sulfonate ester initiators yields poly(carbamoyliminoethylene)s (**6**) (Scheme II) via the usual ring-opening polymerization of the oxazoline ring since the counteranion derived from the initiator, a sulfonate ion, has no catalytic activity toward isomerizations due to a lack of nucleophilicity.[2] The polymerization of **1a** with 2 mol % of methyl trifluoromethanesulfonate in benzonitrile at 150 °C quantitatively produced an insoluble gelish product after 100 h, whose IR spectrum showed the presence of urea groups ($\nu_{C=O}$ = 1630 cm^{-1}) and unreated oxazoline groups ($\nu_{C=N}$ = 1660 cm^{-1}). Obviously, two oxazoline moieties in **1a** polymerize independently, which results in the branching and cross-linking of polymer.

Double Isomerization Polymerization of 1b. The polymerization of bis(2-oxazolin-2-yl)homopiperazine (**1b**) having a seven-membered diimino ring with benzyl bromide also produced a linear polymer, **3**, in good yields (Table I).

If the polymerization mechanism for **1a** shown in Scheme IV is also applicable to **1b**, two unit structures are possible for poly(**1b**). After the formation of **7b** by a similar initiating reaction, consecutive isomerizations yield **8a**-like species and, then, **9b** (Scheme VI). The ionic spiro species **9b** has three electrophilic reaction sites, i.e., the 2- and 7-positions of the homopiperazine ring and the methylene carbon of the diazolidinone ring. Among these three positions the attack on the diazolidinone ring has never been found.[2] The attack of the counteranion on the 2-position forms a bromoethyl derivative, **10c** (route C in Scheme VI), while attack at the 7-position produces a bromopropyl derivative **10b** (route B). By successive isomerizations and the consequent propagation described above, the 1,3-diazolidin-2-on-1,3-diylethylene-5,6-dihydro-4*H*-1,3-diazin-2-on-1,3-diylethylene unit (the unit of **3**) will be produced from **10b** and the 1,3-diazolidin-2-on-1,3-diylethylene-1,3-diazolidin-2-on-1,3-diyltrimethylene unit (the unit of **13**) from **10c**. Therefore, the structure of the resulting polymer from **1b** will be **3** or **13** or will consist of both **3** and **13** units.

The structure of the polymer of **1b** was most clearly characterized by IR spectroscopy since the C=O carbonyl stretching frequency of a five-membered cyclic urea is higher than that of a linear or six-membered cyclic urea having similar substituents.[2] The IR spectrum of poly(**1b**) is shown in Figure 1b. Two C=O stretching bands appear at 1676 and 1630 cm^{-1}, indicating the presence of both types of urea groups. The former band is acribed to a five-membered cyclic urea from the comparison with the IR chart of **2** and the latter to a six-membered one: the carbonyl stretching band of 1,3-dimethyl-5,6-dihydro-4*H*-1,3-diazin-2-one (*N*,*N*′-dimethyltrimethyleneurea) appears at 1640 cm^{-1}.

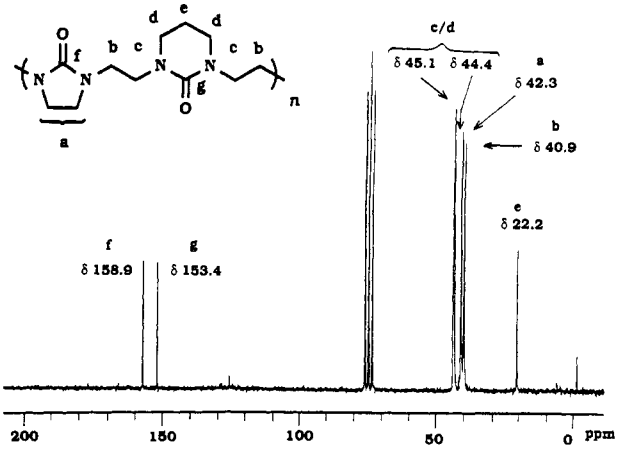


Figure 4. 22.6-MHz ^{13}C NMR spectrum of **3** ($CDCl_3$/TMS).

Scheme VI

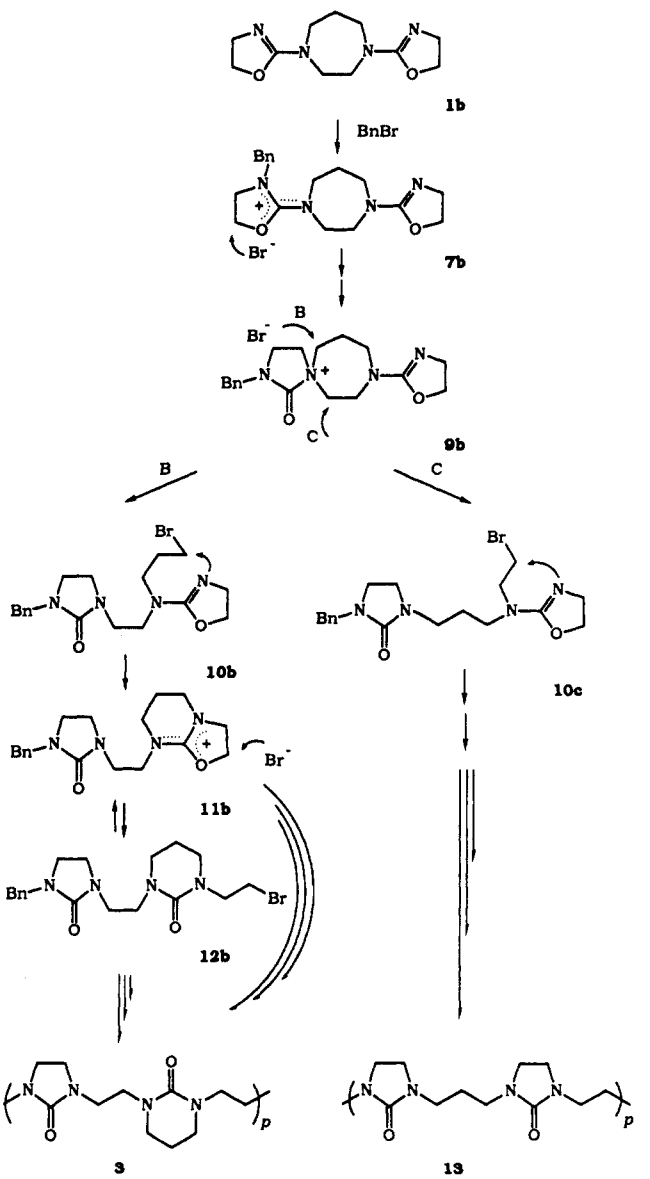


Figure 4 shows the ^{13}C NMR spectrum of poly(**1b**), in which seven main peaks are observed. The peaks ascribed to the carbonyl groups are observed at 153.4 and 158.9 ppm. The former is ascribed to five-membered cyclic urea carbonyl carbons from comparison with the NMR chart

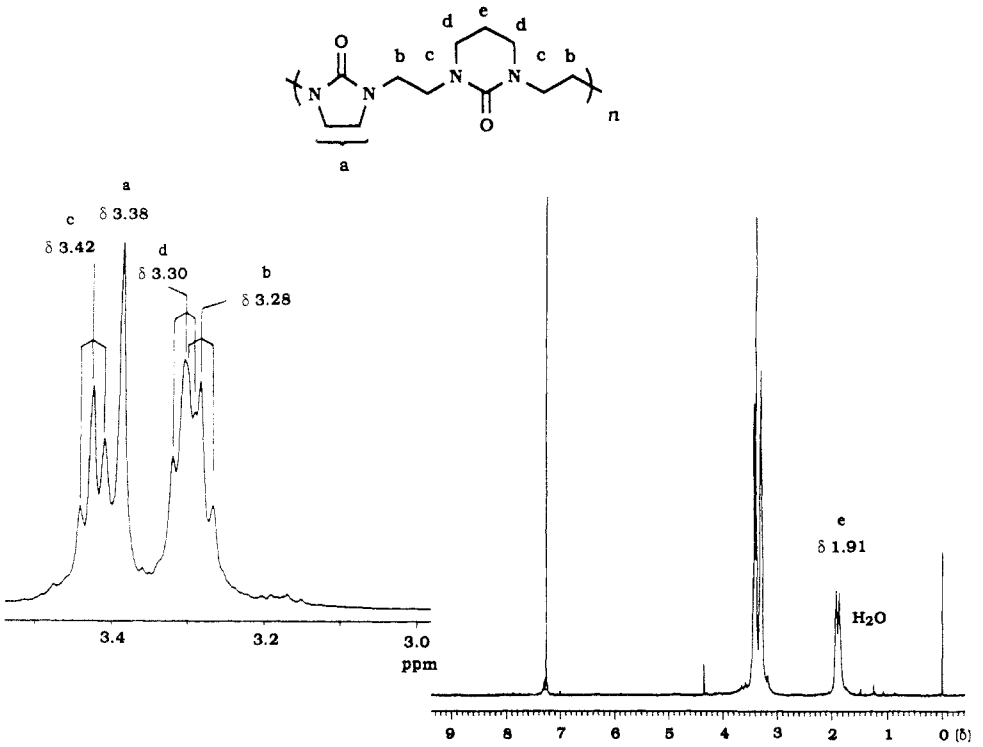
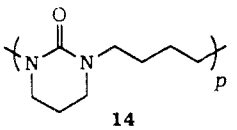


Figure 5. 400-MHz ^{1}H NMR spectrum of **3** ($CDCl_3$/TMS).

of **2** and, consequently, the latter is ascribed to six-membered ones.

Polymers containing six-membered cyclic urea units can be prepared by the DIP of 2-amino-5,6-dihydro-4*H*-1,3-oxazines.[8] In the ^{13}C NMR spectrum of a polymer of 2-(1-pyrrolidinyl)-5,6-dihydro-4*H*-1,3-oxazine (**14**), peaks as-



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cribed to six-membered rings appeared at 22.8 (N–C–*C*), 44.7 (N–C), and 153.3 (C=O) ppm. The coincidence between these chemical shifts of carbonyl peaks also supports the presence of six-membered cyclic urea units in **3**. From the almost equal intensity of these carbonyl peaks in Figure 4 and the absence of minor peaks except for those ascribed to the initiating benzyl group at around 126 ppm, it is concluded that the polymer structure is pure **3** and it contains no **13** unit. Other peaks are ascribed to each carbon as shown in Figure 4 in due consideration of the data of **2** and **14**. Peaks c and d could not be distinguished from each other.

The 400-MHz ^{1}H NMR spectrum of **3** also supports the polymer structure (Figure 5). Although the identification of each peak is very difficult due to their analogous chemical shifts, the peaks are reasonably ascribed as shown in Figure 5 in due consideration of the peak assignments for **2** and **14**. The singlet at δ 3.38 is ascribed to the methylene protons of the five-membered urea ring (a). Therefore, the peak at δ 3.36 in the ^{1}H NMR spectrum of **2** (Figure 2) is assigned to methylenes a and the other peak at δ 3.29 is, hence, ascribed to methylenes b. Back to Figure 5, the triplet at δ 3.28 is assigned to methylenes b. In the ^{1}H NMR spectrum of **14** peaks ascribed to six-membered ring protons appeared at δ 1.91 ($NCCH_2$) and 3.31 (NCH_2). Therefore, the peaks at δ 1.91 and 3.30 are ascribed to methylenes c and d, respectively.

The exclusive formation of **3** by the polymerization of **1b** means bromide anion attacks selectively the 7-position of the homopiperazine ring. It is tentatively explained by either a steric effect caused by the 2-oxazoline ring located at the 4-position or by an electronic effect of the urea group. However, it is generally known that substituents in the β- or γ-position do not have much effect on S_N2 rates.[9] More studies would be necessary to discuss this problem further.

The observed molecular weights of **3** determined from VPO again agreed well with the calculated ones. Polymer **3** is soluble in water, nitromethane, methanol, benzonitrile, dichloromethane, and chloroform but insoluble in acetonitrile, DMF, acetone, THF, diethyl ether, carbon tetrachloride, and hydrocarbons. Polymers **2** and **3** are highly crystalline materials whose melting points are 210 (**2**) and 223 °C (**3**).

The polymerization of cyclic pseudoureas yields the new type of polyureas. Polymers consisting of five-membered cyclic urea rings and ethylene or tri-, tetra-, penta-, or hexamethylene units can be prepared by the DIP of **1a**, 2-(1-azetidinyl)-2-oxazoline, 2-(1-pyrrolidinyl)-2-oxazoline, **4a**, or **4b**, respectively.[2,4] These polymers can be considered as polymeric models for *N,N,N',N'*-tetramethylurea or 1,3-dimethyl-1,3-diazolidin-2-one (*N,N'*-dimethylethyleneurea). Analogous examples are polymers of 2-alkyl-2-oxazolines, which are polymeric models for *N,N*-dimethylformamide or *N,N*-dimethylacetamide. Polymers of 2-alkyl-2-oxazolines have been known to possess high compatibility to commodity polymers and to have excellent amphiphilic properties and are applicable as, for example, antielectrostatic agents,[10] hydrogels,[11] and nonionic surfactants.[12,13]

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