Communications to the Editor

Double Isomerization Polymerization of 2-Amino-2-oxazolines: A Novel Ring-Opening Polymerization Accompanying Isomerization of Growing Species

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In the present paper is described a novel ring-opening isomerization polymerization of cyclic pseudoureas (1; Scheme I), 2-oxazolines having cyclic imine substituents at their 2-position. The polymerization of 1 gives two polymers quite different from each other via cationic (electrophilic) mechanisms. One is poly[(*N*-carbamoylimino)ethylene] (2) produced by the usual cationic ring-opening isomerization polymerization of 1 with methyl trifluoromethanesulfonate (triflate) or methyl *p*-toluenesulfonate (tosylate). In this polymerization the 2-oxazoline ring is opened as in the well-known case of 2-alkyl- or 2-aryl-2-oxazolines.[1] 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. In the latter polymerization, the isomerization of propagating species occurs during the propagation:the 2-oxazoline ring in the monomer rearranges to a 5-membered cyclic urea unit, and the cyclic imine moiety suffers ring opening. Although both modes of polymerization of 1 are to be classified into the same category of isomerization ring-opening polymerization, hereafter, the second mode of polymerization involving the opening of the cyclic imine ring is expressed by the term of "double isomerization polymerization (DIP)", meaning "the *isomerization polymerization* accompanying the *isomerization* of propagating species", to distinguish it from the first mode of polymerization.

A series of 2-amino-2-oxazolines has been proven to undergo this DIP, which includes 2-pyrrolidino-2-oxazoline (**1a**), 2-piperidino-2-oxazoline (**1b**), and 2-(1-azepanyl)-2-oxazoline (**1c**). None of the 5-7-membered cyclic amine derivatives has ever been known to undergo the ring-opening polymerization until now.

The monomers 1 were easily prepared by the condensation of 2-ethoxy-2-oxazoline with the corresponding cyclic secondary amines catalyzed by *p*-toluenesulfonic acid in benzene.[2] Although the synthesis of **1a** and **1b** has been reported in a previous patent,[3] no investigation on their polymerization has even been done.

The polymerization of 1 in benzonitrile was carried out in a sealed tube under nitrogen. After heating at the designated temperature, the polymer was isolated by precipitation from chloroform (solvent) to an equivolume mixture of diethyl ether with hexane (nonsolvent).

The results of the ring-opening polymerization of **1a** with a sulfonate ester or an alkyl halide as cationic initiator are shown in Table I. In most cases the polymeric products were obtained almost quantitatively. Very interestingly, the structure of the resulting polymer depends on the type of initiator. With methyl triflate (MeOTf) or tosylate (MeOTs) (run nos. 1-4), the polymer having urea pendant groups, **2a**, was obtained. On the other hand, with benzyl chloride or bromide (run nos. 7-9), the polymer consisting of a 5-membered cyclic urea ring and tetramethylene units, **3a**, was produced. With methyl iodide initiator, the polymerization of **1a** afforded a polymer consisting of both of **2a** (17%) and **3a** units whose composition was determined by ^{1}H NMR spectroscopy (run no. 5).

The structural difference between **2a** and **3a** was most clearly characterized by IR spectroscopy (Figure 1) since the C=O carbonyl stretching frequency for a 5-membered cyclic urea was higher than that for a linear or 6-membered cyclic urea having similar substituents as in the cases of lactams and lactones.[4] Namely, the C=O stretching band of **3a** appears at 1676 cm^{-1}, whereas that of **2a** appears at 1622 cm^{-1} in Figure 1.

The 400-MHz ^{1}H NMR spectra of **2a** and **3a** are shown in Figure 2. The peak ascribed to β-methylene protons of the tetramethylene unit in **3a** (peak c′) appears at δ 1.51 in Figure 2B while that of the pyrrolidino ring in **2a** (peak c) is observed at δ 1.81 in Figure 2A, which also strongly supports the structure of **3a**.[5]

The polymer **2a** is a crystalline yellow material with a melting point of 223 °C which is soluble in methanol, dichloromethane, and chloroform. On the other hand, **3a** is a hygroscopic, yellow semicrystalline material with a melting point of 163 °C which is soluble in nitromethane and in the same solvents for **2a**.

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-CC$_6$H$_5$) 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 I. 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 (run nos. 2, 3, and 6) suggests the occurrence of chain transfer. The broader molecular weight distributions in these runs also support it. It is in

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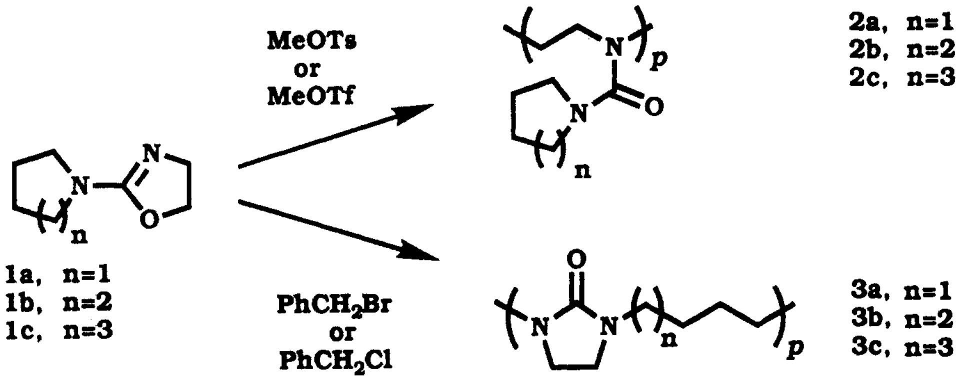
Scheme I



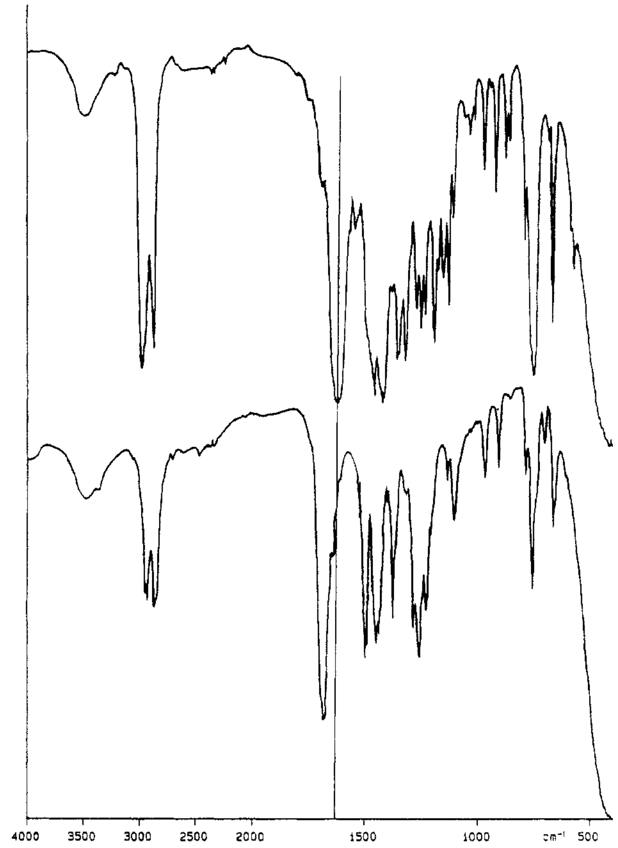


Figure 1. IR spectra of **2a** and **3a** (KBr).

good contrast to our previous findings that the polymerization of cyclic imino ether proceeds via a living mechanism to give a polymer of low polydispersity (<1.2).[1]

The polymerizations of **1b** and **1c** with methyl iodide respectively gave **3b** and **3c**, while those with methyl tosylate or triflate yielded polymers having urea pendant groups, **2b** and **2c**, in a similar manner (run nos. 10–13).

Preparation and Isomerization of 1:1 Adducts of 1a with Initiator. To investigate the mechanism of this peculiar polymerization, 1:1 adducts of **1a** with methyl tosylate and with methyl iodide were prepared. The reaction of **1a** with an excess amount (2.6-fold) of methyl tosylate in benzonitrile at 36 °C yielded 3-methyl-2-pyrrolidino-2-oxazolinium tosylate (**4a**; Scheme II) as colorless crystals (mp 47–48 °C) in 88% yield.[6] It was stable in the absence of moisture or **1a**, remaining unchanged in nitrobenzene at 80 °C after 8 h.

An analogous oxazolinium salt having an iodide counteranion, **4b**, was also isolated as orange needles by the reaction of **1a** with the 3.7-fold amount of methyl iodide under similar conditions (mp 55 °C (DSC)) in 86% yield.

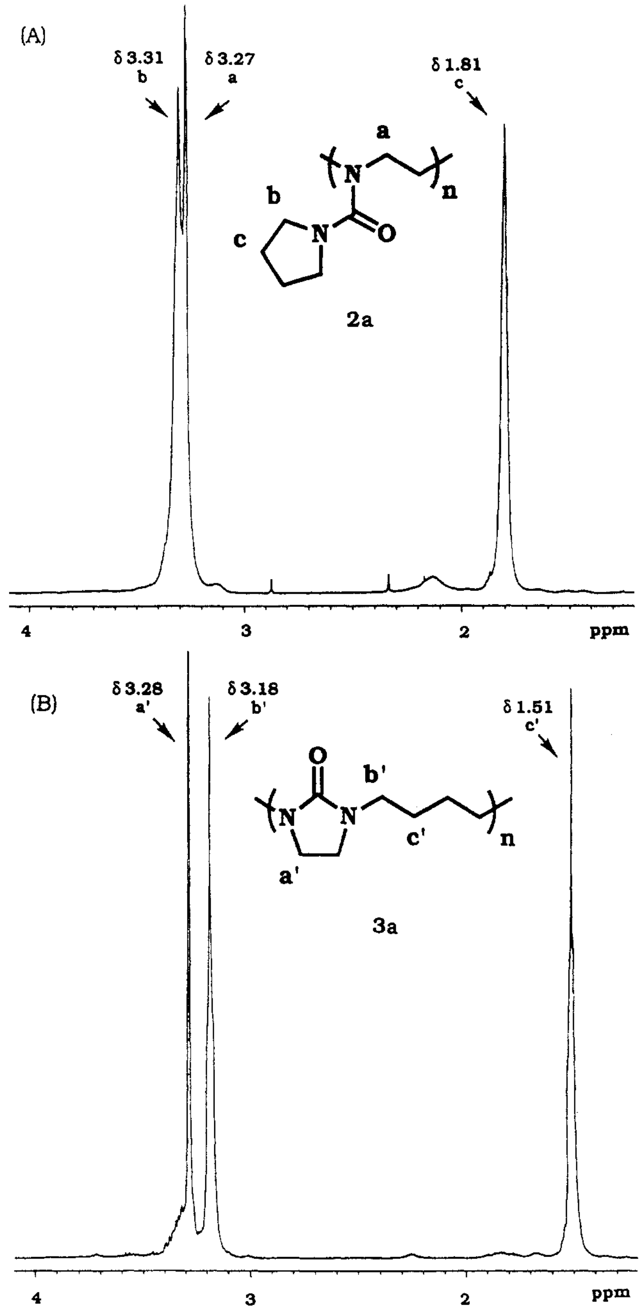


Figure 2. 400-MHz ^{1}H NMR spectra of **2a** (A) and **3a** (B) (in CDCl$_3$ containing 0.05% of TMS).

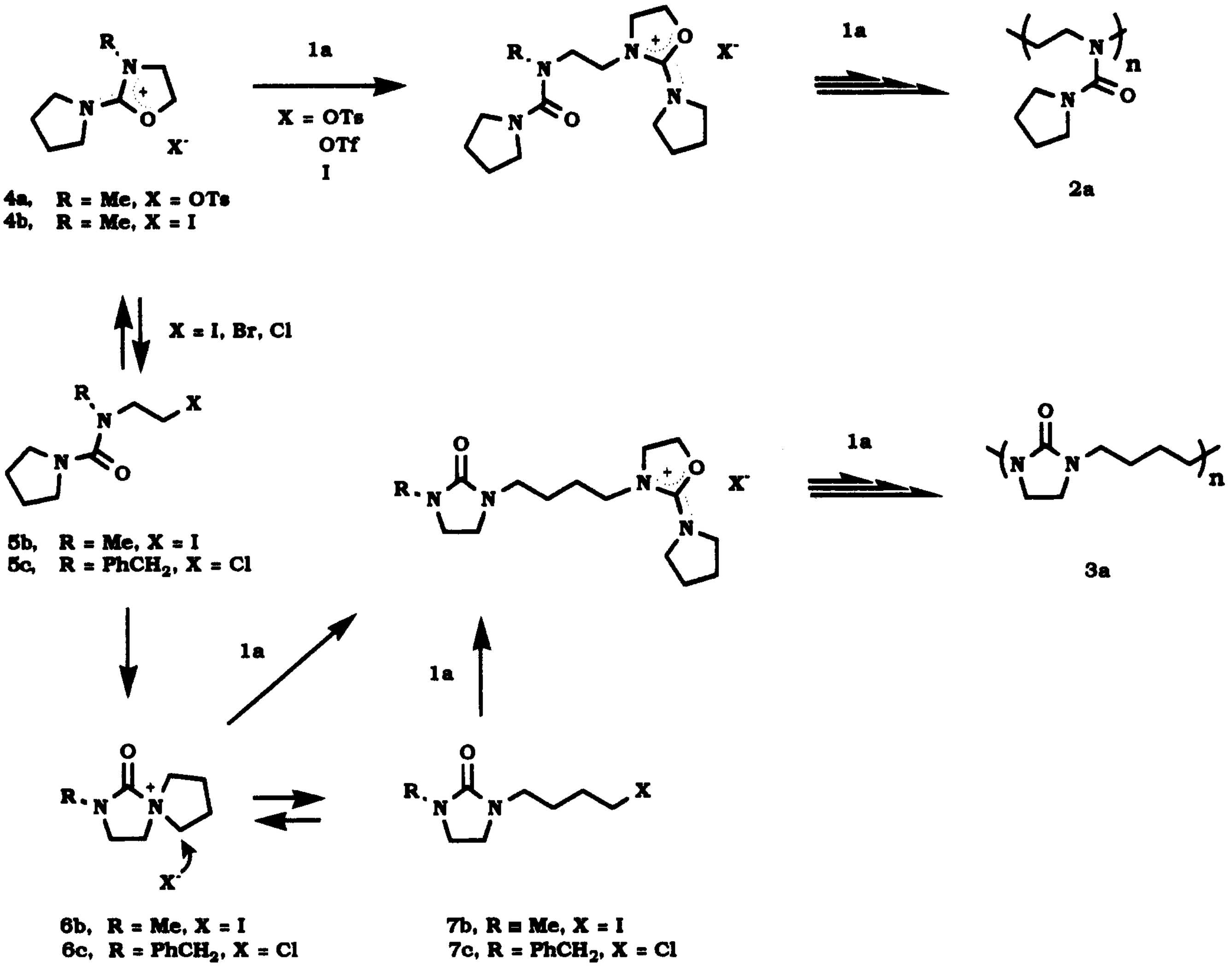
In contrast to **4a**, **4b** is thermally unstable. When **4b** was dissolved in benzonitrile-d_5 and kept at 80 °C, the in situ ^{1}H NMR measurement of the solution showed ca. 60% of **4b** isomerized into two new species (**6b** and **7b**) after 10 min. During the cooling at −40 °C, **6b** was crystallized

Table I
Ring-Opening Polymerization of 5-Membered Cyclic Pseudoureas

run no.	1	initiator	[M]/[I]	temp, °C	time, h	polymer: yield, %	structure	M_n[a]	M_w/M_n[a]	$M_{n,theor}$[b]	M_n[c]	M_n[d]
1	**a**	MeOTs	10.7	80	24	100	**2a**	730	1.15	1500	1700	1600
2	**a**	MeOTs	49.8	105	15	97	**2a**	3000	1.52	6980	2500	
3	**a**	MeOTs	99.2	105	15	87	**2a**	5500	1.49	13900	4300	16000
4	**a**	MeOTf	9.8	80	24	97	**2a**	800	1.11	1370	1400	1300
5	**a**	MeI	9.9	80	16	97	**2a/3a**[e]	1100	1.36	1390	2000	1900
6	**a**	MeI	47.3	100	168	74	**2a/3a**[e]	3600	1.80	6630	3200	
7	**a**	$PhCH_2Br$	9.5	80	47	93	**3a**	2100	1.32	1330		
8	**a**	$PhCH_2Br$	48.0	100	100	95	**3a**	8300	1.32	6730	5700	6800
9	**a**	$PhCH_2Cl$	9.8	140	30	93	**3a**	2000	1.23	1370	1900	1800
10	**b**	MeOTs	11.7	100	170	44	**2b**	880	1.26	1810		
11	**b**	MeI	9.7	120	48	99	**3b**	2100	1.41	1490		
12	**c**	MeOTf	9.5	80	20	90	**2c**	1580	1.03	1590		
13	**c**	MeI	9.5	80	40	91	**3c**	3440	1.22	1590		

[a] Determined by GPC with polystyrene standards. [b] Theoretical molecular weight calculated from the feed ratio of monomer to initiator. [c] Determined by VPO in chloroform at 35 °C. [d] Determined from the integral ratio of the peaks ascribed to N-CH_3 (or N-CC_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. [e] Consisting of the both **2a** (17%) and **3a** units, whose contents were determined by ^1H NMR.

Scheme II



from the mixture, which was collected by filtration as pale yellow needles (mp 132 °C). The structure of **6b** was identified from ^1H and ^{13}C NMR and IR spectroscopies as an ionic spiro compound having a quarternary N-alkylated urea group, 3-methyl-1-azonia-3-azaspiro[4.4]nonan-2-one iodide.[7]

When the isolated **6b** was once more dissolved in nitrobenzene-d_5 and heated at 80 °C, it was slowly converted 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 and the equilibrium constant ([**7b**]/[**6b**]) was estimated as 2.2 at 80 °C from ^1H NMR.

The isomerization of **4** to **6**, from an O-alkylated salt of urea to an N-alkylated one is quite a new reaction not only in polymerization chemistry but also in organic chemistry. However, analogous isomerizations of a kinetically preferred product to a thermodynamically favored one have been known. For example, a ketene silyl enol ether isomerized to an α-silyl ester and an O-alkylated salt of urethane to an N-alkylated one.[8,9]

Polymerization Mechanism. Considering the above experimental results, the polymerization mechanism of the present DIP was explained as follows. In all of the present systems, an oxazolinium salt species **4**, and O-alkylated salt of urea, was first formed by the reaction of the monomer with each of the initiators. 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 propagation. Hence, the propagation via oxazolinium species secures the usual ring-opening polymerization process.

However, when the counteranion of the salt is nucleophilic enough as in the case of halides, it catalyzes the rearrangement of the O-alkylated salt **4** to the N-alkylated salt **6** according to the following scheme. 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. 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 found between 3,5-dimethyl-2-oxazolinium iodide, a 1:1 adduct of 5-methyl-2-oxazoline with methyl iodide, and *N*-methyl-*N*-(2-iodoethyl)formamide.[10]

A minor part of **5b** converts to an 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 electrophilic enough to suffer the attack of the counteranion or the monomer. Although **6b** possesses two electrophilic reaction sites, i.e., α-positions of the pyrrolidinium ring and the methylene carbon of the diazolidinone ring, the attack of the counteranion occurs exclusively at the pyrrolidinium ring, and the covalent ethyleneurea species **7b** generates selectively.

With benzyl chloride as the initiator, the formation of **5c** is preferable since chloride ion is more nucleophilic than iodide ion in organic solvents and its leaving ability is lower than iodide.[11] By the nucleophilic attack of the nitrogen atom, **5c** is transformed to **6c**, which is also unstable and immediately converts to **7c**.

The propagating species in 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 species to the **6**-like one is fast enough, the propagation exclusively occurs via **6**- or **7**-like species as in the case of the benzyl chloride or bromide initiator. With methyl iodide initiator, the propagation via the **4b**-like species cannot be negligible because of the relatively low nucleophilicity and the high leaving ability of the iodide anion, which results in the contamination of the **2a** unit in the polymer. Our kinetic study using **4b**–**7b** as model compounds for the propagating species revealed that the propagation to yield the **3a** unit mainly proceeds via the covalent **7b**-like species in the polymerization with methyl iodide at 80 °C.[12]

The present work is quite interesting not only from the view point of polymerization chemistry but also from that of material science since the produced polymers **2** and **3** are novel types of polymers. Moreover, it is also quite interesting that **3a** can be readily convertible to polyamine having alternate units of iminoethylene and iminotetramethylene by hydrolysis. The results of the formation of polyamine as well as the kinetic study on DIP will be described soon.

References and Notes

(1) For example, see: Kobayashi, S.; Saegusa, T. *Ring-Opening Polymerization*; Elsevier Applied Science Publishers: New York, 1985; Vol. 2, Chapter 11.

(2) Rein, K.; Goicoechea-Pappas, M.; Anklekar, T. V.; Hort, G. C.; Smith, G. A.; Gawley, R. E. *J. Am. Chem. Soc.* **1989**, *111*, 2211.

(3) Peet, N. P.; Sunder, S. U.S. Patent 4064348 (*Chem. Abstr.* **1977**, *88* (17), 121154d.

(4) Nakanishi, K. *Infrared Absorption Spectroscopy—Practical*; Chapter 2. Holden-Day and Nankodo Company Ltd.: San Francisco and Tokyo, 1962.

(5) The structures of **2a** and **3a** were also confirmed from ^{13}C NMR spectroscopy (in $CDCl_3$): **2a**, δ 25.8 (β-CH_2 carbons of the pyrrolidine ring), 47.3, 48.3, 160.9 (C═O); **3a**, δ 24.3 (β-CH_2 carbons of the tetramethylene unit), 41.8, 43.0, 159.5 (C═O).

(6) **4a**: ^{1}H NMR ($CDCl_3$) δ 1.63–2.13 (m, 4 H, β-CH_2 protons of the pyrrolidine ring), 2.33 (s, 3 H, CH_3Ar), 3.37 (s, 3 H, CH_3N), 3.47–4.27 (m, 6 H, CH_2N), 4.72 (t, 2 H, CH_2N); ^{13}C NMR ($CDCl_3$) δ 20.8 (CH_3Ar), 25.0 (β-CH_2 carbons of the pyrrolidine ring), 33.9 (CH_3N), 49.0 and 52.1 (α-CH_2 carbons of the pyrrolidine ring and C_4), 67.4 (C_5), 124.0, 126.7, 137.7, and 143.1 (Ar), 156.4 (C_2); IR (in $CHCl_3$) 2984, 1683 ($\nu_{C=N}$), 1522, 1298, 1201 cm^{-1}. The ^{1}H and ^{13}C spectra of **4b** were essentially the same as those of **4b** except for the absence of the peaks ascribed to tosylate: IR (in $CHCl_3$) 2955, 1683 ($\nu_{C=N}$), 1519, 1458, 1294 cm^{-1}.

(7) **6b**; ^{13}C NMR ($CDCl_3$) δ 22.4 (β-CH_2 carbons of the pyrrolidine ring), 32.5 (NCH_3), 43.8 (4-position of the oxadiazolidinone ring), 53.9 (5-position of the oxadiazolidinone ring), 61.9 (α-CH_2 carbons of the pyrrolidine ring), 151.4 (C═O); IR (in CH_2Cl_2) 3039, 2959, 1813 ($\nu_{C=O}$), 1494, 1450, 1431, 1292, 1103, 1004, 937 cm^{-1}.

(8) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473.

(9) Ahmed, M. G.; Alder, R. W. *Chem. Commun.* **1969**, 1389.

(10) Kobayashi, S.; Morikawa, K.; Shimizu, N.; Saegusa, T. *Polym. Bull.* **1984**, *11*, 253.

(11) Parker, A. G. *Chem. Rev.* **1969**, *69*, 1.

(12) To determine the individual electrophilicity of the equilibrated **6b** and **7b** toward **1a**, **6a** (a tosylate salt) and *n*-butyl iodide were respectively used as model compounds.