Polymerization via Zwitterion. 10. Alternating Cooligomerization of 2-Methyl-2-oxazoline with Ethylenesulfonamide

Takeo Saegusa,* Shiro Kobayashi, and Jun-ichi Furukawa

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. *Received March 12, 1976*

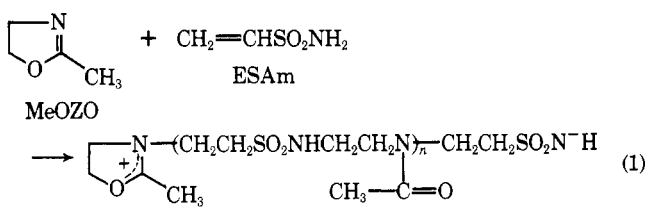
ABSTRACT: An alternating cooligomerization of 2-methyl-2-oxazoline (MeOZO) with ethylenesulfonamide (ESAm) was studied. The cooligomerization took place without any added initiator to produce cooligomers of MeOZO and ESAm. The structure of the cooligomer was determined by ir and NMR spectra, elemental analysis, as well as an alkaline hydrolysis experiment. A zwitterion (betaine) derived from MeOZO and ESAm, which was an intermediate of the cooligomerization, was isolated at a lower temperature. A reaction scheme of the cooligomerization proceeding via a zwitterion (eq 4–6) was proposed.

Various combinations of copolymerizations between nucleophilic monomers (M_N) and electrophilic monomers (M_E) which occur without any added catalyst have been found by us.[1-9] A zwitterion, $^+M_N-M_E^-$, which is the key intermediate of copolymerization, is formed by the interaction of M_N and M_E. In many cases the so-called alternating copolymers were produced. In the present study, 2-methyl-2-oxazoline (MeOZO) and ethylenesulfonamide (ESAm) were employed as M_N and M_E, respectively. At 130 °C, MeOZO and ESAm were reacted with each other to produce alternating cooligomers. At a lower temperature, a zwitterion was isolated as a result of combining the two monomers.

Results and Discussion

Cooligomerization between MeOZO and ESAm. An equimolar mixture of MeOZO and ESAm (5 mmol each) in DMF (1.5 ml) containing 0.02 mmol of *N*-phenyl-2-naphthylamine as a radical inhibitor was heated at 130 °C under nitrogen. After 37 h, the reaction mixture was poured into a large amount of diethyl ether to precipitate polymeric materials. The cooligomer was dried in vacuo to give 0.80 g of a glassy, white, and hygroscopic solid (83% yield), the molecular weight of which was measured as 357 by vapor pressure osmometry in DMF at 55 °C.

The ir spectrum of the oligomer shows strong absorption bands at 1630 cm^{-1} for the amide carbonyl group at 1560 cm^{-1} for C=N, at 1315 and 1150 cm^{-1} for the sulfonamide group, and at 1280 cm^{-1} for C–O–C stretching. The NMR spectrum of the cooligomer in D_2O shows a broad signal at δ 4.7–3.8 due to methylene protons of the oxazolinium ring, of $-CH_2CH_2SO_2NHCH_2CH_2N-$, and of $CH_2CH_2SO_2N^-H$, and a sharp singlet at δ 2.80 due to methyl protons attached to the oxazolinium ring and a broad signal at δ 2.6 due to the acetyl group, which is formed by opening the oxazolinium ring. From the peak ratio of the methyl and methylene signals the ratio of MeOZO and ESAm in the oligomer was determined as 1.00:1.04. A signal due to NH was not observed in D_2O.



MeOZO ESAm

1 (1)

The cooligomer composition of MeOZO and ESAm was calculated from an elemental analysis of S (%) content to be 1.00:1.06, which is very close to that obtained from NMR. The structural determination was made in more detail with the cooligomer prepared from a zwitterion (vide infra).

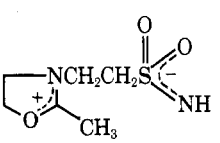
Similarly, the cooligomerization of MeOZO with ESAm was performed under various conditions (Table I). The composition of cooligomers showed the tendency of ESAm in excess in the cooligomerizations with DMF and $PhNO_2$ solvents. However, the tendency reversed in PhCN and CH_3CN solvents. The cooligomers are usually soluble in highly polar solvents such as water, methanol, and DMF but insoluble in less polar solvents: benzene, chloroform, and diethyl ether. The solubility of the oligomers is dependent on the molecular weight, the higher molecular weight product being insoluble in methanol (No. 5 in Table I).

Isolation of Zwitterion. The diethyl ether layer, from which cooligomer 1 was separated, gave white crystals after standing overnight at room temperature. The structure of the crystals was determined by ir and NMR spectroscopy, molecular weight measurement, and elemental analysis. The ir spectrum of the crystal (Figure 1a) shows strong absorption bands at 1560 cm^{-1} for $\nu_{C=N}$, at 1280 cm^{-1} for ν_{SO_2} and ν_{C-O-C}, and at 1140 cm^{-1} for the SO_2 band.

The NMR spectrum of the crystal in D_2O shows a multiplet at δ 4.7–3.9 due to methylene protons of oxazolinium ring and of NCH_2CH_2S and a sharp singlet at δ 2.80 assigned to methyl protons attached to oxazolinium ring (Figure 2). The result of the elemental analysis of the crystal supports the 1:1 composition of MeOZO and ESAm. Anal. Calcd for $C_6H_{12}N_2O_3S$: C, 37.49; H, 6.29; N, 14.57; S, 16.68. Found: C, 37.31; H, 6.54; N, 14.75; S, 16.42.

The molecular weight of the crystals by vapor pressure osmometry in DMF at 55 °C is 191 which is very close to the calculated value of 192.1.

Based on the above data the structure of the white crystals is assigned to a zwitterion (betaine) 2 formed from MeOZO and ESAm.



2

The crystal melts at 132–4 °C and is soluble in highly polar solvents such as DMF, methanol, acetonitrile, and water but insoluble in toluene, benzene, and diethyl ether.

It should be noted that zwitterion 2 is so stable as to be still present as a living species after the above work-up procedures. It is therefore very likely that cooligomer 1 contains 2.

Preparation and Oligomerization of Zwitterion 2 and Characterization of Cooligomer. Since it was found above that zwitterion 2 could be isolated as a stable species the facile preparation of 2 became important. We have found that 2 could successfully be prepared at lower temperatures from

Table I
Cooligomerization of MeOZO with ESAm[a]

No.	Solvent	Temp, °C	Time, h	Cooligomer % yield[b]	Cooligomer % S	Cooligomer MeOZO/ESAm[c] from NMR	Cooligomer MeOZO/ESAm[c] from % S	Cooligomer Mol wt[d]
1	DMF	130	37	83	16.96	1/1.04	1/1.06	357
2	DMF	150	98	100	17.82	1/1.11	1/1.24	594
3	PhCN	130	44	79	12.99	1/0.62	1/0.64	307
4	CH_3CN	120	192	83	11.97	1/0.59	1/0.54	340
5	$PhNO_2$	150	194	82	19.43	1/1.33	1/1.58	810
				15[e]	18.53	1/1.19	1/1.39	1900[e]

[a] The charged MeOZO and ESAm were 5.0 mmol in 1.5 ml of solvent. [b] {[The amount of cooligomer (g)]/[the charged amount (g)]}100. [c] The MeOZO/ESAm ratio of the cooligomers was determined by NMR spectra and the elemental analysis (% S), respectively. [d] Determined by VPO in DMF at 55 °C. [e] MeOH insoluble part.

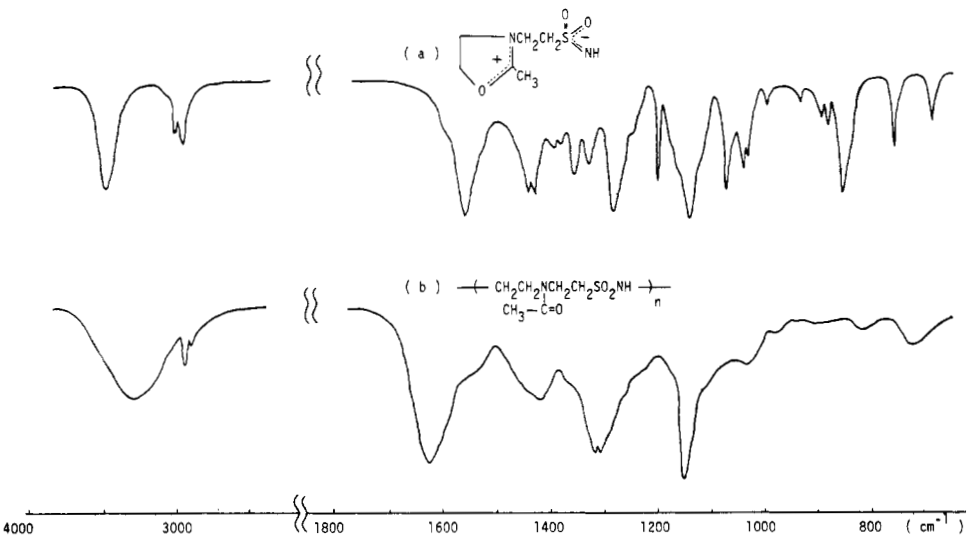


Figure 1. Infrared spectra of the MeOZO–ESAm betaine (a) and cooligomer (b) (KBr).

MeOZO and ESAm. An equimolar mixture of MeOZO and ESAm (10 mmol each) in CH_3CN (3 ml) containing 0.04 mmol of *N*-phenyl-2-naphthylamine as a radical inhibitor was heated at 100–105 °C under nitrogen. After 12 h the reaction mixture was poured into a large amount of diethyl ether to precipitate a white solid material. The solid was collected by filtration and the filtrate further gave rise to white crystals after standing overnight. The crystals were collected by filtration. The two solids were combined and recrystallized from an acetonitrile–diethyl ether mixture. After two crystallizations white crystals were obtained (0.93 g, 48% yield), mp 132–4 °C.

The oligomerization was examined with the use of **2** as "monomer". A solution of **2** (0.70 g) in DMF (1 ml) was heated at 150 °C under nitrogen. After 120 h the reaction mixture was poured into a large amount of diethyl ether to precipitate polymeric material. The precipitate was dried in vacuo to give 0.65 g of solid (93% yield). The structure of the solid was confirmed by ir, NMR, and elemental analysis to be analogous to cooligomer **1**. The molecular weight was 911.

The ir spectrum of the oligomer shows strong absorption bands at 1630 cm^{-1} for the amide carbonyl group and at 1315 and 1150 cm^{-1} for the sulfonamide group (Figure 1b). The C=N band at 1560 cm^{-1} had nearly disappeared. The NMR spectrum of the cooligomer in D_2O shows a broad signal at δ 4.7–3.8 ($-CH_2CH_2NCH_2CH_2-$, 8 H) and a doublet like signal at δ 2.6 (CH_3, 3 H) (Figure 3a). From the peak ratio of the methyl and methylene signals the ratio of MeOZO and ESAm in the oligomer was determined as 1.00:1.00. A signal due to NH was not observed in D_2O. In DMSO-d_6, however, two signals at δ 7.4 and 6.9 assignable to NH (total 1 H) appeared in addition to the methyl and methylene signals (Figure 3b).

The elemental analysis of the cooligomer supported the 1:1 composition of MeOZO and ESAm. Anal. Calcd for $(C_6H_{12}N_2O_3S)_n$: C, 37.49; H, 6.29; N, 14.57; S, 16.68. Found: C, 37.21; H, 6.51; N, 14.75; S, 16.38.

Alkaline hydrolysis of the cooligomer was carried out to confirm structure **1**. The NMR spectrum of the reaction mixture (Figure 4a) showed that the hydrolysis was completed. The hydrolysis products consisted of a 1:1 mixture of the Na salts of β-[(β-aminoethyl)amino]ethanesulfonic acid, **3**, and of acetic acid, i.e., NMR peaks (Figure 4a) at δ 3.1–2.8 (broad, 4 H) and 2.7–2.5 (broad, 4 H) are due to protons of $-NCH_2CH_2N-$ and $-CH_2CH_2S-$, respectively. Methyl protons of the copolymer (δ 2.0) were almost completely deuterated. Furthermore, the small triplet peak at δ 3.6 due to terminal

$$1 \xrightarrow[D_2O]{NaOH} D_2NCH_2CH_2\underset{\displaystyle D}{\underset{|}{N}}CH_2CH_2SO_3Na + CH_3CO_2Na$$

Na salt of **3**

$$+ DOCH_2CH_2\underset{\displaystyle D}{\underset{|}{N}}CH_2CH_2SO_3Na \quad (2)$$

Na salt of **4**

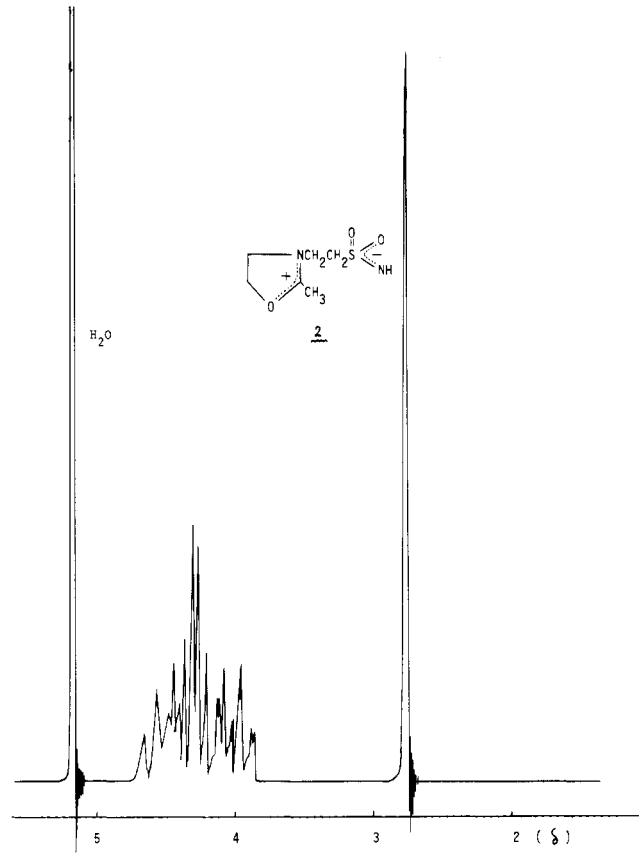


Figure 2. NMR spectrum of the MeOZO–ESAm betaine in D_2O.

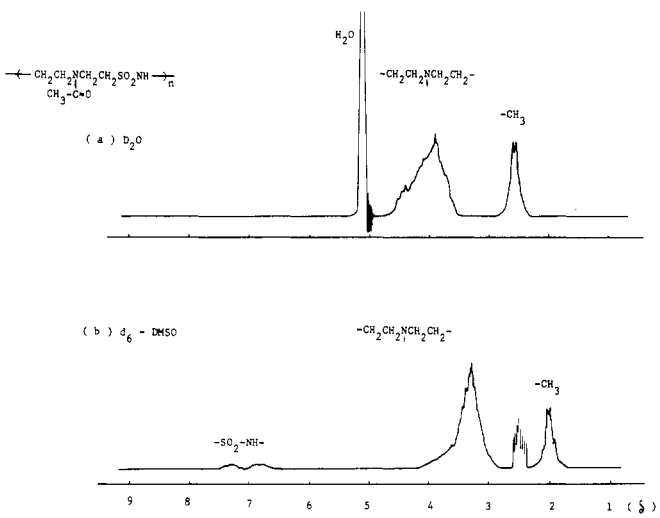


Figure 3. NMR spectra of the MeOZO–ESAm cooligomer in (a) D_2O and (b) DMSO-d_6.

CH_2O group formed from the oxazolinium ring is seen because the molecular weight of the cooligomer is not too high. The CH_2O signal represents the presence of Na salt of β-[(β-hydroxyethyl)amino]ethanesulfonic acid **4**. The other methylene signals of **4** overlap with those of **3**.

The assignment was further confirmed by the comparison of the spectrum of the alkaline hydrolysis mixture (Figure 4a) with that of an equimolar mixture of Na salts of an authentic sample of **3** and acetic acid in NaOH–D_2O solution (Figure 4b). It is evident that the spectra (Figures 4a and 4b) resemble each other. **3** was prepared by the reaction of ethylenediamine and ethylenesulfonic acid, mp 88 °C. Anal. Calcd for $C_4H_{12}N_2O_3S$: C, 28.57; H, 7.19; N, 16.65; S, 19.06. Found: C, 28.31; H, 7.33; N, 16.38; S, 19.00.

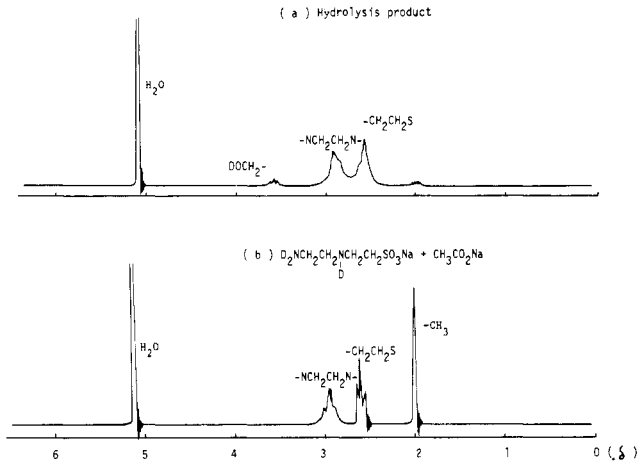
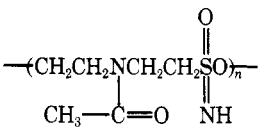


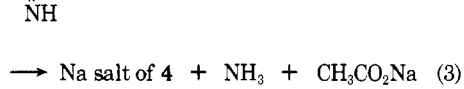
Figure 4. NMR spectra of (a) the alkaline hydrolysis product of the MeOZO–ESAm cooligomer and (b) a mixture of Na salts of **3** and of acetic acid in D_2O.

The oligomerization of **2** was also carried out in $PhNO_2$ solvent and without solvent (Table II). The oligomerization in solvent gave oligomer of higher molecular weight than that without solvent because of the high viscosity during reaction at 150 °C in the latter case.

There are two possibilities for the structure of the cooligomer unit derived from MeOZO and ESAm, the amide–sulfonamide **1** and the amide–sulfilimine **5** structures. However, no detection of NH_3 (by Nessler's reagent) in the alkaline hydrolysis products is taken to exclude the possibility of structure **5**.

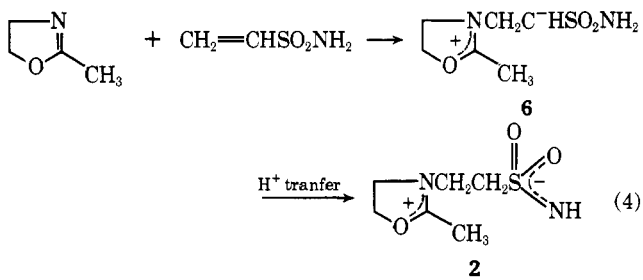


5



(3)

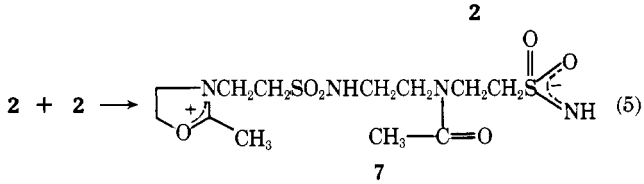
Cooligomerization Mechanism. On the basis of the above data a zwitterion mechanism below is proposed to rationalize the present cooligomerization. The course of the MeOZO–ESAm cooligomerization is schematically formulated in eq 4–6.



6

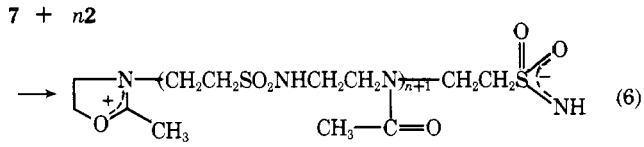
(4)

2



(5)

7



(6)

1

The first step is the formation of a Michael adduct **6** from MeOZO and ESAm, which is followed by a proton-transfer

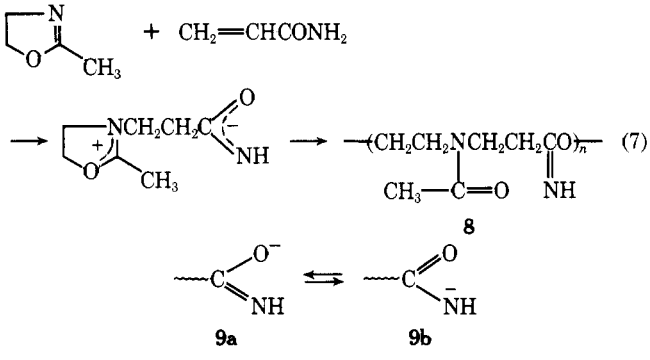
Table II
Oligomerization of Zwitterion 2 at 150 °C

No.	Solvent	Time, h	Mol wt[a]	
6	DMF	120	911	Yield > 90%
7	$PhNO_2$	130	887	MeOZO/ESAm = 1.00[b]
8	none	258	390	

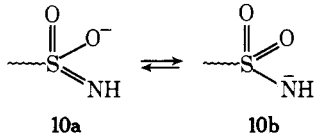
[a] Determined by VPO in DMF at 55 °C. [b] Determined by the % S content and NMR spectroscopy.

process. The formation of **2** is very rapid compared with the subsequent steps of eq 5 and 6. Then, two molecules of **2** afford a dimeric zwitterion **7**. The propagation proceeds via the successive attack of **2** onto **7** to form a macrozwitterion **1**.

The present cooligomerization is interestingly compared with the copolymerization of acrylamide (AM) with MeOZO which gave a copolymer of the amide–imidate structure **8** via the regiospecific reaction at the oxygen anion **9a** of an ambident anion (**9a** ↔ **9b**).[6]

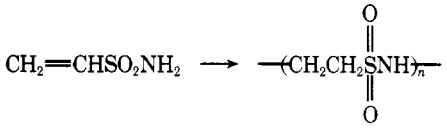


On the other hand, ESAm gives a sulfonamide unit in the oligomer **1** via the regiospecific reaction at the nitrogen anion **10b** of an ambident anion (**10a** ↔ **10b**).



10a **10b**

The sulfonamide anion of **2**, **7**, and **1** is an ambident anion of oxygen (**10a**) and nitrogen (**10b**). It should be noted that the regiospecific reaction took place exclusively at the nitrogen anion **10b** in eq 5 and 6 to give the sulfonamide unit. This fact is similar to the homopolymerization of ESAm by base catalysts first found by Breslow et al.[10] in which ESAm gave a polymer of the sulfonamide structure **11** via a hydrogen-transfer process.



11

Experimental Section

Reagents. MeOZO was purchased from Aldrich Chemical Co. and purified by distillation, bp 110 °C.[11] ESAm was synthesized according to the well-known method,[12] mp 24 °C (lit.[12] mp 24 °C). DMF was purified by distillation twice under nitrogen using CaH_2 as dehydrating agent. Benzonitrile, acetonitrile, and nitrobenzene were distilled on P_2O_5 under nitrogen.

β-[(β-Aminoethyl)amino]ethanesulfonic acid (**3**) was prepared by the reaction of an excess of ethylenediamine with ethylenesulfonic acid at 110 °C for 5 h and purified by thin layer chromatography: mp 88 °C; ir 1630 cm^{-1} (ν_{N-H}), 1200 and 1045 cm^{-1} (SO_2 bands).

β-[(β-Hydroxyethyl)amino]ethanesulfonic acid (**4**) was obtained by the reaction of an excess amount of monoethanolamine with ethylenesulfonic acid at 120 °C for 3 h as a white hygroscopic solid: mp 189 °C; ir 1200 and 1045 cm^{-1} (SO_2 band).

Cooligomerization Procedure. To 1.5 ml of solvent in a test tube MeOZO and ESAm (5.0 mmol each) were added at room temperature under nitrogen and the tube was sealed. The mixture was then kept at a desired temperature. After the reaction the tube was opened and the reaction mixture was poured into a large amount of diethyl ether to precipitate the cooligomer. A white glassy material was obtained after drying in vacuo.

Hydrolysis of Cooligomer. To 0.05 g of cooligomer was added 0.5 ml of 15% D_2O solution of NaOH at room temperature and the mixture was heated at 90 °C for 15 h. The reaction mixture was then subjected to NMR measurement.

References and Notes

(1) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 354 (1972).
(2) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **7**, 1 (1974).
(3) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **7**, 139 (1974).
(4) T. Saegusa, Y. Kimura, K. Sano, and S. Kobayashi, *Macromolecules*, **7**, 546 (1974).
(5) T. Saegusa, Y. Kimura, S. Sawada, and S. Kobayashi, *Macromolecules*, **7**, 956 (1974).
(6) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **8**, 374 (1975).
(7) T. Saegusa, S. Kobayashi, Y. Kimura, and H. Ikeda, *J. Macromol. Sci., Chem.*, **9**, 641 (1975).
(8) T. Saegusa, S. Kobayashi, and J. Furukawa, *Macromolecules*, **8**, 703 (1975).
(9) T. Saegusa, Y. Kimura, N. Ishikawa, and S. Kobayashi, *Macromolecules*, submitted.
(10) D. S. Breslow, G. E. Hule, and A. S. Mallach, *J. Am. Chem. Soc.*, **79**, 3760 (1957).
(11) T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, **4**, 87 (1973).
(12) (a) A. A. Goldberg, *J. Chem. Soc.*, 464 (1945); (b) A. S. Matlack, *J. Org. Chem.*, **23**, 729 (1958).