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Effects of Additives on the Alternating Copolymerization of Aziridines with Cyclic Imides

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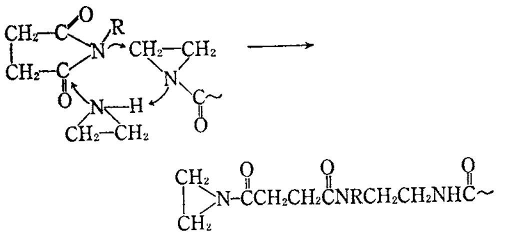
The effect of the addition of 2-methyl-2-oxazoline, which is an isomer of the growing chain end, was examined. The rate of the copolymerization of ethylenimine with succinimide increased upon the addition of 2-methyl-2-oxazoline. On the basis of this result and of the NMR spectrum of the copolymer, the mechanism of propagation *via* an activated state similar to oxazoline was proposed. The copolymerization was accelerated by the addition of sodium iodide, which is the catalyst of the isomerization of the growing chain end. The property of the copolymer obtained was different from that of the copolymer obtained without sodium iodide. Sodium iodide also affected the copolymerization of *N*-ethylethylenimine with succinimide, while it did not affect that of ethylenimine with *N*-ethylsuccinimide. The reduced viscosity of the copolymer increased with the reaction time. The reaction mechanism of the copolymerization in the presence of the catalyst was discussed on the basis of the facts mentioned above.

The present authors have previously reported[1,2] that the growing chain end in the alternating copolymerization of ethylenimine with cyclic imides was the *N*-acylethylenimine ring and that the propagation proceeded *via* a six-membered ring by means of the hydrogen migration of the ethylenimine and the ring opening of cyclic imide.



In this mechanism, it is also plausible that the oxygen atom of *N*-acylethylenimine coordinates to the hydrogen atom of ethylenimine. In relation to this coordination, it has been reported[3] that this growing chain end, *N*-acylethylenimine, easily isomerized to the oxazoline ring with a catalyst such as sodium iodide. In this isomerization, it is considered that the oxygen atom of the carbonyl group and the carbon atom of the ring coordinate

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[1] T. Kagiya, M. Izu, T. Adachi and K. Fukui, *J. Polym. Sci., Part A-1,* **7**, 2659 (1969).

[2] T. Kagiya, T. Adachi and K. Fukui, *ibid.*, **7**, 2651 (1969).

[3] T. Kagiya, S. Narisawa, T. Maeda and K. Fukui, *Kogyo Kagaku Zasshi*, **69**, 732 (1966).

to the cation and anion of the catalyst respectively.

In order to examine the coordination of the oxygen atom, the effect of the oxazoline or isomerization catalyst on the copolymerization was studied.

Experimental

The methods of preparing and purifying the monomers were described in a previous paper.[1] The 2-methyl-2-oxazoline was prepared by the isomerization of *N*-acetylethylenimine according to the literature.[3] The sodium iodide and *N*,*N*-dimethylformamide were obtained commercially (G.R. grade) and were used without further purification.

A measured amount of the cyclic imide and a solid additive were placed in a glass ampoule. After the mixture had been dried under reduced pressure, a certain volume of aziridine and a liquid additive were placed in the ampoule with a syringe under a nitrogen atmosphere. The ampoule was then sealed and kept in a constant-temperature bath for a definite period. The reaction products were washed with acetone to remove the residual monomers and then dried *in vacuo*.

The composition of the copolymer was determined by elementary analysis. The infrared spectra were obtained by the potassium-bromide-pellet technique on a Shimadzu infrared spectrophotometer, Model IR-27. The NMR spectra were recorded in D_2O at room temperature with JEOL model JNM-3H-60 at 60 MHz. The reduced viscosity of the copolymer was calculated from the viscosity measurement of a 0.5% solution of formic acid at 35°C.

Results and Discussion

(1) Effect of 2-Methyl-2-oxazoline. In order to examine the oxygen coordination mechanism described above, 2-methyl-2-oxazoline was added to the system of the copolymerization of ethylenimine with succinimide. The results are shown in Table 1.

TABLE 1. EFFECT OF ADDITION OF 2-METHYL-2-OXAZOLINE*

Expt. No.	2-Methyl-2-oxazoline g (mol)	Reaction time min	Yield g	Rate** g/min
1	—	24.0	1.808	0.075
2	0.051 (0.0006)	19.5	2.028	0.104
3	0.128 (0.0015)	11.5	2.037	0.177
4	0.255 (0.0030)	10.0	1.987	0.199
5***	*N*-Acetylethylenimine 0.256 (0.0030)	9.2	2.323	0.252

* Monomer: Ethylenimine 1.291 g (0.03 mol)
Succinimide 2.973 g (0.03 mol)
Reaction temperature: 70°C

** Reaction was stopped at almost the same yield, and a reaction rate was expressed in a value of yield divided by time.

*** Shown as a reference.

The copolymerization was accelerated by the addition of 2-methyl-2-oxazoline, and the copolymer obtained was a white, powdery polymer. The rate was almost the same as that of the copolymerization in the presence of the same amount of *N*-acetylethylenimine (Exp. No. 5). The NMR spectrum of the copolymer shown in Fig. 1-a displayed peaks which could be assigned to the methylene proton of the repeating unit, $-(-C\underset{a}{\underline{H}}_2C\underset{a}{\underline{H}}_2-NHCOC\underset{b}{\underline{H}}_2C\underset{b}{\underline{H}}_2-CONH-)-$, at $\tau=6.72$ (a), 7.48 (b).[1] It also displayed peaks assignable to the end groups of *N*-acylethylenimine ($\tau=7.56$) and *N*-substituted succinimide ($\tau=7.25$). The peak intensity of the latter was quite small compared with that in the spectrum (Fig. 1-b) of the copolymer obtained without additives. This phenomenon was also observed in the NMR spectrum (Fig. 1-c) of the copolymer obtained by the copolymerization of ethylenimine and succinimide in the presence of *N*-acetylethylenimine. Since the copolymer initiated by 2-methyl-2-oxazoline or *N*-acetylethylenimine has no amide end, it is difficult for the cyclization reaction[2] at the polymer end to form the structure of *N*-substituted succinimide to occur.

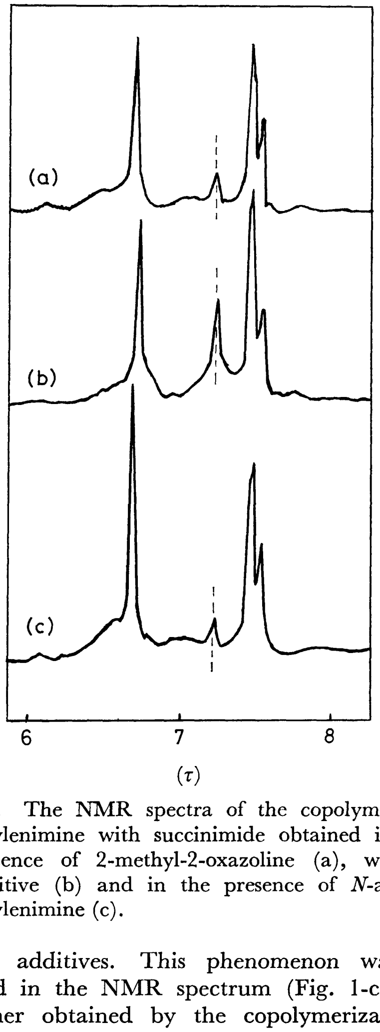
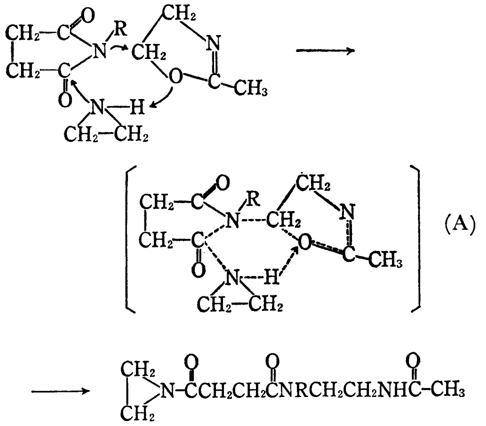
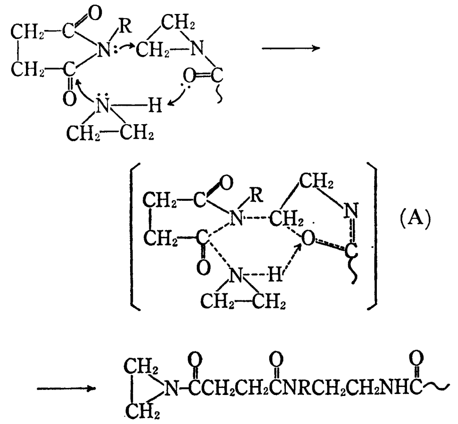


Fig. 1. The NMR spectra of the copolymers of ethylenimine with succinimide obtained in the presence of 2-methyl-2-oxazoline (a), without additive (b) and in the presence of *N*-acetylethylenimine (c).

On the basis of the facts that the acceleration by 2-methyl-2-oxazoline was almost the same as the acceleration by *N*-acetylethylenimine, that the peaks which should be assignable to the oxazoline ring were not observed in the spectrum (a) and that the structure of the copolymer was the same as the structure of the copolymer obtained in the presence of *N*-acetylethylenimine, the following mechanism for initiation by oxazoline is proposed: the oxazoline ring quickly opens *via* the activated state (A) and the *N*-acylethylenimine end is yielded. Moreover, the effect of 2-methyl-2-oxazoline on the copolymerization is similar to that of *N*-acetylethylenimine.



On the basis of the above consideration, the mechanism of the propagation reaction may be considered to be analogous: (i) it is not the nitrogen atom, but the oxygen atom, of the *N*-acylethylenimine end of polymer that coordinates to the hydrogen of ethylenimine, and (ii) the hydrogen-migration-propagation reaction proceeds *via* an activated state (A) similar to that in the oxazoline structure.



(2) Effect of Isomerization Catalyst. It has been reported that *N*-acylethylenimine is isomerized to oxazoline by a catalyst such as sodium iodide.[3] In case the reaction proceeds *via* the mechanism proposed above and the isomerization is the rate-determining step, it can be expected that the propagation reaction will be accelerated by the addition of sodium iodide. The results shown in Table 2 are in accordance with this expectation.

These findings seem to support the mechanism proposed above, but the copolymer obtained was a yellow or brown, hygroscopic or greasy polymer, and the properties of the copolymer were different from those of a copolymer obtained without sodium iodide. The infrared spectrum of the copolymer displayed the characteristic peaks of amide, but the NMR spectrum (Fig. 2) of the copolymer displayed an extra peak at $\tau=7.07$ which had not been found in the specturm of the copolymer shown in Fig. 1-b.

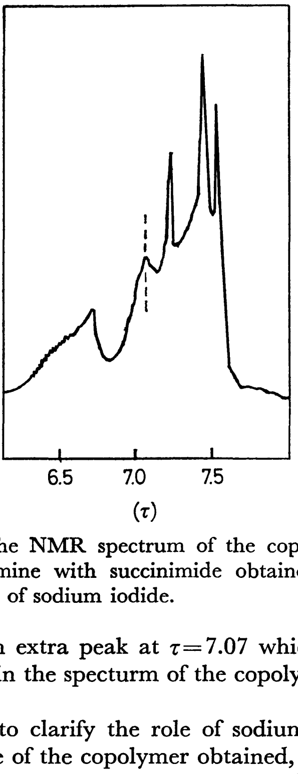


Fig. 2. The NMR spectrum of the copolymer of ethylenimine with succinimide obtained in the presence of sodium iodide.

In order to clarify the role of sodium iodide in the structure of the copolymer obtained, the following experiments were performed (Table 3). Ethylenimine or succinimide was not polymerized by sodium iodide. Moreover, *N*-acetylethylenimine neither copolymerized with succinimide nor homopolymerized in the presence of sodium iodide. Therefore, it can be concluded the structure of the copolymer is neither $-(-CH_2CH_2-\underset{\displaystyle CO\sim}{N}-COCH_2CH_2CONH-)-_n$ nor $-(-CH_2CH_2-\underset{\displaystyle CO\sim}{N}-)-_n$.

In view of the fact that sodium iodide acts as a catalyst of the isomerization of the *N*-acylethylenimine end to oxazoline, the reaction of succinimide with 2-methyl-2-oxazoline was carried out and examined, with particular care. From the

TABLE 2. EFFECT OF SODIUM IODIDE

Expt. No.	Monomers, g (mol)		NaI mol×10^4	Temp. °C	Time min	Yield g	Composition (mol%)		η_{sp}/c* dl/g
	Ethylenimine	Succinimide					Imine	Imide	
1	1.291 (0.03)	2.973 (0.03)	—	70	24.0	1.808	50.15	49.85	—
2	1.291 (0.03)	2.973 (0.03)	6	70	13.0	2.985	56.25	43.75	0.073
3	0.646 (0.015)	2.973 (0.03)	3	70	20.0	1.410	54.46	45.54	—
4	0.646 (0.015)	1.487 (0.015)	—	30	240	0.000	—	—	—
5	0.646 (0.015)	1.487 (0.015)	3	30	240	0.081	—	—	—
6	1.291 (0.03)	1.487 (0.015)	3	30	240	0.052	—	—	—
7	0.646 (0.015)	2.973 (0.03)	3	30	240	0.058	—	—	—
8	0.646 (0.015)	1.487 (0.015)	15	30	26.0	1.376	—	—	—

* 0.5% solution of formic acid at 35°C.

TABLE 3. REACTIVITIES OF POLYMERIZATION OF VARIOUS MONOMERS BY SODIUM IODIDE*

Expt. No.	Monomer** (mol)		Additive (mol)	Reaction time hr	Yield g
1	Ethylenimine (0.03)		NaI 0.0006	216	0.000
2***	Succinimied (0.01)		NaI 0.0002	44	0.000
3	AEI (0.01)	Succinimide (0.01)	—	119	0.000
4	AEI (0.01)	Succinimide (0.01)	NaI 0.0002	148	0.000
5	AEI (0.01)		NaI 0.0002 Succinimide 0.0002	216	0.000
6	AEI (0.01)		NaI 0.0002	41	0.000
7	Succinimide (0.01)	2-Methyl-2-oxazoline (0.01)	—	69	0.000

* Reaction temperature: 70°C

** AEI=*N*-Acetylethylenimine

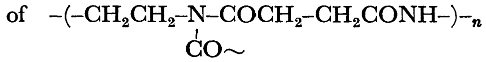
*** Solvent: Acetonitrile 5 cc

TABLE 4. EFFECT OF SODIUM IODIDE ON THE COPOLYMERIZATION OF *N*-SUBSTITUTED MONOMERS*

Expt. No.	Momoners (mol)**		NaI mol	Reaction time hr	Yield g
	Imine	Imide			
1	Ethylenimine (0.01)	ESI (0.01)	—	65	0.444
2	Ethylenimine (0.01)	ESI (0.01)	0.0005	70	0.465
3	EEI (0.01)	Succinimide (0.01)	—	170.5	0.000
4	EEI (0.01)	Succinimide (0.01)	0.001	70	0.133

* Reaction temperature: 70°C

** ESI=*N*-Ethylsuccinimide, EEI=*N*-Ethylethylenimine

fact that no polymer was obtained, it may be concluded that sodium iodide does not give the structure of  $-(-CH_2CH_2-\underset{CO\sim}{\underset{|}{N}}-COCH_2-CH_2CONH-)-_n$ which is that of the copolymer of succinimide with an oxazoline ring.

On the other hand, it is plausible that sodium iodide does not only affect the *N*-acylethylenimine, but also activates either succinimide or ethylenimine to give the copolymer with a different structure. In the light of the mechanism described above, the effect of sodium iodide on the copolymerization of ethylenimine with *N*-substituted succinimide was also examined (Table 4, Nos. 1 and 2). No effect was, however, observed. As has been mentioned in a previous paper.[2] *N*-ethylethylenimine did not copolymerize with succinimide. However, in the presence of sodium iodide, this copolymerization occurred to give a greasy polymer. This result is similar to that in the copolymerization of *N*-ethylethylenimine with succinimide by water.[2]

On the basis of these results, it may be considered that sodium iodide does not affect the ring opening of succinimide, but that it does affect the ring opening of ethylenimine to yield *N*-(*β*-aminoethyl)-succinimide, which is then able to give a polyamide by polyaddition reaction in analogy with the copolymerization by water.

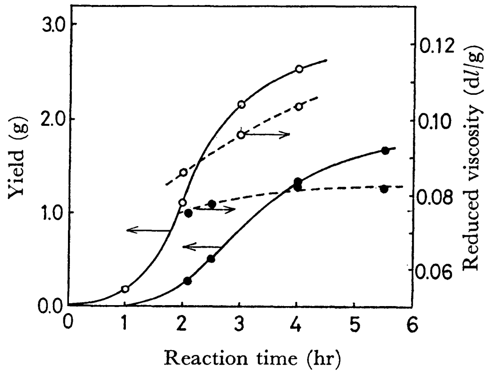
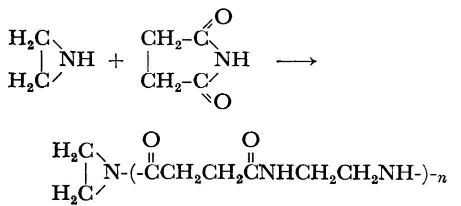


Fig. 3. The plots of polymer yield or reduced viscosity *vs.* reaction time.
Monomers: Succinimide 2.973 g (0.03 mol)
Ethylenimine 1.291 g (0.03 mol)
Additive: ○ NaI 0.0015 mol
● No additive
Solvent: *N*,*N*-Dimethylformamide 5 cc
Temperature: 70°C

The copolymerization of ethylenimine with succinimide was carried out quantitatively in an *N*,*N*-dimethylformamide solution in order to verify the polyaddition mechanism. The polymer yield and the reduced viscosity of the polymer obtained were then plotted against the reaction time (Fig. 3). In the early stage, an acceleration of the rate was observed. The reduced viscosity of the copolymer obtained in the absence of sodium iodide was almost constant regardless of the reaction time, while that obtained in the presence of sodium iodide increased. After the copolymer obtained by sodium iodide was again dissolved in *N*,*N*,-dimethylformamide and kept at 70°C for 47 hr, the reduced viscosity increased from 0.103 to 0.131 (d*l*/g). These two facts suggest that the reaction between polymers, namely, polyaddition reaction, occurs, at least in part.

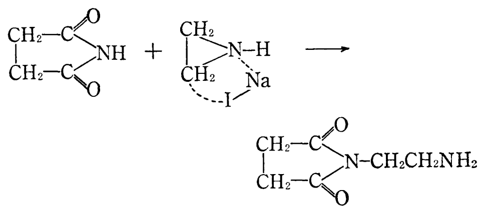
On the basis of the facts presented above, the following is proposed as a possible reaction mechanism in the presence of sodium iodide:

(i) The same reaction as that which occurs without a catalyst.

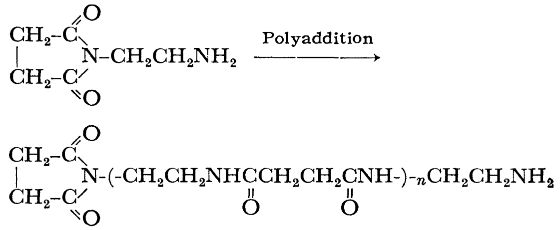


(I)

(ii) Polyaddition of *N*-(*β*-aminoethyl)succinimide. *N*-(*β*-Aminoethyl)succinimide is formed by the ring-opening reaction of ethylenimine with sodium iodide.

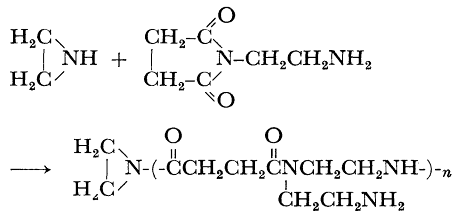


N-(*β*-Aminoethyl)succinimide is considered to give a polyamide by a polyaddition in which the ring of succinimide opens with amine.[2,4,5]



(II)

(iii) Copolymerization of ethylenimine with *N*-(*β*-aminoethyl)succinimide.



(III)

Since ethylenimine is able to copolymerize with *N*-substituted succinimide, *N*-(*β*-aminoethyl)succinimide may be considered to act as an active *N*-substituted succinimide.

The NMR spectrum of the copolymer obtained by sodium iodide at 30°C displayed the peak assigned to *N*-acylethylenimine. On the other hand, at 30°C, the copolymerization without sodium iodide did not occur (*cf.* Table 2, No. 4). This indicates that the (i) reaction did not occur. Therefore, the *N*-acylethylenimine end was considered to be produced by the reaction (iii). Moreover, the peak of the NMR spectrum at $\tau=7.07$ in Fig. 2 might be assignable to the methylene proton of the *N*-(*β*-aminoethyl) group.

Therefore, it may be concluded that the copolymer obtained by a catalsyt of the isomerization of *N*-acylethylenimine, such as sodium iodide, is a mixture of the copolymers (I), (II), and (III).

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[4] T. V. Sheremeteva, V. A. Gusinskaya and V. V. Kudryavtsev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1963**, 1821; *Chem. Abstr.*, **60**, 2809 (1964).

[5] T. Kagiya, S. Narisawa, K. Manabe, M. Kobata and K. Fukui, *J. Polym. Sci., Part A-1*, **4**, 2081 (1966).