The Preparation of Poly(ethylene N,N′-Disubstituted Ureas) by the 1,4-Addition Type Ring-opening Polymerization of 2-Imino-1,3-oxazolidines

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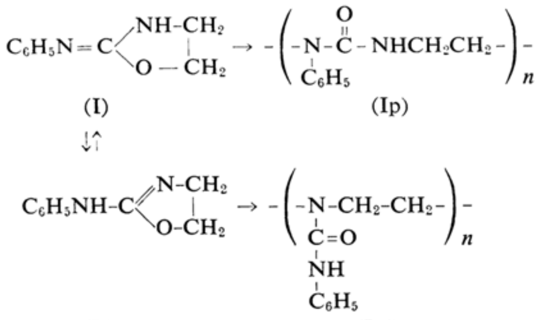
A new type of ring-opening polymerization of ethylene iminocarbonates, cyclic ketene acetals and 2-iminotetrahydrofurans, to give polyurethans, polyesters and polyamides respectively, has been reported in preceding papers.[1,2] It was shown there that the polymerization of 2-phenylimino-1, 3-oxazolidine (I) gives a polymer with urea linkage; however, both the melting temperature and the intrinsic viscosity of the resulting polymer are low. Moreover, a troublesome problem remained concerning the structure of the polymer, since there are two possible pathways for the polymerization to yield poly(ethylene *N*-phenyl urea) (Ip) and the polyethylene imine-type polymer (Ip′), which have been attributed to the existence of two tautomeric forms, 2-phenylimino-1, 3-oxazolidine (I) and 2-anilino-2-oxazoline (I′), respectively. In this connection, in the present investigation, the polymerizations of 2-imino-3-substituted-1, 3-oxazolidines, which have no labile hydrogen atom at the 3-position, have been studied in order to establish the ring-openig polymerization which yields polyureas of the type Ip.



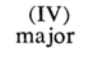
Several methods for the preparation of *N*, *N*′-disubstituted-2-imino-1, 3-oxazolidines (III) have been reported: from β-hydroxyethyl thioureas by the action of mercuric oxide,[3] from guanidinoethanols by refluxing in xylene,[4] or from β-chloroethylureas by the action of potassium hydroxide.[5] Although the last route seems to be the most convenient, the yields of the desired compounds are low, and the corresponding cyclic ureas IV have resulted as main products.

It has now been found that II gives the cyclic pseudo ureas III in good yields when treated with hot water and neutralized with sodium hydroxide.

On the other hand, the cyclic pseudo ureas with an unsubstituted imino group (III, R=H) were prepared from ethanolamines and cyanogen bromide through the hydrobromides.[6]

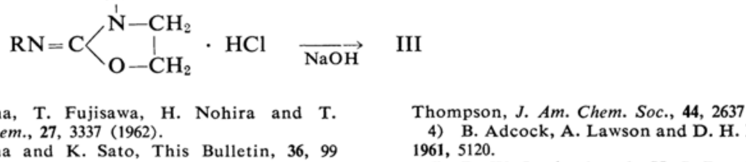
When III was heated with benzoic acid in benzene, ring-opening adducts V were obtained in fairly good yields.

$$\mathrm{III} + C_6H_5COOH \rightarrow$$



$$RNH\text{-}\overset{O}{\overset{\|}{C}}\text{-}NR'CH_2CH_2\text{-}O\overset{O}{\overset{\|}{C}}C_6H_5$$

(V)



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[1] T. Mukaiyama, T. Fujisawa, H. Nohira and T. Hyugaji, *J. Org. Chem.*, **27**, 3337 (1962).

[2] T. Mukaiyama and K. Sato, This Bulletin, **36**, 99 (1963).

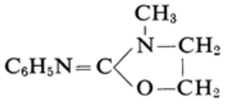
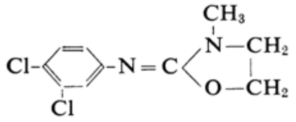
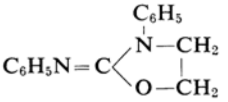
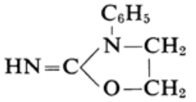
[3] F. B. Dains, R. Q. Brewster, J. S. Blair and W. C. Thompson, *J. Am. Chem. Soc.*, **44**, 2637 (1922).

[4] B. Adcock, A. Lawson and D. H. Miles, *J. Chem. Soc.*, **1961**, 5120.

[5] R. W. Luckenbaugh, U. S. Pat. 2902356 (1959).

[6] J. T. Thurston, U. S. Pat. 2479525 (1949).

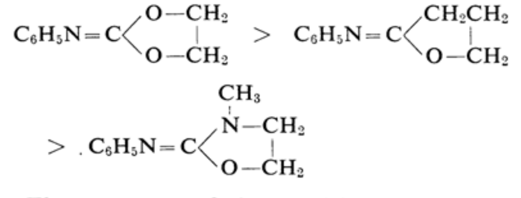
TABLE I. BULK POLYMERIZATION OF 2-IMINO 1, 3-OXAZOLIDINES (III)

Monomer	Polymerization conditions				Properties of polymers		
	Catalyst	%	Temp. °C	Time hr.	Yield %	P. M. T. °C	$[\eta]^{30°}_{\text{chloroform}}$
	BF_3[E]	1.0	120	4	90(a)	187～190	0.14
	BF_3[O]	1.0	140	3	95(b)	190～193	0.26
	BE_3[O]	1.0	160	2	95(b)	184～187	0.20
					63(a)	184～187	0.33
	BF_3[E]	0.3	85	36	90(b)	125～140	0.06
	$AlCl_3$	0.3	85	36	20(b)	125～140	—
	$TiCl_4$	0.3	85	36	20(b)	105～140	—
	BF_3[E]	1.1	140	1	85(c)	345～350	0.50 (*m*-cresol)
	BF_3[O]	1.1	160	0.33	100(c)	350～353	0.33 (*m*-cresol)
	BF_3[O]	0.2	160	1	60(c)	348～355	0.55 (*m*-cresol)
	BF_3[E]	1.0	140	4	50(d)	130～160	0.10
	H_2SO_4	1.0	140	4	40(d)	120～140	0.05
	BF_3[O]	1.0	160	3	80(d)	100～130	0.03

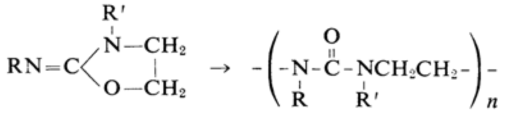
P. M. T., Polymer melting temperature; BF_3[E], Boron trifluoride etherate; BF_3[O], Boron trifluoride 2-imino-3-phenyl-1, 3-oxazolidine complex (VI); (a)—(d): reprecipitating media (a), chlroform-acetone; (b), chloroform-petroleum ether; (c), *m*-cresol-acetone; (d), chloroform-ether

This reaction is similar to those of ethylene iminocarbonates or 2-iminotetrahydrofurans with acids reported in the previous papers,[1,2] and it suggests the possibility of a 1, 4-addition type ring-opening polymerization of the iminooxazolidines.

Successful ring-opening polymerizations of the iminooxazolidines in question were carried out when these oxazolidines were heated in the presence of a cationic catalyst such as boron trifluoride etherate at a temperature between 85 and 160°C. Higher temperatures were necessary for this polymerization than for the polymerization of the ethylene iminocarbonates (25～100°C) and the 2-iminotetrahydrofurans (60～100°C). This result agrees with that of a kinetic study[7] of the 1, 4-addition type ring-opening reaction of three typical cyclic imino-compounds with carboxylic acids, where the order of the reactivities was shown to be as follows:



The structure of the resulting polymers was confirmed to be of the polyethylene-urea-type (IIIp) by means of infrared spectroscopy. That is, the monomers show an absorption in the range 1670～1680 cm^{-1} due to the exo-imino group of the five-membered ring, while all polymers absorb at the region about 1650 cm^{-1}, the same region as that where non-cyclic substituted ureas absorb.



(III) (IIIp)

The polymerization conditions and properties of the resulting polymers are listed in Table I.

2-Phenylimino-3-phenyl-1, 3-oxazolidine (III, R, R′ = C_6H_5) gave a hard, tough polymer with a fairly high polymer-melting temperature of 350°C. It was soluble in *m*-cresol, but insoluble in acetone, chloroform, methylene dichloride and dimethylsulfoxide. These properties may be attributable to the high density and to the symmetrical arrangement of phenyl groups along the ethylene urea linkages. The unsubstituted imino oxazolidine (III, R = H, R′ = C_6H_5–) gave a polymer with a low polymer melting temperature and a low viscosity in low yields. In addition, the oxazolidine was found to give a stable complex with boron trifluoride when it was mixed with boron trifluoride etherate in a dilute ether solution:

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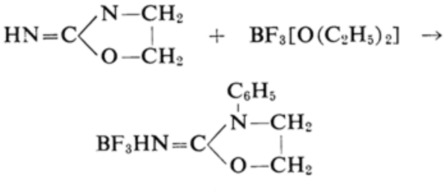
7) T. Mukaiyama, Y. Tamura and T. Fujisawa, This Bulletin, 37, 628 (1964).



(VI)

The difficulty of the polymerization of the oxazolidine may be connected with the stability of the complex VI as this complex can be weighed in small quantities, an attempt was made to use this as a catalyst in the polymerization of the other disubstituted imino oxazolidines. It was found that the complex VI was as effective as boron trifluoride etherate in these polymerizations.

2-Imino-3-methyl-1, 3-oxazolidine (III, R=H, R'=CH_3) did not give any solid polymers, even when it was heated at 120°C for 5 hr.

Experimental

1-(2-Chloroethyl)-3-phenyl-1-methyl Urea (II, R=C_6H_5, R'=CH_3) and 1-(2-Chloroethyl)-3-(3, 4-dichlorophenyl)-1-methyl Urea (II, R=3, 4-$Cl_2C_6H_3$, R'=CH_3).—These compounds were prepared from the corresponding hydroxyethyl ureas and thionyl chloride according to the methods described in the patent literature.5)

By an analogous method, 1-(2-chloroethyl)-1, 3-diphenyl urea (II, R, R'=C_6H_5) was obtained from 1-(2-hydroxyethyl)-1, 3-diphenyl urea (which had been prepared from phenyl isocyanate and *N*-phenyl ethanolamine in dioxane as a viscous liquid) and thionyl chloride in a 65% yield. It was recrystallized from ligroin (70 parts) and benzene (30 parts). M. p. 71°C.

Found; C, 65.43, H, 5.47; N, 10.43. Calcd. for $C_{15}H_{15}ClN_2O$: C, 65.57, H, 5.50; N, 10.19.

2-Phenylimino 3-Methyl 1, 3-Oxazolidine (III, R=C_6H_5, R=CH_3).—Eleven grams of 1-(2-chloroethyl)-3-phenyl-1-methyl urea was heated with 50 ml. of water with vigorous stirring in a boiling water bath for 30 min. After cooling, the solution was neutralized with aqueous sodium hydroxide. The precipitate was recrystiallized from ligroin. Yield, 7.2 g. (80%); m. p. 74.5~75.5°C (lit.4) m. p. 82°C). The infrared spectrum (KBr) showed strong absorptions at 1678 cm^{-1} (N=C) and 1039 cm^{-1} (O−C).

Found: C, 68.16, H, 6.86; N, 15.90. Calcd. for $C_{10}H_{12}N_2O$: C, 68.01, H, 7.04; N, 16.10%.

2-(3, 4-Dichlorophenylimino)-3-methyl-1, 3-oxazolidine (III, R=3, 4-$Cl_2C_6H_3$, R'=CH_3) was prepared in the same way. Yield, 80%; m. p. 64~65°C (lit.5) m. p. 45~47°C). The infrared spectrum (KBr) showed strong absorptions at 1673 cm^{-1} (N=C) and 1035 cm^{-1} (O−C).

Found: N, 11.58. Calcd. for $C_{10}H_{10}Cl_2N_2O$; N, 11.43%.

2-Phenylimino-3-phenyl-1, 3-oxazolidine (III, R, R'=C_6H_5).—This compound was also prepared by a similar method except for the use of a larger amount of water: Ten grams of 1-(2-hydroxyethyl-1, 3-diphenyl urea was heated with 500 ml. of water for one hour. It was then recrystallized from ligroin. Yield, 5.6 g. (65%); m. p. 124°C. A strong absorption due to the imino group appeared at 1679 cm^{-1} (KBr) in the infrared spectrum. This material was identical in all respects with a sample prepared from 1-(2-hydroxyethyl)-1, 3-diphenyl thiourea and mercuric oxide3).

2-Imino-3-phenyl-1, 3-oxazolidine (III, R=H, R'=C_6H_5) and 2-Imino-3-methyl-1, 3-oxazolidine (III, R=H, R'=CH_3).—These compounds were prepared by the method of Thurston6) except for the use of cyanogen bromide instead of cyanogen chloride.

2-Imino-3-phenyl-1, 3-oxazolidine: Yield, 46%; m. p. 99~100°C, after recrystallization from ligroin (lit.6) m. p. 99~100°C).

2-Imino-3-methyl-1, 3-oxazolidine: Yield, 50%; b. p. 56~57°C 3 mmHg. Found: C, 47.80, H, 8.29; N, 26.74. Calcd. for $C_4H_8N_2O$: C, 47.98, H, 8.05; N, 27.98%.

Ring-opening Adducts of the Imino Oxazolidines with Benzoic Acid. (V)—A mixture of 2-phenylimino-3-methyl-1, 3-oxazolididine (1.0 g.) and benzoic acid (0.85 g.) in 5 ml. of dry benzene was refluxed for 2 hr. The solvent was removed under reduced pressure, and the residual 1-(2-benzoyloxyethyl)-3-phenyl-1-methyl urea (V, R=C_6H_5, R'=CH_3) was washed with aqueous sodium carbonate. It was then recrystallized from ligroin and benzene; yield, 1.1 g. (65%); m. p. 116~117°C. The infrared spectrum (KBr) showed strong absorptions at 1720 cm^{-1} (C=O of ester linkage) and at 1646 cm^{-1} (C=O of urea linkage).

Found: C, 67.42, H, 6.09; N, 9.67. Calcd. for $C_{17}H_{18}N_2O_3$: C, 68.44, H, 6.08; N, 9.39%.

Similarly, 1-(2-benzoyloxyethyl)-3-(3, 4-dichlorophenylimino)-1-methyl urea (V, R=3, 4-$Cl_2C_6H_3$-, R'=CH_3) was obtained from 2-(3, 4-dichlorophenylimino)-3-methyl-1, 3-oxazoline and benzoic acid in a 60% yield (m. p. 103~104°C) after recrystallization from ligoin and benzene. The infrared spectrum (KBr) showed strong absorptions at 1720 cm^{-1} (C=O of ester linkage) and at 1650 cm^{-1} (C=O of urea linkage).

Found: C, 55.86, H, 4.47; N, 7.80, Calcd. for $C_{17}H_{16}Cl_2N_2O_3$: C, 55.60, H, 4.36; N, 7.83%.

The Boron Trifluoride Complex of 2-Imino-3-phenyl-1, 3-oxazolidine (VI).—To a 2% solution of 2-imino-3-phenyl-1, 3-oxazolidine in dry ether cooled in an ice water bath was added, an equivalent amount of boron trifluroride etherate. The resulting precipitate was filtered and washed with dry ether. The yield was almost quantitative. It is very sensitive to moisture and easily deliquesces. It melts at the range 97~105°C.

Found: N, 11.70. Calcd. for $C_9H_{10}N_2OBF_3$: N, 12.17%.

Polymerizations of the above mentioned imino oxazolidines were carried out in bulk polymerizations. The catalysts, polymerizing temperature and time, reprecipitating media, yields, melting temperature and intrinsic viscosities are shown in Table I. The infrared spectra (KBr) of poly(ethylene *N*-phenyl-*N'*-methylurea), poly[ethylene

N-(3, 4-dichlorophenyl) *N'*-methylurea] and poly(ethylene *N*, *N'*-diphenylurea) showed strong absorptions at 1648 cm^{-1}, 1647 cm^{-1} and 1659 cm^{-1} respectively. These are attributable to the noncyclic disubstituted urea linkages.

Summary

Various 2-imino-1, 3-oxazolidines have been prepared from β-chloroethylureas or from ethanolamines and cyanogen bromide.

N, *N'*-Disubstituted 2-imino-1, 3-oxazolidines give poly(ethylene *N*, *N'*-disubstituted ureas) by 1, 4-addition type ring-opening polymerization in the presence of a cationic catalyst such as boron trifluoride etherate. On the other hand, 2-unsubstituted imino-1, 3-oxazolidines polymerize with difficulty and give polymers with low melting temperatures.

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