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The Preparation of Poly(Ethylene Carbamate)

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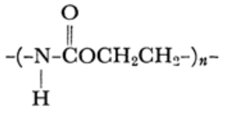
Poly(ethylene *N*-chlorocarbamate) was obtained by the 1, 4-addition-type ring-opening polymerization of ethylene *N*-chloroiminocarbonate with cationic catalysts, such as boron trifluoride etherate or sulfuric acid. Although it is an amorphous, tough elastomer, it is unstable in the air and decomposes to a brittle, pumiceous polymer. The reductions of poly(ethylene *N*-chlorocarbamate) by means of an aqueous solution of arsenic trioxide, butanol-zinc powder, *t*-butanol, and fluorene gave poly(ethylene carbamate), which is a new, stable, hydrogen-bonded polymer.

On the basis of a series of previous studies concerning 1, 4-addition-type ring-opening polymerization,[1-5] it is expected to prepare a new polymer, *i. e.*, poly(ethylene carbamate), which has a strong hydrogen bond in its intermolecules, as the following formula:



$$-(-\underset{\displaystyle H}{\underset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}OCH_2CH_2-)_n-$$

This polymer could be prepared neither by a ring-opening polymerization of cyclic urethane, oxazolidone-2,[6] nor by a condensation polymerization

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

2) T. Fujisawa, Y. Tamura and T. Mukaiyama, This Bulletin, **37**, 793 (1964).

3) T. Mukaiyama and K. Sato, *ibid.*, **36**, 99 (1963).

4) H. Nohira, Y. Nishikawa and T. Mukaiyama, *ibid.*, **37**, 797 (1964).

5) T. Mukaiyama, I. Kuwajima and K. Mizui, *J. Org. Chem.*, **31**, 32 (1966).

6) M. Crowther and W. R. Nummy, U. S. Pat. 2806839; *Chem. Abstr.*, **52**, 4305 (1958).

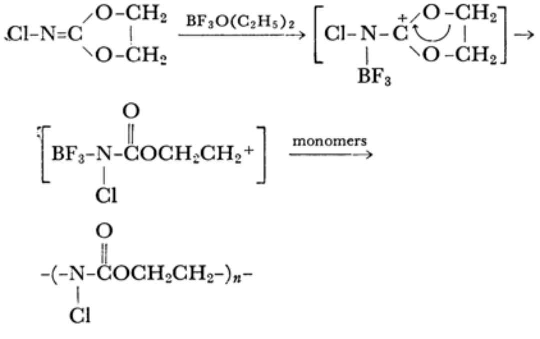
TABLE 1. ELEMENTARY ANALYSIS OF POLY(ETHYLENE *N*-CHLOROCARBAMATE) OF A BRITTLE, PUMICEOUS STATE

	Catalyst	C, %	H, %	N, %
Found	$BF_3O(C_2H_5)_2$	33.61	4.54	12.50
	H_2SO_4 (95%)	30.76	4.03	11.56
Calcd for	$-(-NClCOOCH_2CH_2-)_n-$	29.65	3.29	11.52
	$-(-NHCOOCH_2CH_2-)_n-$	41.38	5.79	16.09

of such a monomer as β-hydroxyethylcarbamic acid.

It has been reported that the *N*-unsubstituted monomer of the 1, 4-addition-type ring-opening polymerization, *i. e.*, ethylene iminocarbonate, could not be isolated.²⁾ In the present experiment, a new route for the preparation of the polymer was successfully established by a reduction of poly(ethylene *N*-chlorocarbamate), which had been obtained by the 1, 4-addition-type ring-opening polymerization of ethylene *N*-chloroiminocarbonate.

Ethylene *N*-chloroliminocarbonate was prepared by the reaction of potassium cyanide with ethylene glycol and chlorine in an alkaline solution. When a solution of the iminocarbonate in chloroform was allowed to stand at 30°C for 10 days in the presence of a catalytic amount of boron trifluoride etherate, a polymer was obtained and was characterized as poly(ethylene *N*-chlorocarbamate) by its infrared spectrum, which has a strong absorption band at 1720 cm^{-1} attributable to urethane linkage, whereas the iminocarbonate has no absorption in this region. This result suggests that the polymerization of ethylene *N*-chloroiminocarbonate proceeds by a 1, 4-addition-type ring-opening polymerization similar to those of ethylene *N*-phenyliminocarbonate,¹⁾ 2-imino-1, 3-oxazolidines,⁴⁾ and 2-iminotetrahydrofurans.³⁾



It was found that the polymerization of the iminocarbonate was greatly influenced by the reaction conditions and the catalysts. When the bulk polymerization of ethylene *N*-chloroiminocarbonate was tried in the presence of boron trifluoride etherate at room temperature, the reaction mixture exploded, resulting in a dark brown tar. The iminocarbonate was also explosively decomposed when it was heated at a temperature above 160°C. On the other hand, the solution polymerization of the iminocarbonate initiated by boron trifluoride etherate at 30°C was successfully carried out in such solutions as chloroform and tetrachloroethane to give poly(ethylene *N*-chlorocarbamate). The monomer was recovered, however, when the polymerization was attempted in toluene, dimethylformamide, and *t*-butanol solutions.

Further, the effect of catalysts was examined in a chloroform solution at 30°C. The yield of the polymer was quantitative with boron trifluoride etherate and 20% with sulfuric acid, and the monomer was recovered with such catalysts as titanium tetrachloride, stannic chloride, aluminum chloride, formic acid, and phosphorus pentoxide, which are good initiators in the polymerization of ethylene *N*-phenyliminocarbonate.¹⁾ In the absence of a catalyst, no noticeable polymerization occurred even when the solution was refluxed. The difference in the reactivities between ethylene *N*-chloro- and *N*-phenyliminocarbonates, which is also found in the reactions with acid,²,⁷⁾ can be explained in terms of the difference in the basicities of the imino groups in the iminocarbonates.

The poly(ethylene *N*-chlorocarbamate) thus obtained is an amorphous, tough elastomer after reprecipitation from ether. This polymer is comparatively unstable in the air, and it is gradually decomposed to yield a brittle, pumiceous polymer with the loss of chlorine. The infrared absorption spectrum of the pumiceous polymer showed characteristic bands in the regions of 3400 and 1540 cm^{-1} attributable to the nitrogen-hydrogen linkage, whereas the amorphous polymer has no absorptions in these regions. The observed values of the elementary analysis (C, H and N) for the pumiceous polymer are between the theoretical values for poly(ethylene *N*-chlorocarbamate) and poly(ethylene carbamate), as is shown in Table 1. This evidence suggested that the chlorine atoms of poly(ethylene *N*-chlorocarbamate) are partially replaced by hydrogen atoms when kept standing in the air. The chlorine atoms are considered to be so-called active halogenes

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7) T. Mukaiyama, T. Fujisawa and T. Hyugaji, This Bulletin, **35**, 687 (1962); T. Mukaiyama, Y. Tamura and T. Fujisawa, *ibid.*, **37**, 628 (1964).

TABLE 2. THE REDUCTION OF POLY(ETHYLENE *N*-CHLOROCARBAMATE)

Reducing reagent	Poly(ethylene carbamate)					
	Yield, %	Decomp. p. °C	$[\eta]^{30°C}_{DMSO}$	Analysis		
				C, %	H, %	N, %
Arsenic trioxide	90	228	0.28	40.15	5.85	15.01
n-Butanol-Zn	90	215	0.17	40.67	5.31	16.14
t-Butanol-Zn	90	215	0.13	39.58	4.75	15.40
t-Butanol	95	215	0.14	40.00	5.96	15.54
Fluorene	90	227	0.20	40.63	5.63	16.00

TABLE 3. POLY(ETHYLENE CARBAMATE)

Polymerization condition of ethylene *N*-chloroimino-carbamate		Poly(ethylene carbamate)*					
Temp., °C	Time hr	Yield, %	Decomp. p. °C	$[\eta]^{30°C}_{DMSO}$	Analysis		
					C, %	H, %	N, %
100	1	90	177	0.24	39.29	5.74	16.41
	2	90	213	0.46	40.32	5.65	14.39
	3	80	223	0.25	38.65	4.95	15.68
50	5	95	212	0.13	40.93	5.72	15.49
	10	95	231	0.17	40.30	5.40	15.97
	20	80	247	0.72	40.54	5.86	15.61
30	20	95	223	0.10	40.78	5.76	14.55
	57	95	215	0.14	40.00	5.96	15.54
	1800	95	219	0.20	40.13	5.46	15.28

* Reduction of poly(ethylene *N*-chlorocarbamate) was carried out with *t*-butanol.

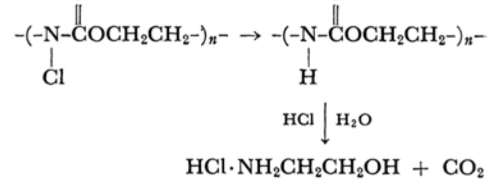
such as that of *N*-chlorosuccinoimide. Therefore, it may be expected that the reduction of poly(ethylene *N*-chlorocarbamate) would be smoothly conducted by various reducing reagents to give stable, hydrogen-bonded poly(ethylene carbamate).

The reduction of poly(ethylene *N*-chlorocarbamate) was carried out without any isolation of the polymer after ethylene *N*-chloroiminocarbonate had been polymerized at room temperature for 57 hr in a chloroform solution with boron trifluoride etherate initiation; when poly(ethylene *N*-chlorocarbamate) was stirred in an aqueous alkaline solution of arsenic trioxide, a white, powdered polymer was separated. Further, the reduction was successfully carried out by treating the polymer with *n*- or *t*-butanol and zinc powder. In these cases, no remarkable difference could be observed between *n*- and *t*-butanols. On the other hand, the reduction by *n*-butanol and triethylamine failed, resulting in a dark brown colored polymer.

It was found that reduction likewise took place, when poly(ethylene *N*-chlorocarbamate) was heated under refluxing in a large excess of *t*-butanol. Moreover, in order to establish milder reduction conditions, fluorene was chosen as the reducing reagent. When poly(ethylene *N*-chlorocarbamate) was kept standing at room temperature for 90 days with fluorene in chloroform, the white polymer was obtained in a good yield together with 9-chlorofluorene.

The reduction conditions, and the physical properties and elementary analysis of the resultant polymer are listed in Table 2. As shown there, the observed values of the elementary analysis of the reduced polymer almost coincide with the theoretical values for poly(ethylene carbamate). The infrared spectra of the polymer showed absorption bands attributable to the nitrogen-hydrogen linkage (3400 and 1540 cm^{-1}), urethane linkage (1700 and 1230 cm^{-1}), and methylene group (2900 and 1460 cm^{-1}).

The structure of the polymer was confirmed to be poly(ethylene carbamate) by its hydrolytic degradation, which was carried out by refluxing it in hydrochloric acid. This resulted in the formation of ethanolamine hydrochloride in a yield of 85% with the evolution of carbon dioxide.



$$-(\underset{\mathrm{Cl}}{\mathrm{N}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH_2CH_2}-)_n- \rightarrow -(\underset{\mathrm{H}}{\mathrm{N}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH_2CH_2}-)_n- \xrightarrow[\mathrm{H_2O}]{\mathrm{HCl}} \mathrm{HCl\cdot NH_2CH_2CH_2OH} + \mathrm{CO_2}$$

Poly(ethylene carbamate), which has the highest intrinsic viscosity (0.72 d*l*·g^{-1}), was obtained by the reduction of the poly(ethylene *N*-chlorocarbamate) prepared by the polymerization of ethylene *N*-chloriminocarbonate in a tetrachloroethane solution with boron trifluoride etherate initiation at 50°C for 20 hr, followed by refluxing in *t*-butanol for 5 hr.

The poly(ethylene carbamate) thus obtained was a white powder which was decomposed at 200—250°C without melting. The higher decomposition point of the reduced polymer than that of poly(ethylene *N*-chlorocarbamate) is presumably to be attributable to the hydrogen bond in its intermolecules. Poly(ethylene carbamate) was only soluble in dimethylsulfoxide; it was insoluble in other organic solvents and in water.

Experimental

The Polymerization of Ethylene *N*-Chloroiminocarbonate. Into a solution of 1.0 g of ethylene *N*-chloroiminocarbonate2) in 1 m*l* of dry chloroform there was added a catalytic amount of boron trifluoride etherate. After the solution had been allowed to stand at room temperature for 10 days, poly(ethylene *N*-chlorocarbamate) was reprecipitated from ether; yield, 0.98 g (98%); decomp. p. 60°C; $[\eta]^{30°C}_{CHCl_3}$ 0.14. Its infrared absorption bands are at 1720 (s), 1400 (s), 1380 (ms), 1340 (ms), 1230 (s), 1150 (s), and 1070 (s) cm^{-1}.

When the polymer was kept standing at room temperature in the air, the polymer gradually decomposed to yield a brittle, pumiceous polymer which has infrared absorption peaks at 3400 (m), 1720 (s), 1530 (m), 1400 (s), 1340 (ms), 1230 (ms), and 1070 (ms) cm^{-1}.

Similarly, poly(ethylene *N*-chlorocarbamate) was obtained in a yield of 20% by treating ethylene *N*-chloroiminocarbonate with a sulfuric acid initiator by the above method.

The Reductions of Poly(Ethylene *N*-Chlorocarbamate). The solution of poly(ethylene *N*-chlorocarbamate) employed in the course of the experiment on reductions was prepared by the following procedure: One gram of ethylene *N*-chloroiminocarbonate was polymerized in 1 m*l* of a chloroform solution with a catalytic amount of boron trifluoride etherate at room temperature for 57 hr; then the solution was diluted with 15 m*l* of chloroform.

The poly(ethylene carbamate) obtained in accordance with the following reductions was dissolved in 30 m*l* of dimethylsulfoxide and reprecipitated from methanol-ether. The polymer was dried *in vacuo* (0.01 mmHg) at 100°C. The yields, physical properties, and results of elementary analysis for poly(ethylene carbamate) are shown in Table 2. Its infrared absorption bands are at 3400 (s), 2900 (m), 1700 (s), 1540 (ms), 1460 (m), 1230 (s), and 1150 (ms) cm^{-1}.

By Arsenic Trioxide. The solution of poly(ethylene *N*-chlorocarbamate) in chloroform was added to a solution of 2.0 g of arsenic trioxide and 5.0 g of potassium hydroxide in 20 m*l* of water with vigorous stirring under ice cooling. Poly(ethylene carbamate) was separated from the reaction mixture and filtered.

By n- or t-Butanol and Zinc Powder. Into the chloroform solution of poly(ethylene *N*-chlorocarbamate) there were added 2.0 g of zinc powder and 5 m*l* of *n*- or *t*-butanol. The reaction mixture was then refluxed for 1 hr, and filtered. The residue was washed with ether and rinsed with dimethylsulfoxide at 50°C. The filtrate and washings were then collected and poured into water to precipitate poly(ethylene carbamate).

By t-Butanol. The chloroform solution of poly(ethylene *N*-chlorocarbamate) was diluted with 60 m*l* of *t*-butanol and refluxed on a water bath for 1 hr. After the polymer had been separated by the fractionation of chloroform, *t*-butanol was decanted off. The polymer was dissolved in 20 m*l* of dimethylsulfoxide and refluxed again in 60 m*l* of *t*-butanol. The same treatment as above was carried out 5 times to give completely reduced poly(ethylene carbamate).

The poly(ethylene *N*-chlorocarbamate) resulting from the polymerization of ethylene *N*-chloroiminocarbonate in chloroform solution with boron trifluoride etherate as an initiator under various reaction conditions was reduced by a method similar to that described above. The polymerization conditions, and the yields, physical properties, and results of elementary analysis for the reduced poly(ethylene carbamate) are indicated in Table 3.

By Fluorene. Into the solution of poly(ethylene *N*-chlorocarbamate) in chloroform there were added 2.0 g of fluorene. After it had stood at room temperature for 90 days, the solution was poured into ether to precipitate poly(ethylene carbamate).

The polymer was filtered off, and the filtrate was treated by column chromatography (Al_2O_3-ether) to separate 9-chlorofluorene, which was then recrystallized from petroleum ether; yield, 1.45 g; mp 90—91°C.

The Hydrolysis of Poly(Ethylene Carbamate). A mixture of 1.0 g of poly(ethylene carbamate) and 15 m*l* of 9 N of hydrochloric acid was refluxed on an oil bath for 20 hr, during this period carbon dioxide was generated; its identity was confirmed by the use of an aqueous solution of barium hydroxide. After the evaporation of the hydrochloric acid *in vacuo*, ethanolamine hydrochloride was solidified and recrystallized from methanol; yield, 1.4 g (85%); mp 75°C.

The authors wish to express their hearty thanks to Miss Toshiko Aoyagi for her microanalysis.