

Controlled-Release Pesticides : 1. Dithiocarbamate Derivatives

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Controlled-Release Pesticides

1. Dithiocarbamate Derivatives

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Poly(ethyleneimine *S*-alkyldithiocarbamate)s were prepared from poly(ethyleneimine sodium dithiocarbamate) and alkyl chlorides, aralkyl chlorides, substituted alkyl esters of chloroacetic acid, β -chloroethyl esters of carbamic and carboxylic acids, and *N*-substituted chlorocarboxamides, respectively. The poly(ethyleneimine) derivatives thus obtained were decomposed physically and chemically to release sulfur and sulfur-containing substances, and acted as controlled-release herbicides or fungicides.

INTRODUCTION

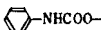
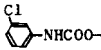
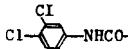
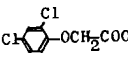
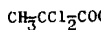
There are a lot of papers on the chemical modification of synthetic and natural polymers in the medicinal field (Ascoli *et al.*, 1967; Bichowsky-Slomnicki *et al.*, 1956 ; Cornel and Donaruma, 1965 ; Dumitru *et al.*, 1973). But, pesticidal polymers for controlled-release have not been studied well. Lately, roach tape (Plant, 1974), and others containing insecticides such as diazinon or chlorpyrifos in synthetic polymers were manufactured as controlled-release insecticides. On the other hand, controlled-release pesticides which can release active substances by chemical decomposition have been investigated by Allan *et al.* (1971) and others (Volkober and Varga, 1963). Beasley and Collins (1970) prepared controlled-release pesticide with a salt linkage. The authors prepared poly(ethyleneimine *S*-alkyldithiocarbamate)s which might be gradually decomposed in the field to give pesticidally active substances. To our knowledge, this is the first report on controlled-release pesticides which are polymers bound covalently with bioactive group.

MATERIALS AND METHODS

Preparation of alkyl chloride derivatives

β -Chloroethyl derivatives shown in Table 1 were synthesized by known methods. β -Chloroethyl *N*-alkyl or arylcarbamate was obtained from the reaction of alkyl or aryl isocyanate and ethylene chlorohydrin in dry tetrahydrofuran. The β -chloroethyl ester of 1,1-dichloropropionic acid and that of 2,4-dichlorophenoxyacetic acid were prepared from 1,1-dichloropropionyl or 2,4-dichlorophenoxyacetyl chloride and ethylene chlorohydrin in a dry tetrahydrofuran-pyridine mixture. *N*-(3',4'-dichlorophenyl)chloropropionamide was prepared from 3,4-

Table 1. β -Chloroethyl derivatives RCH_2-CH_2-Cl .

Compd. No.	R	Yield (%)	M.p., b.p.*	UV λ_{max}^{MeOH} nm (ϵ)	IR $\nu_{max}^{CHCl_3}$ (cm ⁻¹)			References
			("C") Recryst. Solvent					
1		83	47/THF	280(120) 234(3310)	3400, 1520, 990,	1730, 1440, 690	1601, 1300,	Sprinson (1941)
2		90	46/THF	276(220) 239(3360)	3400, 1600, 1270,	2950, 1520, 1090,	1730, 1420, 640	McKey and Braun (1951)
3		68	101/C ₆ H ₆	290(1410) 223(11490)	3400 1530, 1190,	3050 1490, 1110	1730 1340,	McKey and Braun (1951)
4		31	108/7mm*	205(80)	3450, 1510, 1030,	2950, 1240, 630	1730, 1230,	Sprinson (1941)
5		76	92/C ₆ H ₆	253(3840) 213(5030)	3400 1580, 650	3000 1510, 1080,	1680, 1080,	Good(1961)
6		16	171-6/7mm*	283(2270) 228(8490) 222(8440)	2900, 1430, 1100, 640	1760, 1300, 1090,	1480, 1180, 870,	McNew and Hoffmann (1950)
7		21	60-1/35mm*	206(443)	2950, 1240, 1000,	1750, 1120, 900,	1440, 1080, 650	Scheuerer <i>et al.</i> (1960)

dichloroaniline and β -chloropropionyl chloride at the molar ratio of 2 : 1 in dry benzene.

Chloromethyl derivatives shown in Table 2 were obtained on usual processes. *N*-(3',4'-dichlorophenyl) or alkyl chloroacetamide was synthesized from chloroacetyl chloride and 3,4-dichloroaniline or alkylamine at the molar ratio of 1 : 2 in dry benzene. 2,4-Dinitro-5-methyl-6-phenyl chloroacetate was prepared from sodium 2,4-dinitro-5-methyl-6-phenolate and chloroacetyl chloride in dry acetone.

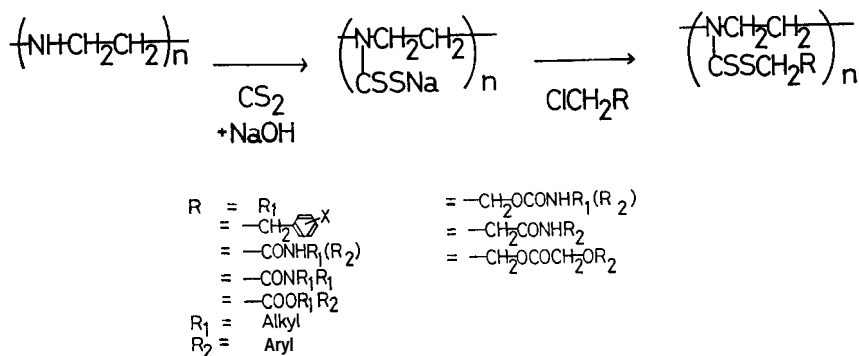
2-(*p*-Chlorophenoxy)ethyl chloroacetate was synthesized as follows ; sodium 2-(*p*-chlorophenoxy)ethylate was prepared from 25 g of 2-(*p*-chlorophenoxy)-ethanol and 3.3 g of metallic sodium in 200ml of dry benzene. Then, 16.2 g of chloroacetyl chloride was gradually added to the ethylate suspension at 0°–5°C, and the mixture was further stirred for 7 hours at room temperature avoiding moisture. Colorless precipitates formed were removed from the reaction mixture. The filtrate treated with activated carbon was evaporated under reduced pressure to give two oily layers. The lower layer was separated, washed with *n*-hexane and distilled at 160°–164°C (0.2 mm Hg) to give yellow oil. Anal. Found (%): C, 49.00; H, 4.13. Calcd. (%) for C₁₀H₁₀O₃Cl₃: C, 48.88; H, 4.08. Yield 31 %.

Table 2. Chloromethyl derivatives $\text{RCOCH}_2\text{-Cl}$.

Compd. No	R	Yield (%)	M.p., b.p.* (°C) Recryst. Solvent	UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm(ϵ)	IR $\nu_{\text{max}}^{\text{CHCl}_3}$ (cm^{-1})	References
8	$(\text{CH}_3)_2\text{CHNH-}$	70	82/4mm*	207(1370)	3400, 2950, 1660, 1520, 1470, 1410, 1260, 600	Fu and Birnbaum (1953)
9	$(\text{CH}_3\text{CH}_2)_2\text{N-}$	57	132/2.8mm*	219(4130)	2950, 1640, 1470, 1440, 1240, 1120, 650	Hannah(1955)
10		49	112/MeOH	242(6200)	3050, 1790, 1600, 1540, 1340, 1180, 1170, 910, 800	Bates <i>et al.</i> (1962)
11		30	160-4/0.2mm*	278(1550) 224(9270) 210(5180)	2950, 1760, 1600, 1490, 1280, 1240, 1170, 1090, 970, 820, 660	Clark <i>et al.</i> (1958)
12		41	106/ C_6H_6	253(3480) 214(450)	3350, 1690, 1580, 1510, 1480, 1130, 1020, 810, 610	Hofer(1959)

Synthesis of poly(ethyleneimine S-alkyldithiocarbamate)s

Twenty two poly(ethyleneimine S-alkyldithiocarbamate)s were prepared, as shown in Scheme 1, from poly(ethyleneimine sodium dithiocarbamate) and alkyl chlorides, benzyl chlorides, alkyl chloroacetates, and chloromethyl or β -chloroethyl derivatives containing pesticidal groups listed in Table 1 and 2, respectively. The reaction were carried out by heating the starting materials in dimethylformamide for several hours at 50°C with stirring. The isolation of the modified polymers was performed by precipitation (by adopting dimethylformamide-methanol, tetrahydrofuran, chloroform, ether and so on) in the addition of a small amount of saturated sodium chloride solution. The properties of these polymers obtained were shown in Table 3.

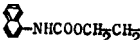
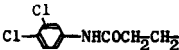
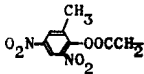
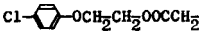
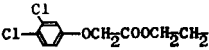


Scheme 1. General synthetic methods of polymers.

Table 3. Poly(ethyleneimine S-alkyldithiocarbamate) $\left(\begin{array}{c} \text{---}(\text{N-CH}_2\text{-CH}_2\text{---})\text{---} \\ | \\ \text{CSSR} \end{array} \right)_n$

Compd. No.	R	UV $\lambda_{\text{max}}^{\text{DMF}}(\text{nm})$	IR $\nu_{\text{max}}^{\text{KBr}}(\text{cm}^{-1})$	Analysis (%)	
				Found	
				N	Ash
13	$(\text{CH}_3)_2\text{CH-}$	281	3350, 2900, 1670, 1480, 1360, 1220, 1110, 980	11.99	---
14	$\text{CH}_2=\text{CHCH}_2$	282	3050, 2900, 1480, 1470, 1400, 1210, 1130, 980	11.67	
15	HOCH_2CH_2	281	3150, 2950, 1630, 1480, 1460, 1350, 1120, 980	11.19	+
16	$\text{CH}_3\text{CH}_2\text{OOCCH}_2$	288	3359, 2950, 1730, 1480, 1440, 1360, 1290, 1210, 1150, 1020	9.67	
17	$\text{CH}_2=\text{CHCH}_2\text{OOCCH}_2$	288	3350, 2900, 1720, 1630, 1480, 1400, 1320, 1210, 1130, 980	9.70	
38	$\text{O}_2\text{N-}\langle\text{C}_6\text{H}_4\rangle\text{-CH}_2$	279	2950, 1600, 1510, 1480, 1400, 1340, 1110, 990, 860	9.73	
19	$\text{Cl-}\langle\text{C}_6\text{H}_4\rangle\text{-CH}_2$	280	3150, 1480, 1400, 1210, 1090, 1020, 830	7.96	
20	$\text{Cl-}\langle\text{C}_6\text{H}_3\rangle\text{-CH}_2$	279	3150, 2900, 1470, 1460, 1400, 1210, 1120, 3030, 990	8.02	
21	$\text{H}_3\text{C-}\langle\text{C}_6\text{H}_4\rangle\text{-CH}_2$	275	3150, 2900, 1480, 1400, 1220, 1110, 1030, 990, 820	8.44	
22	$\langle\text{C}_6\text{H}_5\rangle\text{-COCH}_2$	281	3050, 2900, 1680, 1600, 1480, 1450, 1280, 1200, 980	7.98	
23	$\text{NO}_2\text{-}\langle\text{C}_6\text{H}_3\rangle\text{-CH}_2$ OH	281	3200, 2900, 1580, 1490, 1370, 1280, 1130, 1080, 820	12.09	
34	$\langle\text{C}_6\text{H}_5\rangle\text{-NHCOOCH}_2\text{CH}_2$	284	3350, 2900, 1720, 1660, 3570, 1510, 1480, 1350, 1290, 1140, 990, 800	15.20	
25	$\text{Cl-}\langle\text{C}_6\text{H}_4\rangle\text{-NHCOOCH}_2\text{CH}_2$	279	3250, 2950, 1720, 1650, 1600, 1480, 1440, 1310, 1070	15.81	---

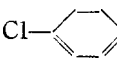
Table 3. (continued)

Compd. No.	R	UV $\lambda_{\max}^{\text{DMF}}$ (nm)	IR $\nu_{\max}^{\text{KBr}}$ (cm^{-1})	Analysis (%)	
				Found N	Ash
26		278	3200, 2900, 1720, 1660, 1590, 1480, 1210, 1160, 770	16.23	
27	$\text{CH}_3\text{NHCOOCH}_2\text{CH}_2$	283	3300, 2950, 1710, 1480, 1440, 1240, 1120, 980	16.22	††
28	$(\text{CH}_3)_2\text{CHNHCOCH}_2$	281	3250, 2950, 2100, 1640, 1530, 1360, 1160, 980	13.57	
29	$(\text{CH}_3\text{CH}_2)_2\text{NCOCH}_2$	283	3150, 2900, 2010, 1660, 1600, 1480, 1440, 1350, 1220, 980	13.81	
30		282	3200, 2900, 1650, 1580, 1480, 1370, 1230, 1120, 1020, 870	12.97	
31		283	3200, 2900, 2100, 1710, 1650, 1480, 1320, 1210, 1130, 980, 880	13.03	
32		285	2950, 1730, 1600, 1480, 1410, 1290, 1240, 1150, 1060, 990, 820	7.81	
33		288	3200, 2900, 1650, 1480, 1430, 1210, 1110, 1010, 830	13.88	
34	$\text{CH}_3\text{CCl}_2\text{COOCH}_2\text{CH}_2$	280	3300, 2950, 1720, 1480, 1400, 1220, 1210, 3140, 1010	13.22	

Poly(ethyleneimine sodium dithiocarbamate) was prepared from poly(ethyleneimine) (Tokyokasei Organic Chemicals), sodium hydroxide, and carbon disulfide (Okawara *et al.*, 1966). η_{sp}/c (0.5 % aq. soln., 20°C)=0.3830. Anal. Found (%): C, 26.40; H, 5.21; N, 10.44. UV $\lambda_{\max}^{\text{H}_2\text{O}}$ (nm): 292 (=N-C=S), 257(-CSSNa), UV $\lambda_{\max}^{\text{DMF}}$ (nm): 298 (=N-C=S). IR $\nu_{\max}^{\text{KBr}}$ (cm^{-1}): 3400-3000 (-NH-, hydrate -OH), 2900 (-CH₂-), 1630 (hydrate -OH), 1460 (=N-C=S), 1120 (C=S) (Fig. 1-B).

The content of dithiocarbamoyl group was determined by LJV spectrometry (12.4 mole %) and by the method of Clark *et al.* (Clark *et al.*, 1951) (14.3 mole %) or A. O. A. C.'s method (Horwitz, 1975) (17.5 mole %).

Poly(ethyleneimine S-[2-(*p*-chlorophenoxy)ethoxycarboxymethyl]dithiocarbamate) was synthesized as follows; when 50 ml of 10 % 2-(*p*-chlorophenoxy)-ethyl chloroacetate solution in dimethylformamide were added to 100 ml of 5 %

poly(ethyleneimine sodium dithiocarbamate) dimethylformamide solution, the mixture reacted exothermally resulting an orange solution (Braun und Engelbertz, 1923 ; Okawara *et al.*, 1966). The colored solution was stirred for 6 hours at 60°C to deposit sodium chloride and others. The reaction mixture cooled to room temperature was filtered off to separate the insoluble substances. The filtrate poured into 1.5 l of methanol was salted out with 10 ml of saturated sodium chloride aqueous solution to give orange precipitates. The precipitates were washed with water, methanol, and ether, then dried under reduced pressure. Yield 4.2 g. UV $\lambda_{\max}^{\text{DMF}}$ (nm): 285 (=N-C=S), IR $\nu_{\max}^{\text{KBr}}$ (cm⁻¹): 3350(-NH-), 2900, 1410(-CH₂-), 1720(-COOCH₂-), 1490, 1470 (-CH=CH-, =N-C=S), 1280-1240 (C1- <=> -OCH₂-), 1150 (-COOCH₂-), 1110 (C=S), 820 (2 substituted Cl--O-) (Fig. 1-A).

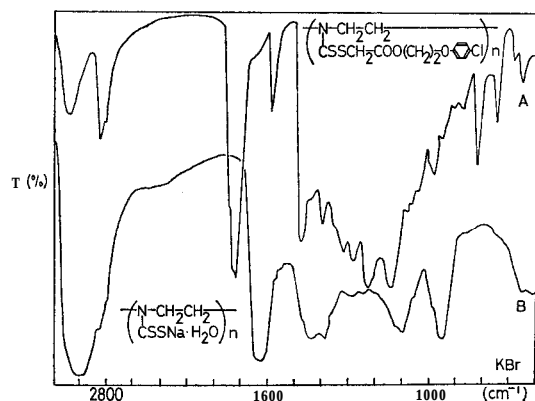


Fig. 1. IR spectra of poly[ethyleneimine S- [2-(*p*-chlorophenoxy)ethoxycarbonylmethyl] dithiocarbamate) (A) and poly(ethyleneimine sodium dithiocarbamate) (B).

Degradation of poly(ethyleneimine sodium or *S*-alkyldithiocarbamate)s by natural light

Dimethylformamide solution of poly(ethyleneimine sodium dithiocarbamate) and poly(ethyleneimine *S*-alkyldithiocarbamate)s were exposed to natural light in the door at room temperature for about 20 days to give a turbid solution and precipitates, and to release sulfur, some sulfur-containing substances and others. The decomposition products of *p*-methylbenzyl compound (21), for example, were detected by TLC (silicagel G, acetone, PdCl₂ or I₂) as 7 spots.

PESTICIDAL BIOASSAY

Herbicidal test

Forty grams of soil (weak acidic upland soil of Kyushu University Farm, pH 6.2) and 10 ml of water were mixed with a 0.2 % poly(ethyleneimine *S*-alkyldi-

thiocarbamate). Twenty seeds of radish (*Raphanus sativus* L. var. *radicular* Dc.) and barnyard millet (*Panicum crusgalli* L.) were respectively put in the treated soil. These plants grew under light keeping wet. The temperature was kept at 25°–28°C for radish and 30°–34°C for barnyard millet at 70–80 % humidity. The medium of barnyard millet was made wetter after germination. The herbicidal activity was defined as the average of growth damage (%) and germination (%) (Blackman, 1951; Ready and Grant, 1947; Sugawara and Koyama, 1971). The results are shown in Table 4.

Table 4. Herbicidal activities of poly(ethyleneimine S-alkyldithiocarbamate)s

Compd. No.	Radish			Barnyard millet		
	Germination (%)	Damage (%)		Germination (%)	Damage (%)	
		19 d	22d		19 d	22d
Control	85	0	6	95	32	63
Positive control #	0	100		0	100	
13	50	20	20	95	28	73
14	40	13	13	90	28	72
15	85**	0	0	85	94	100
16	60*	5	33	95	0	0
17	85	0	6	95	5	10
18	65	8	46	95	21	26
19	85	6	12	95	0	5
20	100	20	25	95	18	18
21	85	0	6	85	6	12
22	85	6	6	95	11	11
23	80	6	13	85	6	12
24	90	6	11	95	79	94
25	55	18	18	95	95	100
26	45	11	11	95	89	100
27	35	57	57	100	25	65
28	70	14	14	100	20	75
29	75	7	7	90	0	11
30	50	0	0	90	83	100
31	5	0	0	95	63	100
32	70	79	93	75	20	53
33	20	100	100	90	61	78
34	65	46	67	90	100	100

$\text{CH}_3\text{-CCl}_2\text{-COOC H}_2\text{-CH}_2\text{-Cl}$ Seedling growth: * repression, ** elongation.

Antifungal test

Disc paper method using the filter papers (Toyokagaku Qualitative No. 2) with 6 mm diameter was employed for the fungicidal test of the polymer (0.5 % dimethylformamide solution) or their light-decomposed materials on *Aspergillus niger*, *Trichoderma viride* and *Pythium debaryanum*. *Asp. niger*, *T. viride* and *P. debaryanum* were cultured on 3 % Czapek-agar and potato-sucrose-agar, respectively at 28°C. The antifungal activity shown in Table 5 was qualitatively evaluated from the ratio of sporulation, inhibiting zone and inhibitory persistence (Golden and Oster, 1947; Sugawara and Koyama, 1971).

Table 5. Antifungal activity of poly(ethyleneimine *S*-alkyldithiocarbamate)s and their decomposed products by light.

Compd. No.	<i>Aspergillus niger</i>		<i>Trichoderma viride</i>		<i>Pythium debaryanum</i>	
	Intact	Decompd.*	Intact	Decompd.*	Intact	Decompd.*
DMF	±		±		±	
CH ₃ -NHCSSNa	‡		‡		‡	
13	±	+	±	±	±	+
14	±	+	±	+	±	+
16	±	+	±	+	±	+
18	±	‡	±	+	±	+
20	±	+	±	+	±	+
21	±	+	±	—	±	+
22	±	±	±	±	±	±
23	±	±	±	±	±	±
24	±	±	±	—	±	—
28	±	±	—	±	±	±
29	±	‡	±	‡	±	±
30	±	±	±	±	±	±
32	±	±	±	+	±	±
33	±	±	—	±	±	±
34	±	±	±	±	±	±
35	‡	‡	‡	‡	‡	‡

Inhibition zone was determined at five to eleven days after inoculation.

‡ zone of inhibition was more than 2 cm,

‡ zone of inhibition was more than 1 cm,

‡ zone of inhibition was less than 1 cm,

— organism failed to grow on disc,

± slight growth of organism on disc,

— no inhibition.

(35) poly(ethyleneimine sodium dithiocarbamate)

* Conditions, see text.

RESULTS AND DISCUSSION

Judging from these experimental data, poly(ethyleneimine sodium or *S*-alkyldithiocarbamate) is thought to be a copolymer with about 15 mole % of dithiocarbamate which decomposes easily to release some substances of lower molecular weight.

S-ethane-2-ol (15) damaged strongly the growth of barnyard millet for 19 days and *S*-arylcarbammates (24, 25, 26) also showed a considerable inhibition on barnyard millet growth. *S*-(3',4'-dichlorophenyl)carbamoylethyl (30) and 2,4-dinitro-5-methyl-6-phenyl *S*-acetate (31) exhibited remarkable selective activity on barnyard millet for a relatively long period. On the other hand, 2-(*p*-chlorophenoxy)ethyl *S*-acetate (32) and *S*-ethyl 2,4-dichlorophenoxyacetate (33) depressed the growth of radish seedling. *S*-ethyl 1,1-dichloropropionate (34) was herbicidally effective on the growth of barnyard millet. Considering from these data, some derivatives of poly(ethyleneimine *S*-alkyldithiocarbamate) whose carbon-sulfur and nitrogen-carbon linkages of dithiocarbamate group can be cleaved by hydrolysis and light might be useful as a controlled-release herbicide.

Poly(ethyleneimine) inhibited the growth of *Asp. niger* and *T. viride*. In addition, water-soluble poly(ethyleneimine sodium dithiocarbamate) (35) was more effective for the inhibition of the growth than poly(ethyleneimine) was. The poly(ethyleneimine sodium dithiocarbamate) decomposed by natural light at room temperature had more inhibitory effect on *Asp. niger* than that of the intact polymer and sodium methyldithiocarbamate. In this case, the lower molecular antifungal compounds released from poly(ethyleneimine sodium dithiocarbamate) were assumed to be sulfur, sodium hydrosulfide, and carbonyl sulfide.

The poly(ethyleneimine S-alkyldithiocarbamate)s could not suppress the fungus growth in the dark for several days. But, the poly(ethyleneimine S-alkyldithiocarbamate)s (solution of dimethylformamide) decomposed by natural light were effective antifungally as shown in S-allyl(14), S-acetate (16), S-m-chlorobenzyl (20), and others. The released substances are still unknown except sulfur, but some sulfur-containing compounds like mono or disulfide derivatives are to be thought. On the whole, these facts suggested that the poly(ethyleneimine sodium dithiocarbamate) and poly(ethyleneimine S-alkyldithiocarbamate)s were chemically and physically decomposed to release antifungal substances.

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