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## Controlled-Release Pesticides

### 4. Synthesis and Decomposition of Poly(*S*-vinyl alkyldithiocarbamate)s

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Poly(*S*-vinyl alkyldithiocarbamate)s were prepared from poly(vinyl chloride) and sodium alkyldithiocarbamates in dimethylformamide. These derivatives were decomposed by exposure to light or by acid or base treatment to give sulfur, sulfur-containing compounds and others. The polymers showed herbicidal and fungicidal activities.

## INTRODUCTION

Recently controlled-release pesticides as a new weapon against insects, weeds and harmful species have been investigated (Allan *et al.*, 1971; Sanders, 1975). For the purpose of development of the herbicidal or fungicidal pesticide such as poly(ethyleneimine *S*-alkyl dithiocarbamate)s, vinylic polymers combined with xanthate, thiocyanate, isothiocyanate or dithiocarbamate, and acrylic polymer with 3-hydroxy-5-methylisoxazolyl group were prepared (Naruse and Maekawa, 1977 a, b, c). A further work on poly(*S*-vinyl alkyldithiocarbamate)s is described in this paper.

## MATERIALS AND METHODS

### 1. Synthesis of sodium alkyldithiocarbamates

According to the Delépine's method (1908), primary and secondary alkylamines (alkyl=Me, Et, n-Pr, i-Pr, n-Bu, i-Bu) were treated with equivalent amounts of carbon disulfide and sodium hydroxide in methanol with stirring at 30°C to produce the corresponding sodium alkyldithiocarbamates. The yield was generally good (Koznetov and Lognova, 1935).

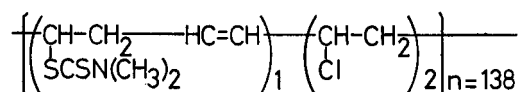
Sodium isopropyl dithiocarbamate. Found : C, 24.46 ; H, 6.07 ; N, 7.03 %. Calcd. for  $C_4H_6NS_2Na \cdot 2H_2O$ : C, 24.35; H, 6.14; N, 7.10 %. UV  $\lambda_{max}^{DMF}$  (nm) : 303 (-NHCS-,  $\epsilon = 14300$ ). IR  $\nu_{max}^{KBr}$  ( $cm^{-1}$ ): 3350, 1630 (hydrate-OH), 3250 (-NH-), 2950, 1450 (-CH<sub>2</sub>-), 1495 (-NHCS-), 1150 (C=S).

### 2. Synthesis of poly(*S*-vinyl alkyldithiocarbamate)s

Poly(*S*-vinyl alkyldithiocarbamate)s (1-9), shown in Table 1, were obtained from the reaction of poly(vinyl chloride) (PVC, n=1100, 0.05 mole) and excess

amount of sodium alkylthiocarbamates in dimethylformamide (DMF) in the dark. The nucleophilic substitution and elimination were run with stirring for several hours at 50°C. The product was isolated by precipitation (DMF-MeOH) and by salting out (Okawara *et al.*, 1963). The removed chloride in this reaction was determined by Volhard's method.

Poly(*S*-vinyl dimethyldithiocarbamate) was synthesized as follows : One hundred ml of 20 % sodium dimethyldithiocarbamate solution dissolved in DMF was mixed with 100 ml of 3.1% PVC solution dissolved in DMF and stirred in the dark for 6 hours at 50°C. The resulting precipitates were discarded and the filtrate was poured into 2.5 l of methanol affording deposits, which were collected by filtration and washed with water and methanol. A tetrahydrofuran solution of the crude product was added to 2l of methanol. From this mixed solution, the product was precipitated by adding a small amount of saturated NaCl solution. The precipitates were filtered, washed with water followed by methanol and ether, then dried *in vacuo* affording 3.2 g of product (Okawara *et al.*, 1966). Lassaigne's test (sulfur), positive. Found : C, 40.04; H, 5.63; N, 4.25 %. Empirical formula :  $(C_{11}H_{13}NS_2Cl_2)_{n=138}$ .  $UV\lambda_{max}^{DMF}$  (nm) : 278 (-NHCS-).  $IR\lambda_{max}^{KBr}$  (cm<sup>-1</sup>) : 3300 (-HC=CH-), 2900, 1380, 1250, 980 (-CH<sub>2</sub>-, -CH-), 1690 (-HC=CH-), 1480 (-NC=S), 1150 (C=S). A structure formula of the product was supposed as follows ;



### 3. Decomposition of the polymer by acid or base

Each suspension of 20 ml of 3 N hydrochloric acid or 5 % potassium hydroxide aqueous solution containing 0.5 g of poly(*S*-vinyl dimethyldithiocarbamate) (7) was warmed for 3 days at 50°C. The reaction mixture was further allowed to stand at room temperature for 155 days. Thin layer chromatographies of the water-soluble materials after 3 and 155 days were carried out (adsorbent, Kieselgel G, Merck ; visualizing agent, iodine or palladium chloride ; developer, acetone, chloroform, tetrahydrofuran). The water-insoluble materials were collected by filtration, washed well with water followed by acetone, and dried *in vacuo*, then analyzed for elements. The reaction mixture after 155 days was extracted with 40 ml of chloroform. The extract was evaporated to dryness under reduced pressure at 40°C to give a little residue of which thin layer chromatography ran on silicagel as noted previously. The chloroform extract obtained from the alkaline treatment was decomposed partly to chloroform-insoluble materials on standing at room temperature. Gas chromatogram of the extract was recorded on a JEOL JGC-750-1100 with a flame-ionizer detector.

### 4. Decomposition of the polymer by natural light

DMF solutions containing 0.5 to 10 % poly(*S*-vinyl alkylthiocarbamate) (1-9) were exposed to light for about 2 weeks indoors at room temperature. The

resulting precipitate was collected by filtration, washed with water followed by acetone, and dried in *vacuo* (Okawara *et al.*, 1964). Elementary analysis of the decomposed polymer (7) was carried out. Thin layer chromatography of the DMF-soluble materials obtained from the decomposed polymer (7) was done with silicagel as mentioned above. The DMF solution of the polymer (7) did not decompose for 3 months in the dark at room temperature.

## PESTICIDAL BIOASSAY

### 1. Herbicidal test

Twenty seeds of radish (*Raphanus sativus* L. var. *radicular* Dc.) and barnyard grass (*Panicum crusgalli* L.) were used for the herbicidal examination with 40 g of upland soil (pH 6.2, Kyushu University Farm) irrigated with 10 ml of water. The sample (0.25 g) was mixed well with the soil and then the seeds were sown under light on it in a 100 ml-glass beaker. The temperature was held at 25-28° C with about 70 % humidity for radish and at 30-34° C with higher humidity for barnyard grass. The soil for barnyard grass was kept wet after germination. The evaluation of the inhibition, as shown in Table 3, was referred to the average (%) of germination and damage of the plant (Sugawara and Koyama, 1971).

### 2. Fungicidal test

DMF solutions containing 0.5 % of poly(S-vinyl alkyldithiocarbamate)s (intact or decomposed by light) were supplied for the fungicidal examination on *Aspergillus niger*, *Trichoderma viride* Pers. ex. Fr. (IFO 5720), and *Pythium debaryanum* Hesse (IFO 5919). The test was achieved by maintaining them at about 80 % humidity and 28°C. The disc papers used were qualitative filter paper with 6 mm diameter (Toyokagaku's product No. 2). The antifungal activity was judged from the inhibition of spore production, inhibiting zone, inhibitory persistence, as shown in Table 4. The medium of the culture was 3 % Czapek-agar for *Asp. niger*, and 3 % potato-sucrose-agar for *T. viride* and *P. debaryanum* (Golden and Oster, 1947; Sugawara and Koyama, 1971).

## RESULTS AND DISCUSSION

Poly(S-vinyl alkyldithiocarbamate)s bearing about 8-38 mole % of dithiocarbamoyl group were obtained from PVC and sodium alkyldithiocarbamates (Table 1). Poly(S-vinyl dimethyldithiocarbamate) was decomposed by acid, base, or natural light to release sulfur and sulfur-containing compounds, or thiuram derivative. These decomposition products were also obtained from sodium dimethyldithiocarbamate by exposure to light (Figs. 1, 2). The formation of these compounds seems to occur by the cleavage of C-S and C-N bonds of the dithiocarbamoyl group by hydrolysis or radical reaction with light. The analytical results of the decomposed polymer were different from those of intact polymer (Table 2). From these results, it was supposed that some substances with a pesticidal activity were presumably released from the polymers after

Table 1. Poly(*S*-vinyl alkyldithiocarbamate)  $\left( \begin{array}{c} \text{---}(\text{CH---CH}_2\text{---})\text{---} \\ | \\ \text{SCSNR}_1\text{R}_2 \end{array} \right)_n$ 

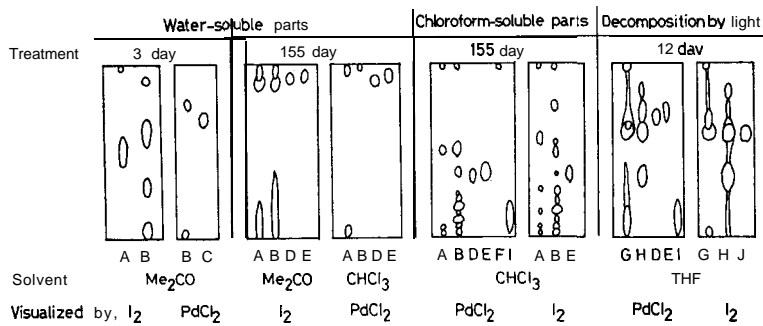
Compd. No.	R <sub>1</sub>	R <sub>2</sub>	Removed Cl(mole %)	UVλ <sub>max</sub> <sup>DMF</sup> (nm)	Analysis
					Found (%)
					N
1	Me	H			
2	Et	H	7.9	265 290	2.59 0.19
3	n-Pr	H	26.1	274	1.66
4	i-Pr	H			
5	n-Bn	H	35.2 7.5	275 270	1.05 1.79
6	<i>i</i> -Bu	H	35.9	290	1.90
7	Me	Me	38.2	278	4.25
8	Et	Et	32.8	280	4.62
9	i-Pr	i-Pr	19.3	285	2.87

 Table 2. Decompositions of poly(*S*-vinyl dimethyldithiocarbamate) by light, acid, and base.

Treatment	Insoluble parts				Soluble parts	
	Analysis Found (%)				Color	Color
	C	H	N	Ash		
None	40.04	5.63	4.25			
3N HCl	39.12	5.13	3.02	—	LB	
5% KOH	39.67	5.20	3.50			LG
Natural light*	40.30	5.41	3.67			

\* at room temp.

LB, light brown; LG, light green; —, colorless.


 Fig. 1. TLC of poly(*S*-vinyl dimethyldithiocarbamate), (compd. 7), decomposed by acid, base, or light.

- A : Poly(*S*-vinyl dimethyldithiocarbamate) treated with 3 N HCl,  
 B : Poly(*S*-vinyl dimethyldithiocarbamate) treated with 5 % KOH aq. soln.,  
 C :  $(\text{CH}_3)_2\text{NCSSNa}$ ,  
 D :  $(\text{CH}_3)_2\text{NCSSSCN}(\text{CH}_3)_2$ ,  
 E :  $(\text{CH}_3)_2\text{NCSSSCN}(\text{CH}_3)_2$ ,  
 F : Sulfur,  
 G : Poly(*S*-vinyl dimethyldithiocarbamate) decomposed by light  
 H :  $(\text{CH}_3)_2\text{NCSSNa}$  decomposed by light,  
 I :  $(\text{CH}_3)_2\text{NCSSH HN}(\text{CH}_3)_2$ ,  
 J :  $(\text{CH}_3)_2\text{NCHO}$ .

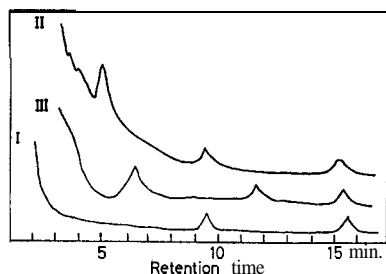


Fig. 2. Gas chromatograms of chloroform-soluble substances from decomposed poly(*S*-vinyl dimethyldithiocarbamate) (compd. 7). I, Decomposed poly(*S*-vinyl dimethyldithiocarbamate) ; II,  $(\text{CH}_3)_2\text{NCSSNa}$  exposed to light; III,  $(\text{CH}_3)_2\text{NCSSSCN}(\text{CH}_3)_2$  exposed to light.

Conditions: FID, Silicone DC-550 (15 w%)/Uniport C (mesh 60/80), 6 mm  $\times$  1 m (glass), 2  $\mu\text{l}$ ,  $\text{N}_2$  gas; 30 ml/min. Temp. ( $^{\circ}\text{C}$ ); column 170 $^{\circ}$ , injection port 170 $^{\circ}$ , detector 190 $^{\circ}$ .

Table 3. Herbicidal effect of poly(*S*-vinyl alkylthiocarbamate)s.

Compd. No.	Radish				Barnyard grass			
	Germination 28 $^{\circ}\text{C}$	Damage (%)			Germination (%)	Damage (%)		
		13 day	21 day	25 $^{\circ}\text{C}$ 35 day		19 day	30 $^{\circ}$ -34 $^{\circ}\text{C}$	
							27 day	32 day
1	95	0	53	60	90	0	22	28
2	95	0	26	50	95	0	0	5
3	65	23	62	19	100	20	20	20
4	80	0	75	53	100	55	65	70
5	45	0	56	65	100	45	75	85
6	80	38	63	41	85	7	12	12
7	90	0	44	56	80	0	6	6
8	95	0	26	50	90	0	0	5
9	85	45	71	65	85	24	59	76
Control	95	0	16	8	95	0	0	0
$\text{EtNHCSSNa}$	0	—	—	—	0	—	—	—
$(\text{Et})_2\text{NCSSNa}$	85	0	100	—	90	11	11	11

these treatments.

As seen from Table 3, poly(*S*-vinyl alkylthiocarbamate)s (1-9) did not inhibit the germination of radish and barnyard grass. But, they were considerably damaged by the polymers. The copolymers were harmful to radish at 10-55% range for 21 days and at 10-60% range for 35 days. Particularly, diisopropyl derivative (9) showed a strong damage on radish. Some derivatives among the polymers revealed herbicidal effect on barnyard grass, too. Isopropyl (4), *n*-butyl (5) and diisopropyl compounds (9) became gradually effective for the damage of barnyard grass from 19 to 32 days at 24-85% range (Table 3).

Intact or decomposed poly(*S*-vinyl alkylthiocarbamate)s (1-9) were examined for the antifungal activity on *Asp. niger*, *T. viride* and *P. debaryanum*. The intact polymers in the dark did not reveal any inhibition zone after several

Table 4. Antifungal activity of poly(S-vinylalkyldithiocarbamate)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.
1	0	2	0	1	0	1
2	0	2	0	1	0	1
3	0	2	0	1	0	1
4	0	3	0	1	0	1
5	0	2	0	1	0	
6	0	2	0	1	0	
7	0	2	0	1	0	
8	0	3	0	1	0	
9	0	2	0	1	0	
DMF	1		1			
CH <sub>3</sub> -NHCSSNa	4		3			

Inhibition zone was observed at four days after inoculation.

4: Zone of inhibition was more than 3. cm.

3: Zone of inhibition was less than 1 cm.

2: Organism failed to grow on disc.

1: Slight growth of organism on disc.

0: No inhibition.

days, but the polymers (1-9) decomposed by natural light inhibited clearly the growth of *Asp. niger*. Thus, the intact polymers in the light were thought to change to the antifungal substance (Table 4).

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