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Controlled-Release Pesticides

3. Herbicidal Synthetic Polymer

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Copoly(S-vinylisothiourea-vinylene-vinyl thiocyanate) was prepared from poly(vinyl chloride) with thiourea as an attempt to develop controlled-release herbicides. The copolymer was decomposed in an aqueous alkaline solution to give thiocyanate and other compounds. The copolymer was also decomposed by acid releasing low molecular compounds. The copolymer was not effective for germination but inhibited the growth of seedlings of barnyard grass on the treated soil for 28 days. The copolymer treated with acid or base was more effective on the germination and the growth of the plant.

INTRODUCTION

Controlled-release pesticides (Sanders, 1975) appeared recently and were thought to have more favorable points than customary low molecular pesticides in spraying time, toxicity, persistency, usage security, and ecological effects. Volkober and Varga (1963) and Allan *et al.* (1971) synthesized a polymer combined with 2,4-D. Beasley and Collins (1970) prepared a polymer bound with herbicidal compound through salt linkage. As an attempt to obtain the controlled-release pesticide, for example a polymer bound covalently with bioactive groups, this paper deals with the preparation of a copolymer bearing isothiourea, vinylene, and thiocyanate groups.

EXPERIMENTAL

1. Preparation of copoly(S-vinylisothiourea-vinylene-vinyl thiocyanate) (I)

Sixty grams of powdered poly(vinyl chloride) (PVC, $n=1100$) were heated with 500g of thiourea for 12 hours at 180°C. After cooling, the reaction mixture was washed well with water and acetone to give brown insoluble materials. The fine powdered material was stirred in water for 36 hours at 60°C, then dialyzed thoroughly against water, and dried under reduced pressure. About 50 g of brown powder was obtained (Speziale, 1963). Sulfur detection with sodium nitroprusside after metallic sodium fusion was positive. Primary amine was detected positively by Van Slyke method. Anal. Found (%) for PVC : C, 38.59; H, 4.96; Cl, 56.71. Found (%) for the product: C, 43.20; H, 5.64; N, 9.93; Cl, 1.61. Empirical formula : $(C_{16}H_{19}N_3S_2)_n$. The results of differential thermal

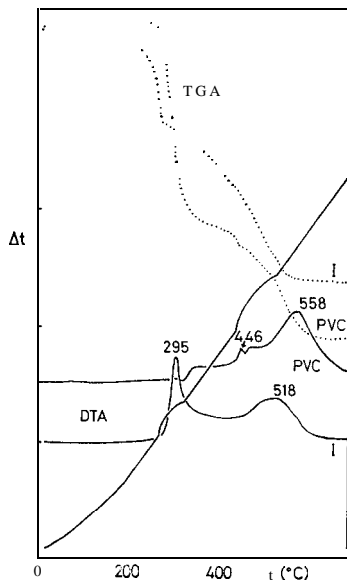


Fig. 1. Differential thermal and thermogravimetric curves of copoly(*S*-vinylisothiourea-vinylene-vinyl thiocyanate) (I) and PVC. Conditions : sample, 5.2 mg ; PVC, 5.7 mg; chart speed, 4 mm/min; heating rate, 20°C/min; temp. range, 10 mV; DTA sensitivity, $\pm 500 \mu\text{V}$; TGA sensitivity, 10 mg; atmosphere, air.

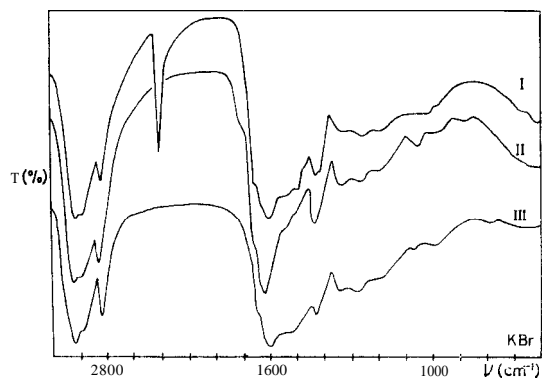


Fig. 2. Infrared absorption spectra of copoly(*S*-vinylisothiourea-vinylene-vinyl thiocyanate) (I), (I) treated with 6 N hydrochloric acid (II), and (I) treated with 5% potassium hydroxide solution (III).

analysis (DTA) and thermogravimetric analysis (TGA) of the product are shown in Fig. 1. Exothermal point ($^{\circ}\text{C}$) for PVC : 446, 558 and for the product: 295, 518. Infrared absorption spectrum of the product, $\text{IR}_{\nu_{\text{max}}}^{\text{KBr}} (\text{cm}^{-1})$: 3300 ($-\text{NH}-$), 3110, 1495 ($-\text{HC}=\text{CH}-$), 2900, 1430 ($-\text{CH}_2-$), 2050 ($-\text{SCN}$), 1690-1450 ($-\text{HC}=\text{CH}-$, conjugated $-\text{HC}=\text{CH}-$, $-\text{C}=\text{NH}$), 630 ($-\text{CH}-\text{Cl}$) (Fig. 2).

2. Decomposition of the copolymer (I) with acid and base

Each suspension of 1.5 g of the copolymer (I) in 100 ml of 6 N hydrochloric acid or 5 % potassium hydroxide aqueous solution was stirred for 19 hours at 70°C. After stirring, the reaction mixture was allowed to stand at room temperature. The resulting precipitates were filtered, washed with water until the filtrate became neutral, then washed further with acetone and tetrahydrofuran, and dried in *vacuo*. Infrared absorption spectra of the insoluble parts (II, treated with acid; III, treated with base) are also shown in Fig. 2. The analytical results of the insoluble parts and soluble parts are summarized in Table 1 and Fig. 3. Released thiocyanate anion was qualitatively detected as ferric thiocyanate formed by adding ferric nitrate to the sample solution acidified with nitric acid. By thin layer chromatography of the base-treated solution, the thiocyanate anion was recognized. The recognition of cyanide anion was done as a Prussian blue. Paper strip sprayed with lead acetate solution was used for the detection of hydrogen sulfide.

Table 1. Decomposition of copoly(S-vinylisothiourea-vinylene-vinyl thiocyanate) (I) with acid and base.

Exp. No.	Treat-ment	Insoluble parts						Soluble parts			
		Color	Analysis Found (%)					IR(SCN) ν ($^{2050}_{\text{cm}^{-1}}$)	Color	Odor	Detection
			C	H	N	S	Cl	Ash			
A	Non	BR	43.20	5.64	9.93	+	1.61	—	+		
	6 N HCl	BR	42.76	5.62	8.15	-I-		+	—	LY	\$ —
	5% KOH aq. soln.	BR	44.37	5.82	7.27	+		##	—	Y	— + —

BR, brown; LY, light yellow; Y, yellow; S, sulfur-like.

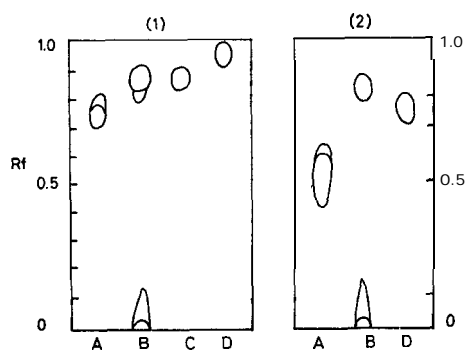


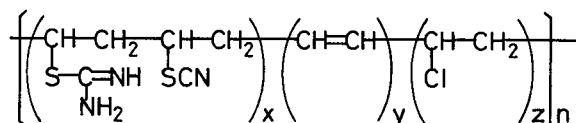
Fig. 3. TLC of the soluble parts from acid or base treatment (in Table 1). A, the soluble parts from 6 N HCl treatment; B, the soluble parts from 5% KOH aq. soln. treatment; C, KSCN; D, $\text{NH}_2\text{C}(\text{S})\text{NH}_2$. Conditions: developer, (1) 95 % ethanol, (2) acetone; adsorbent, Kieselgel G (Typ 60)/Merck, visualized by I_2 , PdCl_2 , or $\text{Na}_2\text{Fe}(\text{CN})_5(\text{NO})$.

3. Herbicidal bioassay

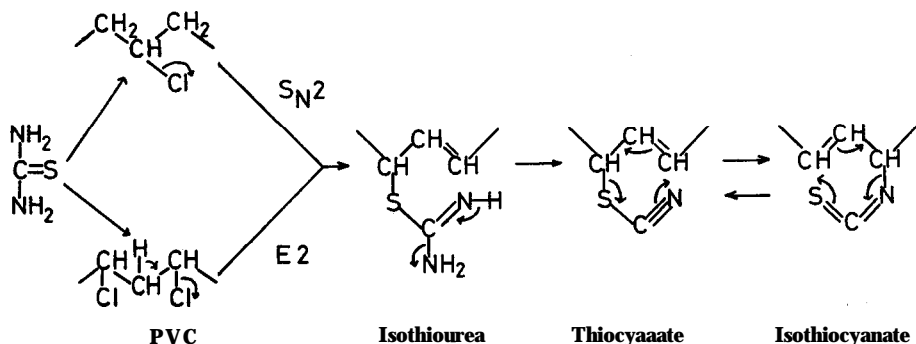
Twenty seeds of radish (*Raphanus sativus* L. var. *radicular* Dc.) and barnyard grass (*Panicum crusgalli* L.) were used for the assay in 40 g of upland soil (pH 6.2, Kyushu University Farm) irrigated with 10 ml of water. One-tenth gram of the sample was mixed well with the soil and the seeds of each plant were sown under light on the soil placed in a 100 ml-glass beaker. The medium for barnyard grass was kept wet after germination. The temperature was kept at 25-28°C under a moderate humidity for radish, and 30-34°C under a higher humidity for barnyard grass. Inhibitory effects were defined as average (%) of germination and damage of each plant (Blackman, 1951; Ready and Grant, 1947; Sugawara and Koyama, 1971).

RESULTS AND DISCUSSION

A structure of the product (I) from PVC and thiourea was proposed as follows from the analytical data;



It was confirmed by differential thermal analysis that the product (I) was not a mixture of PVC and thiourea. The spectrum of (I) in 2050 cm⁻¹ was assigned to thiocyanate group which was thought to be formed from the isothiurea group, which was formed by the nucleophilic substitution for secondary chloride of PVC in molten thiourea. Infrared spectra among PVC, (I), (II), and (III) were different each other. The isothiurea group of (I) was hydrolyzed in potassium hydroxide solution to potassium thiolate of (III). It was found by thin layer chromatography that (I) was decomposed by dilute aqueous alkaline solution to give thiocyanate, that the thiocyanate group of (I) was also decomposed by acid, and that other decomposition products than those



Scheme 1. The formation mechanisms of isothiurea, vinylene and thiocyanate.

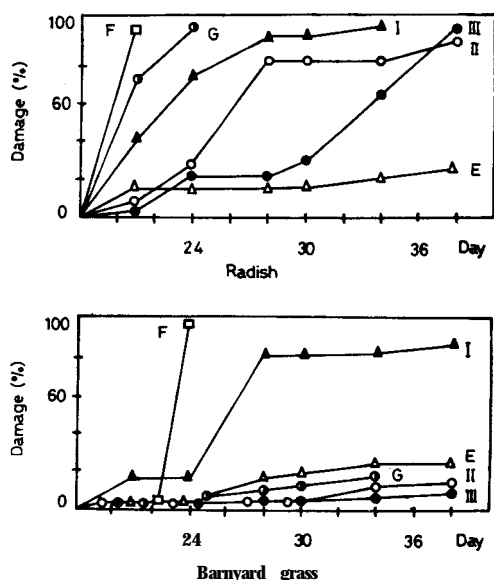


Fig. 4. Herbicidal activity of copoly(*S*-vinylisothiourea-vinylene-vinylthiocyanate) and decomposition products. Conditions, see text. I, copoly(*S*-vinyl isothiourea-vinylene-vinyl thiocyanate) ; II, I treated with acid ; III, I treated with base ; E, control; F, 3-(*p*-chlorophenyl)-1, 1-dimethylurea ; G, *S*-ethylisothiourea hydrobromide.

mentioned above were also released by the acid or base treatment of (I).

The mechanisms of the formation of isothiourea, vinylene, and thiocyanate of (I) were supposed as shown in Scheme 1.

The copolymers (I, II, III) had no effect on the germination of radish and barnyard grass. For 24 days, the copolymer (I) revealed a strong damage to the growth of barnyard grass after sowing, and inhibited radish to grow with about 70 % damage (Fig. 4). It is suggested from these data that the thiocyanate group of (I) is necessary for the reveal of the herbicidal activity.

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