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Pesticide Combined with Synthetic Polymer

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Polyvinylchloride (PVC) was heated with 3-amino-1,2,4-triazole (ATA), 2-imidazolidone (IM) or 2-imidazolidinethione (IMT) above the melting point of each uncleophile from 4 to 96 hours to give products containing the nucleophilic substituent.
It was supposed that hydrogen atom of N-l imine of ATA and amidic hydrogen of IM or IMT were substituted for chlorine of PVC. Among these preparations the polymer combined with ATA exhibited a selective and strong herbicidal activity. Other biological activities of these compounds were described briefly.

INTRODUCTION

There are many papers on synthetic macromolecular compounds with pesticidal or medicinal activity (Utsumi *et al.*, 1967 ; Nakata *et al.*, 1967; Hastings, 1970). Poly (ethylene oxide) was treated with halogen to give halogen-substituted poly (ethylene oxide) with pesticidal activity (Winslow *et al.*, 1963).

Volkober *et al.* (1963) reported that poly (vinyl-2,4-dichlorophenoxy acetate) obtained from polyvinylalcohol and 2,4-dichlorophenoxyacetic acid had the herbicidal activity. Ascoli *et al.* (1957) synthesized poly (acryloyl-5-nitro-2-furfuralhydrazone) from polyacrylhydrazine and 5-nitro-2-furfural and found that the polymer was antifungally active as strong as 5-nitro-furfural was.

Cornel and Donaruma (1965) discovered that poly(2-methacryloxytropone) obtained from polymethacrylic acid and tropolone had a lower ED,, in an antineoplastic activtiy than that of the monomer, and that the polymer displayed a broad spectrum of the antibacterial activity.

Kaneko *et al.* (1969) supposed that substitution and elimination occurred easily in the reaction of PVC with nucleophiles at a liquid-solid phase without formation of cross-linkage.

From these points of view, the authors tried to synthesize pesticidal macromolecular compounds. As an attempt, the reaction of PVC with ATA, IM or IMT and biological activities of the products were investigated.

EXPERIMENTAL

Reaction of PVC with ATA (I-VIII)

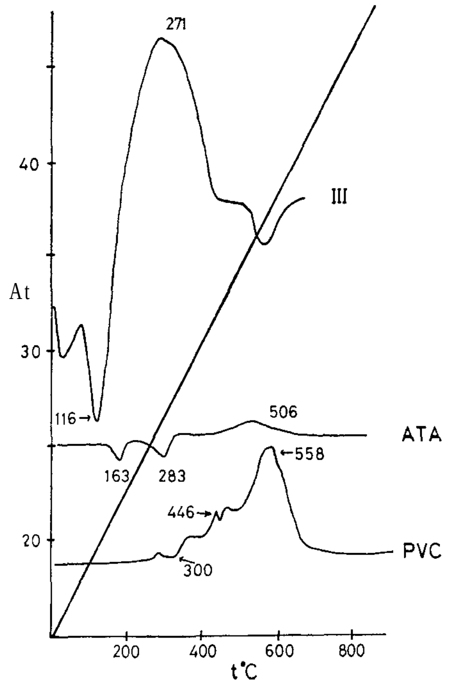
Ten grams of PVC powder ($n=1,100$) were heated with 55 g of ATA for 26 hours at 160°C–170°C. The reaction mixture solidfied by cooling to room temperature was washed completely with water, methanol and tetrahydrofuran, successively. Then the insoluble yellow precipitate was collected and dried ***in vacuo***. Yield 11 g. Chlorine cotent of the product was determined by Volhard's

Table 1. Composition of products obtained from PVC and ATA.

Product No.	Exotherm. decomp. (°C)	Reaction time (hr)	Elementary analysis Found (%) C	H	N	Cl	Color
PVC	446, 472, 558	4	38.59	4.96		56.71	Colorless
I	278, 312	8	49.45	6.11	28.15	15.16	Orangel
II	283, 307	9	49.53	6.28	30.43	13.76	
III	271, 307	16	51.49	6.53	31.08	10.90	Yellow
IV	283, 319	23	48.71.	6.04	33.70	11.55	
V		25	51.07	6.40	32.80	9.73	
V-1		26	50.62	6.47	31.33	11.58	
VI		48				8.02	
VII		71	49.92 49.56	5.93 5.92	36.14 35.67	7.82	
VIII		96	48.31	5.94	38.54	7.21	

Chlorine content of PVC is caicd. value.

III: II treated with 2% NaOH soln. under stirring for 2 hrs at 45°C.



Fig, 1. Differential thermal analysis of III, ATA and PVC. (III); 27 mg, ATA; 5.5 mg, PVC; 5.7 mg, Chart speed :2mm/min, Heating rate :20°C/min, Sensitivity:±500μV, Atmosphere : air.

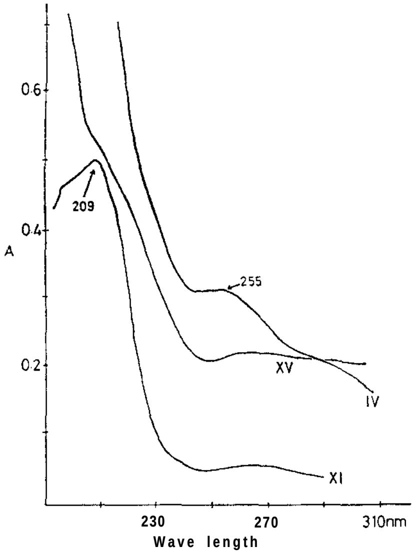


Fig. 2. UV spectra of IV, XI and XV. IV: in 1N HCl, XI and XV: in MeOH.

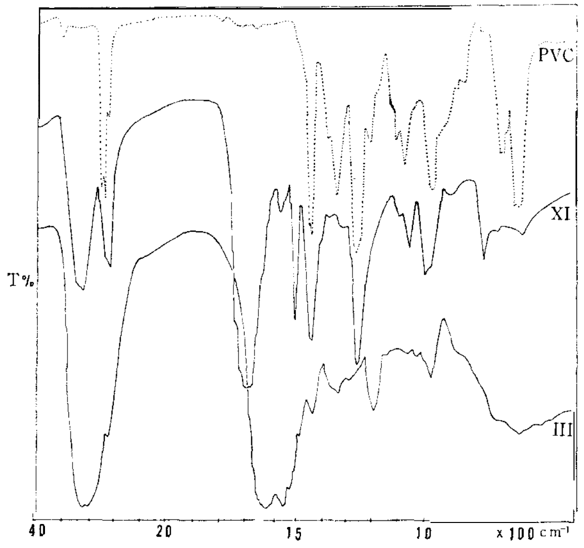


Fig. 3. IR spectra of PVC, III and XI in KBr.

method (1877) after fused with sodium carbonate. Analytical data and exothermal decomposition points of various preparations are listed in Table 1. In a differential thermal analysis (DTA) of (III), an exothermal decomposition at 271°C was observed as shown in Fig. 1. UV spectrum of (IV) in hydrochloric acid solution showed a n-π^* weak absorbance at 255 nm due to carbon-nitrogen double bond (Fig. 2). IR spectrum of (III) in KBr is shown in Fig. 3.

IR $\nu_{max}^{(KBr)}$ cm^{-1} : 3340 (amine NH), 2940-2880 (methylene and methine CH), 3040-3010 (vinyl and conjugated vinyl C=CH), 1680-1620 (vinyl and conjugated vinyl C=C), 1660-1480 (double bond C=N and single bond C-N), and 800-700 (single bond C-Cl).

Preparation of (V-2) **by the treatment of** (VI) **with alkali**

Five grams of (VI) were heated in 100 ml of 2 % potassium hydroxide solution under stirring for 4 hours at 30°C. After the reaction was finished, the precipitate remained was filtered, washed well with water and tetrahydrofuran, then dried *in vacuo.* Yield of yellow solid (V-2) was 4.7 g.

Anal. found (%) : C; 52.81, H; 6.83, N; 33.77, Cl; 8.59

Empirical formula : $(C_{18}H_{25}N_{12}Cl)_{n=91}$

The presence of primary amine in (V-2) was detected by Van Slyke method (Austin, 1950). (V-2) was treated with phenyl isothiocyanate to give a sulfur containing substance whose sulfur was identified by Lassaigne's test.

Reaction of PVC with IM (IX-XIV)

Ten grams of PVC powder (n=1,100) were heated with 66 g of IM for 9 hours at 160°C-170°C. The reaction mixture was cooled to room temperature to solidify. Then the solid mass was washed completely with water, methanol and tetrahydrofuran, successively. The resulting orange solid was dried *in vacuo.* Yield of (XI) was 7.3 g.

Empirical formula : $(C_{11}H_{15}N_2OCl)_{n=137}$

In the DTA curve of (XI), the exothermal peaks were observed at 234°C and 432°C (Fig. 4). UV λ_{max} (MeOH) was 209 nm (Fig. 2). The IR spectrum of (XI) presented absorptions of amide NH, vinylic methine C=CH, methylene and methine CH, amidic carbonyl NH-CO, vinyl and conjugated vinyl C==C, single bond C-N, and methinic chloride C-Cl at 3440, 3040-3010, 2940-2880 and 1450, 1750-1600, 1480, and 700-600 cm^{-1}, respectively (Fig. 3).

Analytical data of products prepared from PVC and IM at different reaction conditions are summarized in Table 2.

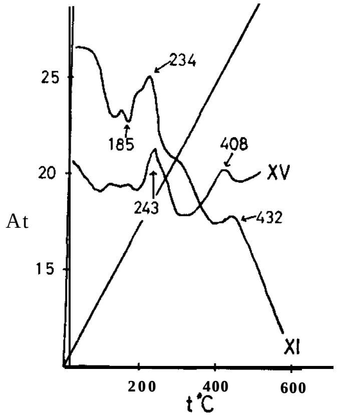


Fig. 4. Differential thermal analysis of XI and XV. (XI) ; 50 mg, (XV) ;30mg, Chart speed :2mm/min, Heating rate : 20°C/min, Sensitivity: ±250μV, Atmosphere : air.

Table 2. Composition of products obtained from PVC and IM.

Product No.	Reaction time(hr)	Reaction temp. ("C)	Elementary analysis Found (%) C	H	N	Cl
IX	5	160 – 170	55.83	6.54	9.25	
X	7					
XI	9	140 160 -- 150 170	54.00 56.75	6.21 6.50	a. 7.89 59	15.14
XII	14	150 – 160	51.86	6.13	6.37	28.52
XIII	27	150 – 160	56.57	6.31	11.69	a.32
XIV	64	150 – 160	62.71	7.76	14.35	

Reaction of PVC with IMT (XV-XVII)

Five grams of PVC powder (n=1,100) were heated with 49 g of IMT for 9 hours on an oil bath at 200°C–205°C. After the reaction was over, the mixture was cooled to afford solid mass. The resulting product was washed with water, methanol, carbon disulfide, acetone and tetrahydrofuran, successively, then dried under reduced pressure. A brown solid product (XVII) was obtained in 2.3 g yield.

The empirical formula of (XVII) was $(C_{16}H_{24}N_4S_2Cl)_{n=100}$.

The DTA of (XV) showed the exothermal decompositions at **243°C** and 408°C. UV spectrum of (XV) is shown in Fig. **2.** IR spectrum of (XVII) in KBr is shown in Fig. 5. IR $\nu_{max}^{(KBr)}$ cm^{-1}: 3450 (thioamide NH), 3040-3010 (vinylic methine C=CH), 2940-2880 (methylene and methine CH), **2050** (isothiocyanate NCS), 1680-1620 (vinyl and conjugated vinyl C=C), 1495 (single bond C-N), 1460–1120 (cyclic thioamide NH-C-N), and 700-600 (single bond C-Cl).

Analytical data of different preparations are illustrated in Table 3.

Table 3. Composition of products obtained from PVC and IMT.

Product No.	Reaction time(hr)	Elementary analysis Found (%) C	II	N	Cl
XV	4	19.56	6.10	14.24	
XVI	4	48.79	6.51	14.30	7.06
XVII	9	51.64	6.32	15.90	10.25
XVIII		52.91	6.61	13.16	
IXX		51.91	6.57	13.20	

XVIII : XVII refluxed in 4% KOH soln.
IXX : XVII refluxed in conc. aq. ammonia.

Hydrolysis of isothiocyanate (XVII) with alkalis

One-fifth grams of (XVII) were refluxed with 50 ml of 4 % potassium hydroxide solution for 8 hours. By cooling, a brown powder (XVIII) was obtained from the reaction mixture. The product was filtered and washed well with water and methanol, and dried *in vacuo*. Yield 0.5 g. The presence of primary

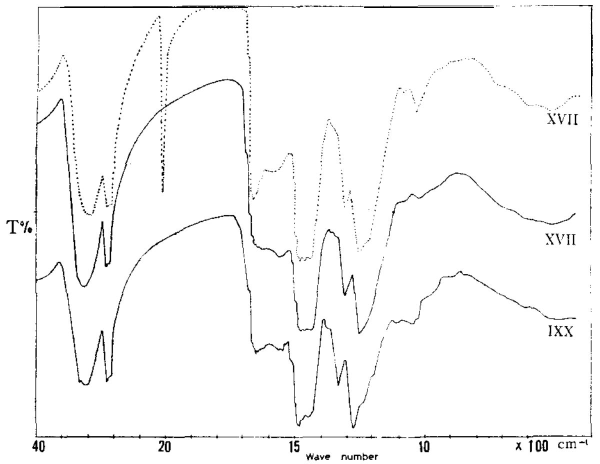


Fig. 5. IR spectra of XVII, XVIII and IXX in KBr.

amine and sulfur in the product was recognized by Van Slyke and Lassaigne's test respectively. (XVIII) did not reveal the presence of absorbance at 2050 cm^{-1} in the IR spectrum due to isothiocyanate.

(XVII) was also hydrolyzed in conc. ammonium hydroxide solution by heating for 16 hours at 90°C to give a solid product (IXX) which was similar with (XVIII). IR spectra of (XVII), (XVIII) and (IXX) are shown in Fig. 5.

BIOASSAY AND BIOLOGICAL ACTIVITY

Herbicidal activity

(V-l) and (V-2) were examined for an effect on seedling growth or germination of radish, rice (NORIN No. 18) and barnyard millet at 100 and 500 ppm as a suspension under light (Crafts et *al.*, 1962). Forty seeds of radish and barnyard millet, and **20** seeds of rice were used for the examination. The assaying temperature was 25°C for radish and 30°C for rice and barnyard millet. The observation was continued for 6 or 15 days. The inhibiting effect was defined as average grown-length of roots, stems and cotyledons of each plant compared with that of the control. An average value was also taken for number of roots of rice. The results are listed in Table 4.

(V-l) had certain effects on the germination and the growth of roots of barnyard millet. Namely, its inhibiting rate was about 40 % at 500 ppm, whereas it accelerated the growth of stems and roots of radish. (V-2) repressed markedly the growth of stems and roots of radish at 100 ppm. On the other hand, (V-l) and (V-2) promoted the growth of cotyledons and roots of rice at 100 ppm.

Therefore, it was elucidated that (V-l) and (V-2) were more selective herbicide than ATA and their effectiveness was stronger than that of ATA.

Table 4. Herbicidal and plant regulatory effects of V-l and V-2.

			Control			Sample			
			H_2O	ATA		V-l		V-2	
Concentration (ppm)				100	500	100	500	100	500
Radish	Germination (%)		100	100	100	90	97.5	80.2	87.5
	Length (cm)	Stem	2.94G	0.95Y	0.5Y	4.1YG	4.1W	0.4YG	0.86G
		Root	3.35W	0.38Y	0.2Y	3.7W	5.4G	0.41W	0. 31W
	Chlorosis of cotyledon (%)		5	100	100	22.5	5	17.5	15
Barnyard millet	Germination (%)		42.5	35	47.5	30	25	45	45
	Length (cm)	Cotyledon	4.7G	0.2Y	0.2Y	6.1G	4.5G	7.4G	4.5G
		Root	2.9W	0.7x	0.15x	3.4W	1.7W	3.3W	3.3W
Rice	Germination (%)		100	100	95	90	100	100	100
	Length (cm)	Cotyledon	0. 78G	4.05Y	0.4Y	3.01G	2.61G	2.54G	1.46G
		Root	5. 7W	2.75Y	0.35Y	5.6W	4.2W	7.27W	5.82W
	Number of root		4.4	0.95	1	1.7	4.4	4.2	4.2

G : Green, W: colorless, Y : yellow, X : lose plant.

Table 5. Effect on metamorphosis of housefly by oral administration.

Time(hr) / Sample*	21	24	27	29	44	46
XI	22	55	64	G7	93	97
XVI	52	69	83	89	94	99
Control	27	51	64	67	94	95

Number of adult emergence from 100 pupae. *Concentration : 1,000 ppm.

Effect on the metamorphosis of housefly

The effect of (XI) and (XVI) on the metamorphosis of housefly was examined under constant humidity at **27°C.** A mixture composed of 50 mg of (XI) or (XVI), 12.5 g of mouse food yeast, 12.5 g of wheat bran and 25 ml of water was used as diets for the oral administration of immature larvae of housefly. The 100 larvae grown in two days after hatching were employed for the assaying. The results are shown in Table 5. (XI) did not reveal any effect on metamorphic changes of pupation and adult emergence, whereas (XVI) promoted the metamorphic change from pupae to adults.

Mammalian toxicity

(XI) and (XVI) of odorless samples were employed as the oral administration in order to examine the toxicity (Rokwski, 1964). Yeast baits contained 0.5 and 1% of (XI) or (XVI) respectively were tabletted to a hard cylinder with $\pi\,\text{cm}^3$ volume. The cylinder baits were orally administered to 4 ddN adult mice maintained at 25°C. The toxic effects were judged from changes of body weight,

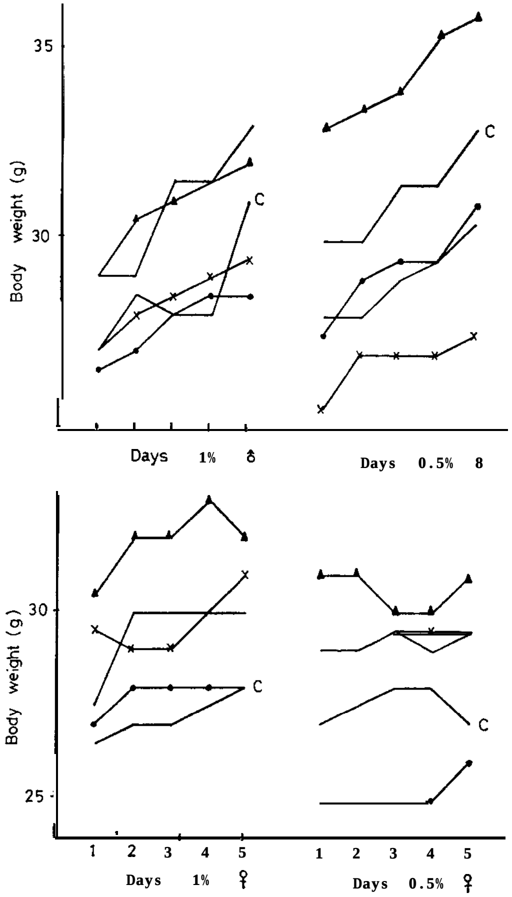
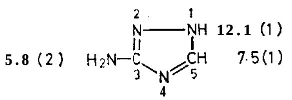


Fig. 6. Toxicity of XI in oral administration for male or female ddN adult mouse. Sample was 1% or 0.5 % bait. C : control.

hair arrangement and mobility. The results are shown in Figs, 6 and 7. Mice survived normally in both sexes and the mobility was also normal. However, (XVI) repressed apparently the increase of body weight of the mice. But (XI) was unlikely to repress that.

RESULTS AND DISCUSSION

The evidence of nucleophilic reactivity of ATA to PVC was given from chemical shifts and integrated values in the NMR spectrum and the integration curve. The chemical shift (δ ppm) and integrated value of proton of ATA are shown as follows :



Integrated values are shown in parentheses.

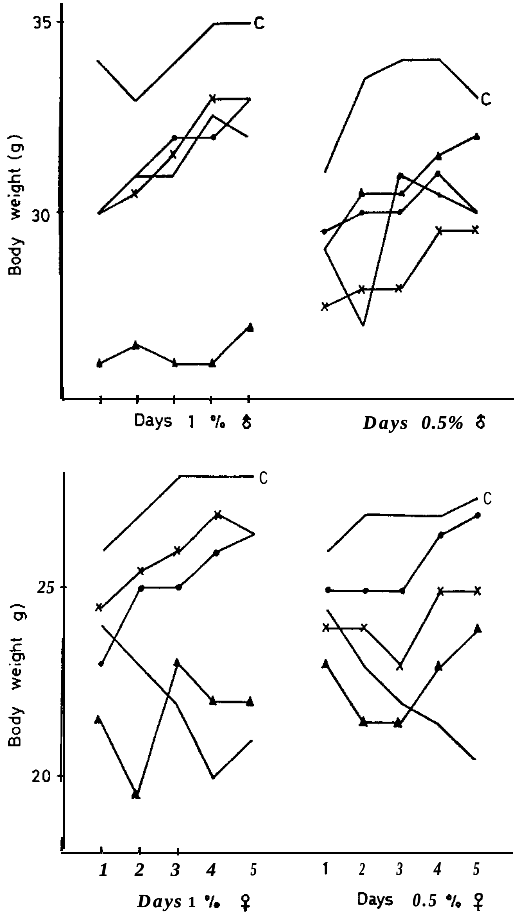


Fig. 7. Toxicity of XVI in oral administration for male or female ddN adult mouse. Sample was 1 % or 0.5 % bait. C : control.

The NMR data suggested that a group at 3-position of ATA had no imine but amine form, that an imine group at 1-position was nucleophilically more reactive than any other atoms in ATA.

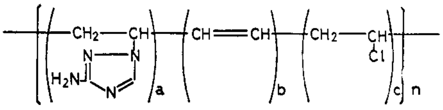
On the other hand, a molecular model of ATA indicated that the ring skeleton of ATA and the amino group at 3-position were located each other on a same plain. From the NMR data and the steric location, it was concluded that the imine of 1-position reacted more easily with PVC methine than the amine of S-position to form carbon-nitrogen bond by the S_N mechanism. In addition, it was supposed that vinyl and conjugated vinyl groups of the product were formed by the nucleophilic attack of ATA to methylenic hydrogen of PVC under an elimination of hydrochloride in an E mechanism.

The product obtained from PVC and ATA showed the presence of primary amine by Van Slyke method and the presence of the absorption (3440 cm^{-1}) due to NH group in IR spectrum. IR spectrum also showed the absorptions at 3040-

3010 cm^{-1} and 1680-1620 cm^{-1} due to vinyl groups.

In the DTA curves, endothermal peaks were 163°C and 283°C and exothermal one was 506°C in ATA, while exothermal points of PVC were 446°C, 472°C and 558 “C. In comparison with DTA curves of PVC, ATA and PVC combined with ATA, these compounds showed quite different curve and exothermal and endothermal peaks. This fact explained that the PVC combined with ATA was not a mixture of two components.

It was deduced that the product contained N-l-substituted ATA, vinyl and conjugated vinyl groups, and unreacted methinic chloride. Although the arrangement of these groups was not clarified, the general structure of the product might be drawn as follows:



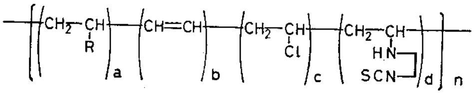
Values of a, b, c and n varied according to the reaction condition. In the case of (V-2), a=3, b=2, c=l and n=91 were calculated from the empirical formula.

In the reaction of PVC and IM, a nucleophilicity of IM to PVC can be estimated from chemical shifts of protons of IM. The chemical shifts of amidic or ethylenic proton were 5.2 or 3.5 ppm at δ value respectively. The chemical shifts suggested that the amidic proton was more reactive than ethylenic proton in the S_N reaction which occurred easily in melted IM.

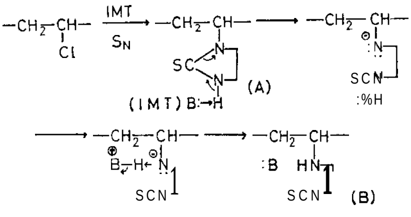
The formations of vinyl and conjugated vinyl groups were expected to go forward under E reaction related to Zipper effect in the action of nucleophilic IM to methylenic hydrogen of PVC.

S_N and E mechanisms in the reaction of PVC and IM were similar to those of PVC and ATA.

IMT also reacted with PVC in the same way as IM. Namely, the structure of the product from PVC and IM or IMT was supposed from analytical data to be as follows: (XI) ; R=IM-H, a = 2, b = 1, c= 1, d= 0, n=137. (XVII); R= IMT-H, a=1, b=2, c=1, d=l, n=100.



The presence of isothiocyanate group in (XVII) was recognized by the IR spectrum (ν_{NCS} 2050cm^{-1}) and hydrolysis with alkalis. The formation of the



isothiocyanate are supposed as follows; IMT-substituted PVC (A) is formed by the reaction of PVC and melted IMT. Then IMT served as both a solvent and a nucleophile in this reaction acts as a basic catalyzer which attacks thioamidic proton of (A). Finally, the isothiocyanate group may be formed.

In general, because of the insolubility of synthetic macromolecular compounds and the resistance to biological decomposition, it might be expected that the products would be biologically inactive. Nevertheless, the combined product showed considerable biological activities.

As mentioned already, there are some reports that pesticides combined with polymer had the activity corresponding to the content of its component. However, there is so far no paper which deals with to elicit a selectivity or increase of an activity by means of combination with polymer.

The selective activity of the PVC-ATA product to the seedling growth and leaf chlorosis of plants was revealed unexpectedly. Considering ATA-content in the polymer, the herbicidal activity of one (V-2) of the PVC-ATA product was 2-3 times greater than that of ATA in the inhibition of growth of radish, whereas it was less effective on the chlorosis of radish than ATA. Therefose, it is thought that the biological effect of the combined product on radish differs from that of ATA.

As for barnyard millet, both of (V-l) and (V-2) accelerated the growth of a cotyledon and a root. Besides, for rice the two products had no effect on the germination, but they promoted the growth of a cotyledon. (V-l) promoted the growth of a root and a stem of radish.

It could be seen from Table 4 that (V-Z) was more selective than ATA was, and that its effective concentration was more dilute than that of ATA. The difference of the activity between (V-l) and (V-2) might be depend on the structure of each compound. While (V-l) is salt of hydrochloric acid, (V-2) is free from hydrochloride.

As to the metamorphosis of housefly and the mammalian toxicity, (XI) had no effect, but (XVI) accelerated about two times within 21 hours in the metamorphic change under the oral administration of immature larvae. However, (XVI) showed the same toxic effects on ddN adult mouse in a few days.

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