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Investigations on Poly(vinyl Chloride). I. Evolution of Aromatics on Pyrolysis of Poly(vinyl Chloride) and Its Mechanism

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Synopsis

Poly(vinyl chloride) (PVC) alone or mixed with 10 wt-% and 50 wt-% TiO_2, SnO_2, ZnO, and Al_2O_3 were pyrolyzed by using a pyrolysis gas chromatograph. Benzene, toluene, ethylbenzene, *o*-xylene, styrene, naphthalene, and various chlorobenzenes were identified. No hydrocarbons could be detected in pyrolysis products of any samples at 200°C. More aromatic hydrocarbons than aliphatic hydrocarbons are released from the PVC–TiO_2 system and in preheated PVC. The contrary result is observed in the PVC–ZnO and PVC–SnO_2 systems. Aromatics having methyl endgroups are easily released from the PVC–ZnO and PVC–SnO_2 systems and at elevated pyrolysis temperature, because methylene groups are easily isolated along the chain by ZnO, SnO_2 and the heating. The release of ethylbenzene *o*-xylene, and chlorobenzenes suggests a repeated dehydrochlorination and recombination of HCl and Cl_2 to double bonds along the chain. Possible decomposition mechanisms of PVC are discussed.

INTRODUCTION

The thermal decomposition of poly(vinyl chloride) (PVC) has usually been represented as involving the dehydrochlorination of the polymer backbone. On the other hand, Stromberg[1] assumed the release of chlorine molecules in his kinetics of the decomposition of PVC. The isolation of small amounts of H_2 and Cl_2 was reported by Tsuchiya[2] on pyrolysis of PVC in an inert gas. Ohta[3] suggested that a part of the hydrogen chloride released from PVC may recombine with the double bonds along the chain introduced by the dehydrochlorination. After pyrolysis of PVC, many kinds of hydrocarbons consisting of aliphatics and aromatics in addition to HCl were detected by Stromberg[1] and other workers.[4–7]

In the present work, PVC, preheated PVC, and PVC containing various metal oxides were pyrolyzed. The pyrolysis products were identified by using gas chromatography and included aromatic hydrocarbons such as benzene, toluene, ethylbenzene, or various aryl chlorides.

Different proportions of volatile products were obtained from the various pyrolyses of PVC. Therefore, it was believed that the pyrolysis products did not depend on the original structure of PVC but on the final structure of polymer releasing their small molecules. In particular, aryl chlorides

may be derived from the recombination of double bonds with chlorine as HCl or Cl_2, assuming that no secondary reactions of the volatile decomposition products take place.

EXPERIMENTAL

Materials

The PVC used in this work was Geon-103EP. Metal oxides were obtained from Kanto Chemical Co., Inc.

Instruments

A Yanagimoto Model GP-1000 pyrolyzer was used to decompose PVC. It was directly attached to the inlet port of a gas chromatograph, Yanagimoto Model GCG-550FP, with double flame ionization detectors. The furnace and stick used to introduce the samples into the furnace were made of quartz.

The precut part in the pyrolyzer was filled with 30 wt-% sodium hydroxide coated on Diasolid H to absorb HCl during the decomposition of PVC and to avoid contaminating or damaging the instruments.

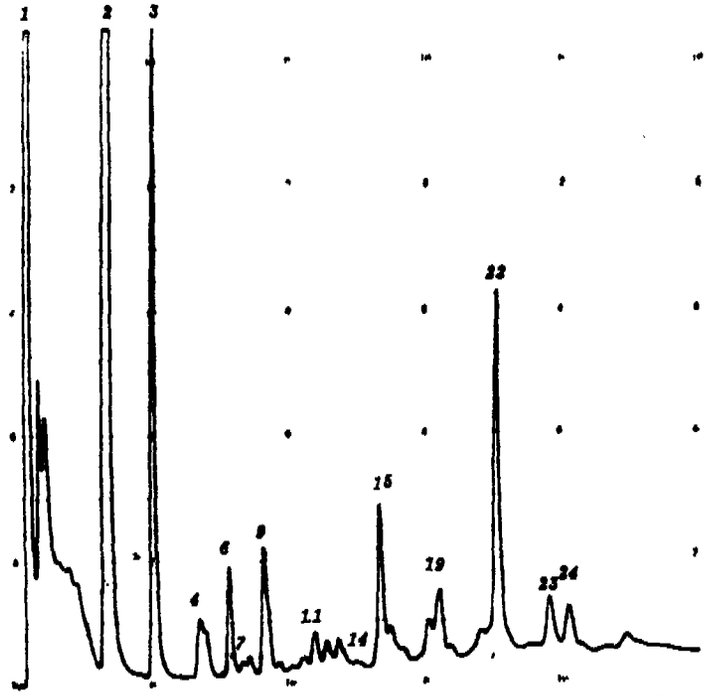

Fig. 1. Pyrogram obtained at 700°C of untreated poly(vinyl chloride).

Pyrolysis

Samples (powder), 1–3 mg, were pyrolyzed in helium gas (flow rate of helium gas, 25 ml/min) at 200–800°C. Separation columns (3 mm id × 2.17 m) containing 20 wt-% PEG-20M coated on Celite 545 were used at a programed increase in temperature from 60°C to 200°C at a rate of 8°C/min. The flow rate of carrier gas (He) was maintained at 25 ml/min at 60°C.

Columns of 20 wt-% SE-30 coated on Celite 545 were used only to identify the pyrolysis products under the same conditions as the separation columns. PVC and the metal oxides were mixed on an agate mortar at room temperature.

RESULTS AND DISCUSSION

PVC samples with or without 10 wt-% and 50 wt-% TiO_2, SnO_2, ZnO, and Al_2O_3 were pyrolyzed at 200–800°C. A sample of PVC preheated at 200°C for 40 min in air was also pyrolyzed similarly. Gas chromatograms of pure PVC and PVC with 10 wt-% SnO_2 pyrolyzed at 700°C shown in Figures 1 and 2 illustrate the effect of active metal oxide on the course of decomposition of PVC.

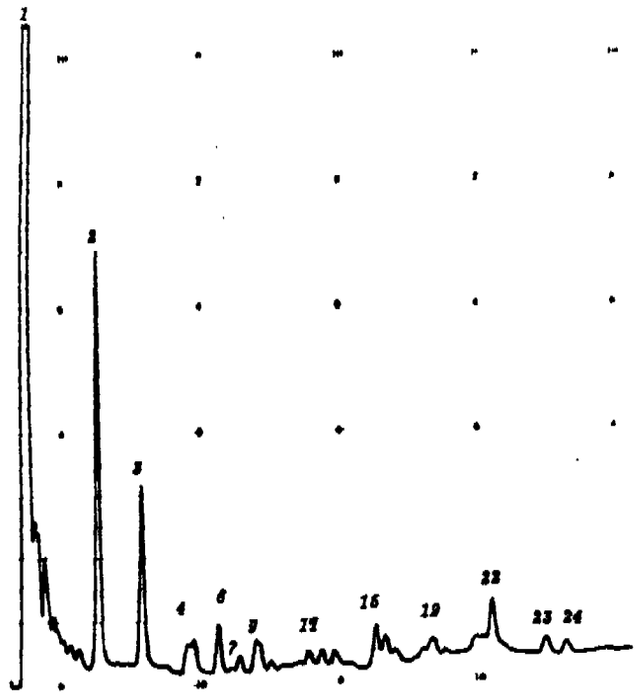

Fig. 2. Pyrogram obtained at 700°C of poly(vinyl chloride)–SnO_2 system (10 wt-% SnO_2).

TABLE IA
γ Values of Pyrolysis Products

Peak	Component	γ					
		Untreated		Preheated		10% TiO_2	
		500°C	700°C	500°C	700°C	500°C	700°C
1	Aliphatic hydrocarbons	3.60	31.87	5.07	33.26	9.35	42.39
2	Benzene	70.23	36.74	71.68	38.35	61.55	31.87
3	Toluene	4.98	9.87	5.40	8.14	6.98	10.57
4	Ethylbenzene	0.76	0.81	0.80	0.50	1.09	0.91
5	A	0.48	0.70	0.00	0.51	0.87	0.97
6	o-Xylene	1.12	1.48	1.33	1.33	1.93	1.78
7	Monochlorobenzene	0.37	0.14	0.30	0.00	0.42	0.12
8	B	0.22	0.27	0.32	0.13	0.42	0.34
9	Styrene	1.63	1.85	1.52	2.08	2.06	1.32
10	C	0.08	0.14	0.12	0.12	0.16	0.19
11	Vinyltoluene	0.47	0.50	0.39	0.55	0.76	0.42
12	D	0.64	0.40	0.67	0.11	0.90	0.38
13	E	0.59	0.33	0.57	0.14	0.71	0.31
14	p-Dichlorobenzene	0.09	0.06	0.08	0.00	0.20	0.06
15	o-Dichlorobenzene Indene	1.58	2.46	1.40	3.19	2.15	1.68
16	F	0.40	0.29	0.53	0.00	0.74	0.71
17	1,3,5-Trichlorobenzene	0.25	0.11	0.39	0.09	0.33	0.19
18	G	0.52	0.39	0.38	0.45	0.85	0.22
19	1,2,4-Trichlorobenzene	1.35	0.66	1.26	0.70	1.33	0.55
20	H	0.13	0.06	0.20	0.00	0.25	0.07
21	I	0.70	0.27	0.26	0.28	0.55	0.32
22	Naphthalene	6.22	7.28	5.39	7.06	3.82	3.46
23	α-Methylnaphthalene	0.94	1.40	0.99	1.16	0.97	0.77
24	β-Methylnaphthalene	0.73	1.14	0.66	1.03	0.63	0.62
25	J	0.18	0.19	0.14	0.09	0.15	0.00
26	K	0.50	0.48	0.45	0.50	0.40	0.00
27	L	0.00	0.00	0.08	0.13	0.00	0.00

At 200°C, no hydrocarbons could be detected in pyrolysis products in any of the samples. There are 11 peaks at 300°C, 20 peaks at 400°C, 26 peaks at 500°C and more at the higher temperatures in the pyrograms of pure PVC. The percentage ratio γ of each peak height to the sum of all peak heights is shown in Table I. Pyrolysis of each sample at each temperature was repeated at least 5–20 times. No variation of peak height ratio γ was observed with pyrolysis periods of 15 sec and 20 min, respectively. The peaks corresponding to lettered components A–L represent unidentified materials. The quantities of these are small and even though these unknown materials are shown to be present, they are not considered in the conclusions of this paper. The lower aliphatic hydrocarbons in the products have been collected into one peak, because PEG-20M was used in the separation columns.

In pyrolyzing PVC, an elevated temperature favors formation of aliphatic hydrocarbons, while aromatics are more easily released than aliphatics at lower temperatures.

TABLE IB
γ Values of Pyrolysis Products

		γ					
		10% SnO_2		10% ZnO		10% Al_2O_3	
Peak	Component	500°C	700°C	500°C	700°C	500°C	700°C
1	Aliphatic hydrocarbons	32.70	64.46	24.26	60.27	7.76	37.25
2	Benzene	34.57	18.49	41.16	15.20	61.62	32.04
3	Toluene	7.24	6.79	6.03	6.67	7.67	10.46
4	Ethylbenzene	2.04	0.44	1.94	1.12	1.20	0.96
5	A	1.38	0.92	0.00	1.40	0.85	0.86
6	o-Xylene	2.46	1.16	1.46	1.13	1.75	1.57
7	Monochlorobenzene	0.57	0.69	0.69	0.18	0.47	0.00
8	B	1.04	0.30	1.11	0.89	0.47	0.33
9	Styrene	2.06	1.45	0.97	0.75	2.14	2.02
10	C	0.37	0.24	0.42	0.48	0.15	0.19
11	Vinyltoluene	0.49	0.60	3.60	0.36	0.70	0.58
12	D	0.73	0.23	2.15	1.20	0.96	0.35
13	E	0.79	0.09	0.28	0.68	0.83	0.38
14	p-Dichlorobenzene	0.45	0.14	1.94	0.13	0.16	0.04
15	o-Dichlorobenzene	0.70	1.25	2.91	1.70	2.15	2.56
	Indene						
16	F	1.10	0.30	0.97	1.25	0.75	0.16
17	1,3,5-Trichlorobenzene	0.59	0.05	1.11	0.37	0.31	0.00
18	G	0.25	0.23	1.39	0.48	0.82	0.44
19	1,2,4-Trichlorobenzene	0.36	0.60	0.83	0.75	1.31	0.76
20	H	0.18	0.13	0.44	0.50	0.21	0.13
21	I	2.50	0.15	1.18	0.36	0.78	0.36
22	Naphthalene	4.79	4.26	3.19	2.04	4.51	5.75
23	α-Methylnaphthalene	1.11	0.86	1.94	1.22	1.06	1.22
24	β-Methylnaphthalene	0.78	0.88	0.00	0.50	0.78	1.01
25	J	0.00	0.00	0.00	0.22	0.18	0.13
26	K	0.00	0.00	0.00	0.17	0.45	0.47
27	L	0.00	0.00	0.00	0.34	0.00	0.00

An important investigation in this work is the effect of added metal oxide on the formation of aromatics. Although preheated PVC and PVC mixed with metal oxides show a temperature effect, aromatic hydrocarbons are more easily released from the polymer than aliphatics in pyrolysis of pure PVC, PVC–TiO_2, or preheated PVC. On the other hand, aliphatic hydrocarbons are more easily released during pyrolysis of PVC with ZnO and SnO_2. In particular, a peak of aliphatics can be found in the pyrograms of PVC–ZnO and PVC–SnO_2 systems at 300°C, while it appears above 400°C in the other systems.

Decomposition yields of some aromatics obtained by the pyrolysis of PVC alone at each temperature are shown in Table II. These data were obtained by gas chromatography with *p*-dichlorobenzene as an internal standard. With increasing temperature, formation of naphthalene increases in comparison with benzene. More aromatics, futhermore, are released from the preheated PVC. These results indicate that the initial

TABLE II
Yields of Decomposition Products (Raw Polymer) with Pyrolysis at Various Temperatures

Product	Yield, wt-%					
	300°C	400°C	500°C	600°C	700°C	800°C
Benzene	3.50	4.67	5.00	5.23	6.30	9.95
Toluene	—	0.21	0.67	0.82	1.55	2.10
Ethylbenzene	—	—	0.16	0.18	0.18	0.23
o-Xylene	—	—	0.16	0.18	0.23	0.25
Styrene	—	0.13	0.22	0.37	0.74	1.06
Naphthalene	—	0.47	0.52	0.73	1.50	3.00

reaction is a dehydrochlorination and then cyclization of polyene in polymer chain begins.

As shown in Table I, trisubstituted benzene or naphthalene is not detected except for aryl chloride, and all the disubstituted aromatics appearing in the main peaks are *ortho* compounds. Accordingly, intermolecular dehydrochlorination or cyclization is not expected during the decomposition of PVC. This supports the results of infrared spectra reported by Ohtani.[8]

A secondary reaction of pyrolysis products with each other, e.g., Friedel-Crafts reaction of toluene with ethylene, might not be involved, because only *ortho* substituents are detected, even in materials obtained from pyrolysis of the PVC–Al_2O_3 system. In this system, Al_2O_3 would be changed to $AlCl_3$, so *ortho* and *para* substituents would be expected to be produced. However, compounds having *para* substituents cannot be detected.

The aromatic pyrolysis products may be classified in three groups: group I contains substances with a molecular structure entirely constructed of conjugated double bonds such as benzene, styrene, and naphthalene; group II contains aromatic hydrocarbons with methyl endgroups, such as toluene, ethylbenzene, xylene, vinyltoluene, β-methylstyrene, and methylnaphthalene; group III contains various aryl chlorides such as mono-, di-, and trichlorobenzene, chlorostyrene, chlorotoluene, and chloronaphthalene. $(\gamma_I)_0$ is defined as

$$(\gamma_I)_0 = (h_I/\sum h)_0$$

where h_I is the sum of peak heights of individual substances belonging to group I, $\sum h$ is the sum of peak heights of all the pyrolysis products. $(\gamma_I)_0$ is the ratio of group I peak heights to all peak heights obtained from the pyrolysis of raw PVC. Similarly there are obtained group I ratios $(\gamma_I)_{MO}$ from the pyrolysis of the preheated PVC and of PVC containing metal oxides.

Δ_I, then, is expressed by $(\gamma_I)_{MO}/(\gamma_I)_0$. The effect of metal oxides on the evolution of group I hydrocarbons from PVC may be estimated from Δ_I value. Δ_{II} and Δ_{III}, similarly, will offer information on evolution of group II and group III pyrolysis products. Furthermore, values of γ

and Δ have been obtained for certain individual pyrolysis products in the same way as for groups I, II, and III.

Figures 3–11 show plots of γ or Δ as a function of temperature for each PVC composition pyrolyzed, specifically Δ_I in Figure 3, γ_{II}/γ_I in Figure 4, $\Delta_{II/I}$ in Figure 5, γ values for ethylbenzene (EB) and toluene (TL) in Figure 6, the ratio of Δ values for the same compounds in Figure 7, γ and Δ value ratios for *o*-xylene (OX) and toluene in Figures 8 and 9, and γ and Δ ratios for group III and group I in Figures 10 and 11.

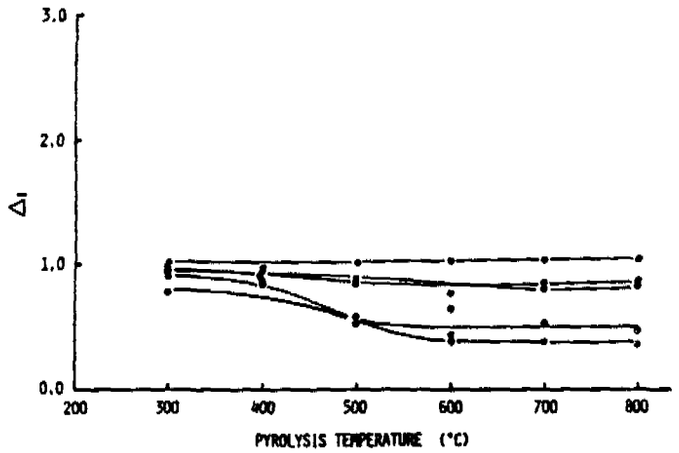

Fig. 3. Plots of Δ_I vs. pyrolysis temperature: (●) preheated PVC; (⊖) 10 wt-% TiO_2–PVC; (◑) 10 wt-% SnO_2–PVC; (⊖) 10 wt-% ZnO–PVC; (◐) 10 wt-% Al_2O_3–PVC.

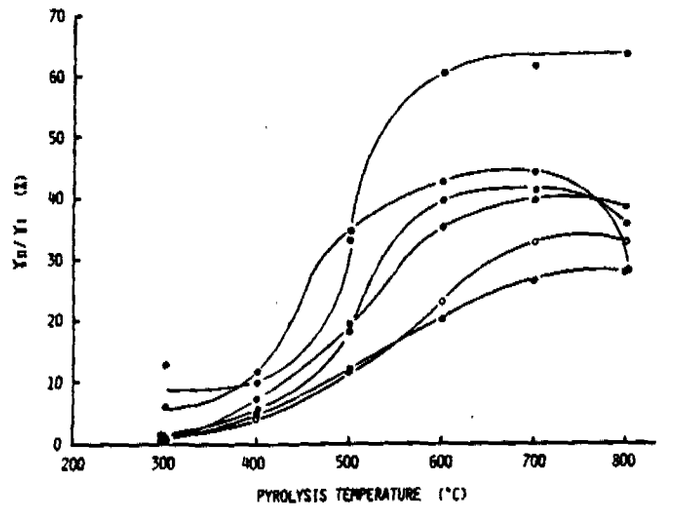

Fig. 4. Plots of γ_{II}/γ_I vs. pyrolysis temperature: (○) untreated PVC; (●) preheated PVC; (⊖) 10 wt-% TiO_2–PVC; (◑) 10 wt-% SnO_2–PVC; (⊖) 10 wt-% ZnO–PVC; (◐) 10 wt-% Al_2O_3–PVC.

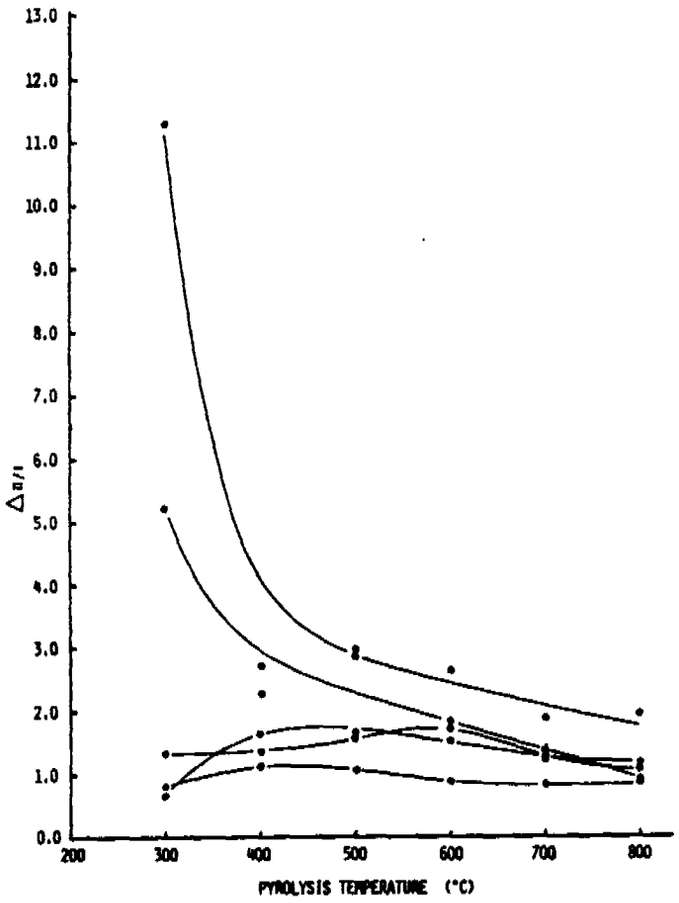

Fig. 5. Plots of $\Delta_{II/I}$ vs. pyrolysis temperature. Symbols as in Fig. 3.

The temperature dependence of Δ_I is illustrated in Figure 3. In the pyrolysis of the PVC–ZnO or the PVC–SnO_2 system, less of the group I products in the evolved materials is found with increasing temperature. It may be that ZnO or SnO_2 is effective in breaking the polymer chains, as evolution of aliphatic hydrocarbons is the result of an extreme rupture of chains. The relation of γ_{II}/γ_I to temperature of pyrolysis is shown in Figure 4. Group II is more easily released than group I at elevated temperature. The relation of $\Delta_{II/I}$ to pyrolysis temperature is shown in Figure 5, where $\Delta_{II/I}$ is the ratio of γ_{II}/γ_I for the polymer–metal oxide system to that of PVC alone. $\Delta_{II/I}$, therefore, measures the effect of addition or preheating upon the rate of formation of group II compounds relative to group I compounds. $\Delta_{II/I}$ values for all experiments are equal to units at higher temperature.

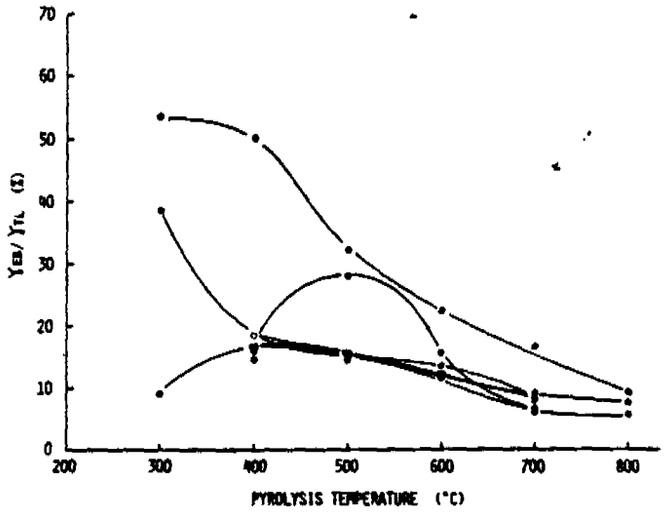

Fig. 6. Plots of γ_{EB}/γ_{TL} vs. pyrolysis temperature. Symbols as in Fig. 4.

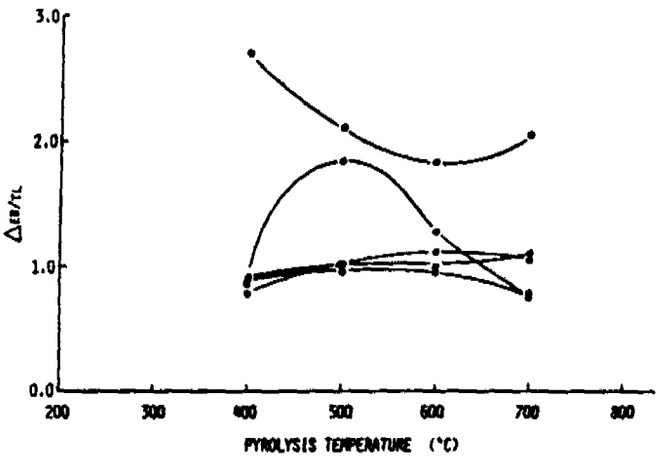

Fig. 7. Plots of $\Delta_{EB/TL}$ vs. pyrolysis temperature. Symbols as in Fig. 3.

Some results for γ_{EB}/γ_{TL} and $\Delta_{EB}/_{TL}$ are illustrated in Figure 6, Table III, and Figure 7 respectively. γ_{EB}/γ_{TL} decreases with increasing temperature, but the curve for ZnO has the steepest slope. The curve for SnO_2 has upward curvature and a maximum at 500°C. $\Delta_{EB}/_{TL}$ has a constant value. For ZnO and SnO_2, the tendency is the same for γ_{EB}/γ_{TL}. The temperature dependences of γ_{OX}/γ_{TL} and of $\Delta_{OX}/_{TL}$ are illustrated in Figures 8 and 9 and Table IV. The rate of evolution of *o*-xylene is unaffected by addition of metal oxides, as shown in Figure 9. γ_{OX}/γ_{TL} decreases with increasing temperature. $\Delta_{OX}/_{TL}$ is unity through

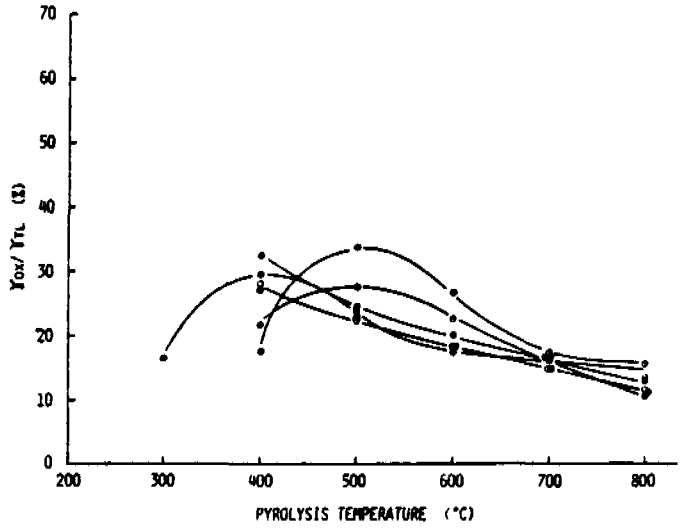

Fig. 8. Plots of γ_{ox}/γ_{TL} vs. pyrolysis temperature. Symbols as in Fig. 4.

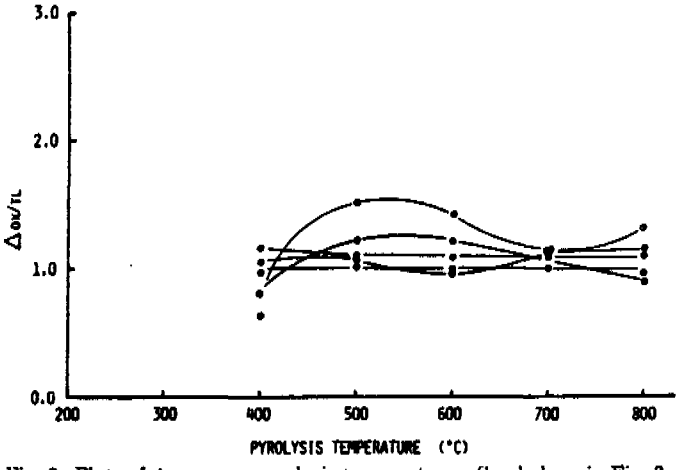

Fig. 9. Plots of $\Delta_{ox/TL}$ vs. pyrolysis temperature. Symbols as in Fig. 3.

for all experiments, as shown by the horizonal line. The release of ethylbenzene is accelerated by ZnO and SnO_2, but that of *o*-xylene is not. The ratio $\Delta_{ox}/_{TL}$ is constant through the various experiments.

ZnO is effective in producing release of group II compounds. Generally, dehydrochlorination of PVC is completed below 400°C, as reported by Matlack[9] and Salovey.[10] ZnO is converted to $ZnCl_2$ by reaction with HCl. This, it is suggested, accelerates dehydrochlorination.[11] At same time, hydrochlorination is also advanced. Therefore, ZnO contributes

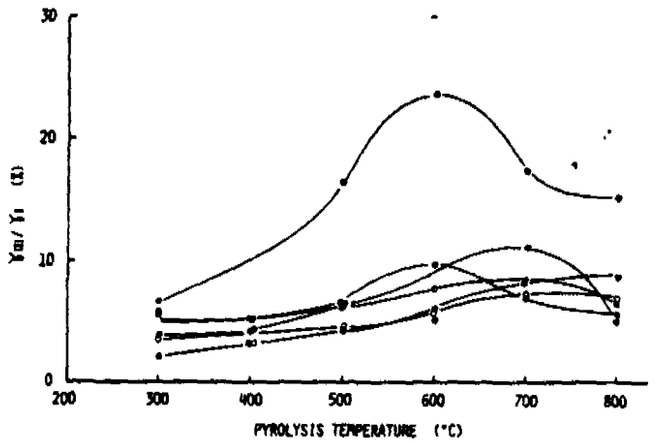

Fig. 10. Plots of γ_{III}/γ_I vs. pyrolysis temperature. Symbols as in Fig. 4.

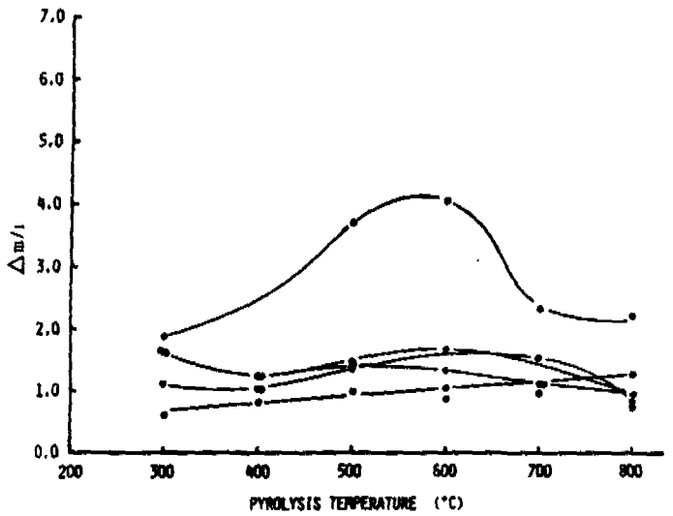

Fig. 11. Plots of $\Delta_{I/III}$ vs. pyrolysis temperature. Symbols as in Fig. 3.

much to the isolation of methylene. It has been pointed out by Stromberg and coworkers[12] that the methylene content in PVC which has undergone a thermal treatment is high. Their conclusion is in good agreement with the results described in this paper. The pyrolysis temperature dependence of γ_{III}/γ_I and of $\Delta_{III}/_I$ is shown in Figure 10 and Figure 11. γ_{III}/γ_I increases at the elevated temperatures. The curve for ZnO has upward curvature and a maximum at 600°C. $\Delta_{III}/_I$ has the same trend as γ_{III}/γ_I. The initial structure of polymer is independent of evolution of aryl chlorides ($\Delta_{III}/_I$ is not equal to unity, as shown in Fig. 11).

TABLE III
$\Delta_{EB/TL}$ for Thermal Decomposition

Pyrolysis temp, °C	$\Delta_{EB/TL}$					
	Untreated	Preheated	10% TiO_2	10% SnO_2	10% ZnO	10% Al_2O_3
300	—	—	—	—	—	—
400	1.00	0.90	0.79	0.89	2.70	0.91
500	1.00	0.97	1.02	1.85	2.11	1.03
600	1.00	0.96	1.12	1.28	1.84	1.00
700	1.00	0.75	1.05	0.79	2.05	1.12
800	—	—	—	—	—	—

TABLE IV
$\Delta_{OX/TL}$ for Thermal Decomposition

Pyrolysis temp, °C	$\Delta_{OX/TL}$					
	Untreated	Preheated	10% TiO_2	10% SnO_2	10% ZnO	10% Al_2O_3
300	—	—	—	—	—	—
400	1.00	1.16	0.78	0.63	1.05	0.97
500	1.00	1.10	1.23	1.51	1.08	1.01
600	1.00	1.09	1.22	1.43	0.97	0.99
700	1.00	1.09	1.12	1.14	1.13	1.00
800	1.00	1.10	0.90	1.32	1.16	0.97

Chlorinated polybutadiene, chlorinated polyethylene, vinyl chloride–vinylidene chloride copolymer, and chlorinated PVC were pyrolyzed previously and their pyrolysis products were described in detail by Tsuge.[12–16]

Chlorinated polyethylene, containing more than 0.71 Cl for every two carbons, was required to release mono- and dichlorobenzene. For chlorinated polybutadiene, it was 1.57 Cl per four carbons, and it was 2.32 Cl for release of tetrachlorobenzene. On pyrolysis of chlorinated PVC, tri- and tetrachlorobenzene were increased. Monochloro-, *m*-dichloro-, and 1,3,5-trichlorobenzene were released from vinyl chloride–vinylidene chloride copolymer.

The recombination of chlorine during the pyrolysis of PVC may be a possible mechanism.

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