

Catalytic Pyrolysis of Polyvinylchloride in the Presence of Metal Chloride

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ABSTRACT: The pyrolysis of polyvinylchloride (PVC) was studied in a quartz reactor with and without the addition of metal chlorides as catalysts. The results indicated that the addition of metal chlorides such as ZnCl_2 or BaCl_2 decreased the temperature of dehydrochlorination of PVC. The introduction of H_2 in pyrolysis enhanced the degradation of PVC at 400°C or higher and decreased the amount of solid residue. Gas chromatography/mass spectroscopy analysis indicated that Zn and Ba chlorides reduced the formation of high molecular weight products. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2464–2471, 2000

Key words: PVC; catalytic pyrolysis; pyrolysis; degradation; metal chloride

INTRODUCTION

Polyvinylchloride (PVC) is one of the most widely used plastics and finds applications in areas as diverse as water pipes, floor and roof tiles, packing films and sheet, etc. Because of its large quantity and chlorine content, the disposal of PVC waste has been a very important topic. The pyrolysis of PVC has been studied in recent years.^{1–3} In general, the mechanism of PVC pyrolysis is believed to be a two-step process.^{4,5} The first step mainly involves dehydrochlorination of the polymer to polyenes.⁶ It occurs at the temperature close to 300°C . At high temperatures, the polymer is pyrolyzed further to low molecular weight hydrocarbons with linear or cyclic structure⁷:



low molecular components and solid residues

Investigations on PVC pyrolysis under oxygen deficient conditions have shown the production of the following classes of pyrolysis products⁸:

1. HCl, which accounts for 56% of products.
2. Aliphatic hydrocarbons.
3. Aromatic hydrocarbons.
4. Chlorinated aliphatics (few).
5. Chlorinated aromatics, such as mono-chlorobenzene, chlorotoluene, and benzyl chloride.⁹

Most of the previous studies have been on the thermal pyrolysis of PVC.^{10–14} However, catalytic pyrolysis of polymers such as polyethylene and polypropylene has been shown to reduce pyrolysis temperature,^{15,16} and to result in sharper product distribution.^{15,17} In the pyrolysis of PVC, the addition of metal chlorides such as AlCl_3 , ZnCl_2 , and

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FeCl_3 can facilitate the dehydrochlorination reaction of PVC.^{18–20} In this study, we further investigated the product distributions characterized by gas chromatography/mass spectroscopy (GC/MS) analysis with and without the addition of chloride additives in PVC pyrolysis. The introduction of H_2 during pyrolysis will also be discussed.

EXPERIMENTAL

PVC powder was obtained from Nan Ya Plastics Corp., Taiwan. PVC-chloride samples were prepared by impregnating the PVC powder with chloride salts such as ZnCl_2 , $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The molar ratios of the PVC repeating unit and metal chloride were 1 : 0.005 or 1 : 0.01. The impregnated samples were dried in a vacuum oven at 90°C for 24 h. Approximately 0.5 g of the PVC or PVC-chloride samples were loaded in a holder hung on the suspension wire of a balance. The sample holder was enclosed in a quartz tube reactor with 2 in. of outside diameter. The reactor was heated by dual furnaces with temperature controllers. Pyrolysis of PVC samples was conducted by raising the temperature at $5^\circ\text{C}/\text{min}$ from room temperature to 550°C with N_2 or N_2/H_2 flowing through the tube reactor at 100 CC/min measured at 1 atm and 0°C . The weight change of the sample was recorded every 25°C . The gaseous products immediately downstream the sample holder can be withdrawn into a quartz collector for GC/mass analysis when needed. Product analysis was conducted with an HP-5890 GC and HP-5972 mass detector. A HP-5MS (0.25 mm \times 30 m) GC column was used for product separation.

In separate experiments, the pyrolysis products were also analyzed by using a pyrolyzer GC/MS instrument system containing a JHP-22 pyrolyzer (Japan Analytical Ind. Co.), 6890 series (Hewlett Packard) gas chromatograph with a HP-5MS capillary column (0.25 mm \times 30 m) and a mass selective detector. The 0.2 g sample was loaded in the system. Temperature of the pyrolyzer was raised quickly to 590°C and kept for 6 s before injecting the pyrolyzed products to GC/MS. The temperature programming of the GC column was as follows: temperature held at 40°C for the first 3 min, increased to 70°C with a heating rate of $2^\circ\text{C}/\text{min}$, held for another 3 min, then increased to 270°C at $10^\circ\text{C}/\text{min}$ and kept at this temperature until the end of the analysis.

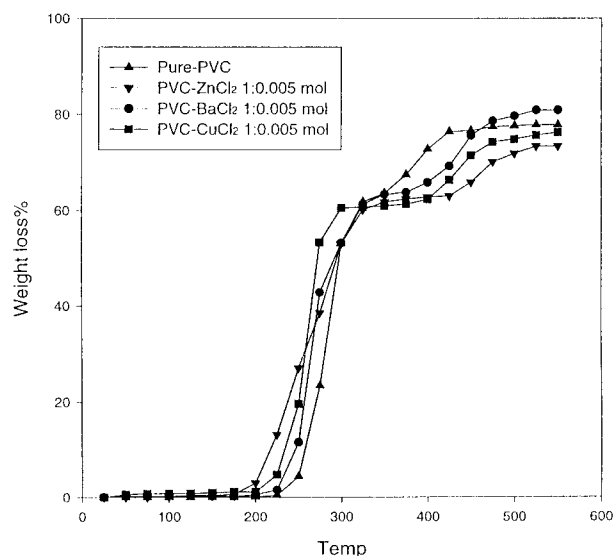


Figure 1 Weight loss of PVC with and without the addition of metal chlorides during pyrolysis in N_2 at a heating rate of $5^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

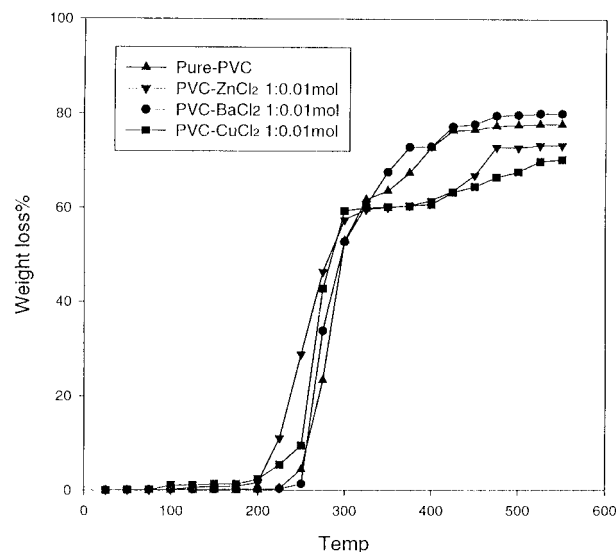
Pyrolysis in Tube Reactor

The pyrolysis of PVC samples was conducted in the tube reactor at a heating rate of $5^\circ\text{C}/\text{min}$. The product distributions analyzed by GC/MS and the weight changes of the sample in different temperature regions are listed in Table I. HCl is the main product at the temperature lower than 250°C . Dehydrochlorination reaction predominated the pyrolysis of PVC at low temperatures and ceased to occur above 400°C . Benzene is the major carbon-containing product below 350°C . The number of products that can be observed increased with the increase of temperature. Little liquid product can be found except that only a small amount of viscous liquid remained on the tube wall after the pyrolysis. The result confirms the previous studies that dehydrochlorination reaction is the first step of the thermal degradation of PVC.

The weight loss of PVC with and without the addition of 0.5 mol % of metal chlorides during pyrolysis up to 550°C is compared in Figure 1. Although the amount of a metal chloride additive is small, its possible small contribution to the weight loss of the sample was deducted by subtracting weight loss of the metal chloride additive from the weight loss of the PVC-metal chloride sample under the same experimental conditions. The results are shown in Figure 1. The dehydro-

Table I Product Distribution in the Pyrolysis of PVC at Various Temperature Ranges

Gas Products	M_w	Peak Area (%)
220–250°C, weight loss: 4.4%		
Hydrochloric acid	36	98.79
Benzene	78	1.215
250–300°C, weight loss: 48.6%		
Hydrochloric acid	36	65.07
Benzene	78	34.32
Toluene	91	0.6
300–350°C, weight loss: 10.6%		
Hydrochloric acid	36	58.1
Benzene	78	39.73
Toluene	91	2.55
Naphthalene	128	0.14
350–400°C, weight loss: 9.8%		
HCl	36	58
Benzene	78	10.71
Toluene	91	11.37
Ethylbenzene	106	2.05
Benzene,1,3-dimethyl	106	0.76
Styrene	104	1.37
P-xylene	106	3.85
Benzene,2-propenyl	120	0.32
Benzene,propyl	120	0.46
Indane	118	0.71
Benzene,butyl	134	0.42
Benzene,1-methyl-2propyl	134	0.403
Naphthalene	128	1.82
Naphthalene,1-methyl	142	0.66
400–450°C, weight loss: 3.8%		
1-Butene	56	26.13
Pentane	72	16.62
Cyclopentene	68	8.94
Hexane	86	11.79
Cyclopentene,3-methyl	82	2.44
Benzene	78	4.26
Toluene	91	9.6
Octane	81	1.59
Heptane	100	1.41
Ethylbenzene	106	3.44
P-xylene	106	7.22
Nonane	128	2.06
Benzene,1-ethyl-2-methyl	120	0.98
Naphthalene	128	0.61
Benzene,propyl	120	0.70
Indane	118	1.05
Benzene,butyl	134	0.66
Benzene,(1-methylpropyl)	134	0.6
Indane,1-methyl	132	0.71
450–500°C, weight loss: 1.0%		
Butane	58	30.5
Pentane	72	20.63
Pentene	72	10.98
Hexane	88	6.94
Benzene	78	5.25
Heptane	95	3.29
Toluene	91	6.42
Ethylbenzene	106	4.06
P-xylene	106	3.38
Benzene,1,2-dimethyl	106	1.65
Benzene,1-ethyl-2-methyl	120	2.32
Benzene,2-propenyl	120	0.98
Naphthalene	128	1.11
Naphthalene,2-methyl	142	0.7

**Figure 2** Weight loss of PVC with or without the addition of metal chlorides during pyrolysis in N_2 at a heating rate of $5^\circ\text{C}/\text{min}$.

chlorination of pure PVC started at about 250°C . However, PVC started to lose weight at lower temperatures when metal chlorides were added. For example, the weight loss of PVC started at about 200°C with the addition of ZnCl_2 . At 250°C , the weight loss increased in the order of pure PVC (4%), PVC- BaCl_2 (12%), PVC- CuCl_2 (19%), and PVC- ZnCl_2 (26%). The addition of 0.5 mol % of BaCl_2 resulted in a slightly smaller amount of solid residue at 550°C than the pure PVC sample. However, ZnCl_2 and CuCl_2 resulted in a slightly larger amount of solid residue. Figure 2 depicts the weight loss of PVC with or without the addition of 1 mol % metal chlorides during pyrolysis in N_2 . The results are similar to those in Figure 1 except that the weight loss of PVC at high temperatures is decreased when metal chlorides are increased to 1 mol %, especially in the case of CuCl_2 . The results suggest the stabilization of PVC at high temperatures when CuCl_2 and ZnCl_2 are added.

The effect of H_2 on the weight change of PVC in pyrolysis is shown in Figure 3. Little change in the onset temperature of dehydrochlorination was found. However, the addition of hydrogen significantly decreased the amount of residue after pyrolysis. There was no significant difference between 5 and 14% H_2 used in pyrolysis. Similar effect of hydrogen on the weight change of PVC was also observed for the PVC- BaCl_2 sample (Fig. 4) and other metal chloride added samples.

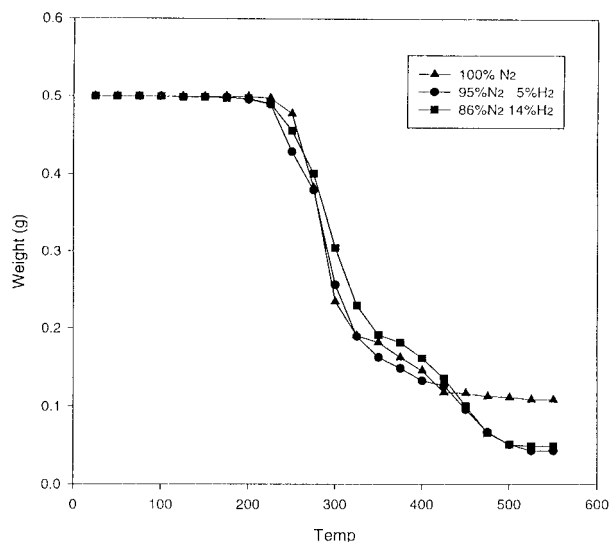


Figure 3 Weight change of PVC sample during pyrolysis in N₂ and in N₂/H₂.

Product Distribution Identified by Pyrolyzer GC/MS

Product distributions of PVC with and without metal chlorides after flash pyrolysis at 590°C were analyzed by pyrolyzer GC/MS equipment. The results are indicated in Table II. If the peak area of a component is larger than 5% of the peak areas of all identified components, the peak is called very strong peak (SS). Similarly, strong peak (S), medium peak (M), weak peak (W), and trace represent the peak areas of 1–5%, 0.5–1%, 0.1–0.5%, and below 0.1%, respectively. The molecular weight distributions of products are compared in Figure 5. The components with molecular weights between 150 and 200 represent the group with the largest peak area. The heavy components with molecular weights higher than 200 substantially decreased when 0.5 mol % BaCl₂ or ZnCl₂ was added to PVC.

DISCUSSION

The dehydrochlorination reaction of PVC occurred largely below 300°C and completed below 400°C (Table I). Benzene and alkyl benzenes were major carbon-containing products below 400°C. Dehydrochlorination of PVC would result in the formation of polyenes.⁷ Aromatization, cracking, and hydrogenation would produce benzene and alkyl and dialkyl benzenes. Aliphatic compounds were produced only above 400°C and was a result

of further cracking and hydrogenation of remaining residue. It should be noted here that a small amount of viscous liquid was found on the tube reactor after the pyrolysis. The viscous liquid can be washed off and dissolved in acetone. The analysis of the resulting liquid by GC/Mass showed the presence of naphthalene, alkyl and dialkyl naphthalenes, fluorene, and alkyl phenanthrenes, etc. It is also interesting to note that HCl and benzene were the major vaporizable pyrolysis products of PVC at temperatures below 350°C (Table I). Only a small amount of toluene and naphthalene were found. Sixty-four percent of PVC weight was lost during temperature programmed pyrolysis up to 350°C. Therefore, it is possible to recover HCl and benzene as chemicals in pyrolysis of PVC. Manzoor et al.²⁰ found that the addition of ZnCl₂ with PVC reduced the activation energy of dehydrochlorination of PVC and temperature required for the reaction. The result is consistent with our study. However, our study also found that the addition of metal chlorides such as ZnCl₂ and CuCl₂ retarded the second-step degradation of PVC. The second-step degradation of pure PVC largely occurred below 400°C (Figs. 1 and 2). However, the metal chloride added samples showed considerable weight loss between 400 and 500°C. The amount of solid residue remaining after programmed heating to 500°C was also higher for the chloride-added samples. High molecular weight hydrocarbons ($M_w > 200$), especially condensed ring aromatic hydrocarbons

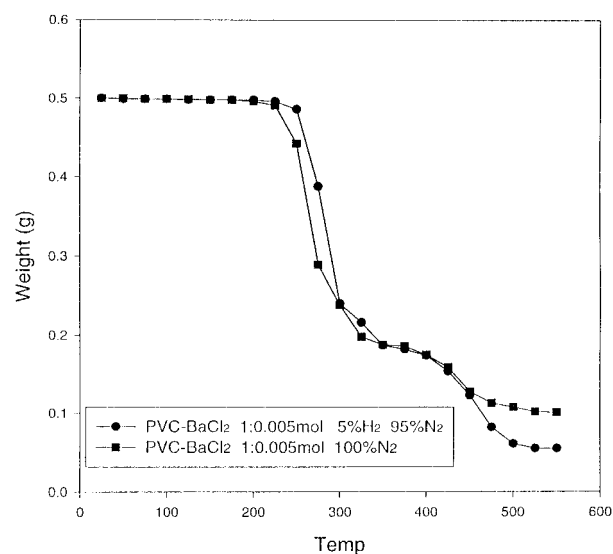


Figure 4 Weight change of PVC in PVC-BaCl₂ sample during pyrolysis in N₂ and in N₂/H₂.

Table II Product Distributions in PVC Flash Pyrolysis With and Without the Addition of Metal Chlorides at 590°C

RT (min)	Library/ID	M_w	Pure PVC	PVC BaCl ₂	PVC ZnCl ₂	PVC CuCl ₂
1.57	Hydrochloride acid	36	SS	SS	SS	SS
1.62	1,3-Cyclopentadiene	66	S	M		
2.05	Furan,tetrahydro	72		M	M	S
2.16	1,3-Cyclohexadiene	80	W			
2.23	Cyclopentene,3-methyl-	82			M	
2.34	Benzene	78	SS	SS	SS	SS
3.65	Cyclohexene,3-methyl	138			W	W
3.99	Toluene	91	S	S	S	S
4.52	Cyclopentanone	80			W	W
6.35	Benzene,chloro	112	W	W		
6.98	Ethylbenzene	106	M	W	M	W
7.32	<i>p</i> -Xylene	106	W	W	W	W
8.20	Benzene,1,3-dimethyl	106			M	
8.28	Styrene	104	S	S	M	W
11.11	Benzene,1-ethenyl-2-methyl-	118	M	W	W	W
11.50	Benzene,propyl	118		W	W	W
12.78	Benzene,1-ethyl-2-methyl-	120				W
15.68	Benzene,1,1'-[1-ethenyl-1,3-propanediyl]	220			W	W
15.91	Benzene,1-propenyl-	118	M	W		
16.34	Benzene,2-propenyl-	118	M	W	M	W
16.93	Indene	116	S	S	S	W
17.61	Benzene,butyl	134			W	W
19.53	Indene,1-methyl-	132			W	W
22.69	(E)-1-phenyl-1-butene	132		W	W	
23.18	1H-Indene,2,3,dihydro-4-methyl	132	W	W		W
	1H-Indene,2,3,dihydro-5-methyl				W	
23.45	2,3,dihydro-1-methylindene	132				W
23.46	Benzene,2-ethenyl-1,4-dimethyl	130			M	
23.57	Benzene,(1-methyl-2-cyclopropen-1	130	M	M	M	
23.66	1H-Indene,3-methyl	130				W
23.83	Cycloprop[a]indene,1,1a,6,6a-tetra	130	M	M	M	
24.12	Naphthalene,1,2-dihydro-	130	S			W
24.04	Naphthalene,1,2,3,4-tetrahydro-	132	W	W	W	W
24.79	Naphthalene	128	SS	S		S
24.82	1H-Indene,2,3-dihydro-1,6-dimethyl	146			W	
25.10	Benzene,(3-methyl-2-butenyl	146				W
25.67	Naphthalene,1,2-dihydro-2-methyl-	144	W	W		
25.80	Naphthalene,1,2-dihydro-6-methyl-	144		trace		
25.81	1H-Cyclopropa Naphthalene,1a,2	144	W		trace	
26.40	1H-Indene,2,3-dihydro-5,6-dimethyl	146			trace	
26.57	1H-Cyclopropa Naphthalene,1a,2	144	W		trace	W
26.85	Naphthalene,1,2-dihydro-3-methyl-	144	W	trace	W	
26.94	Naphthalene,1,2-dihydro-2-methyl-	144		W	W	W
26.95	1H-Indene, 1,1-dimethyl-	144	W	trace	W	
27.01	Benzocycloheptatriene	142		W		
27.08	1H-Indene,2,3-dihydro-5,6-dimethyl	146			W	trace
27.44	Naphthalene, 2-methyl-	142	S	S	M	M
27.54	Naphthalene,1,2-dihydro-6-methyl-	144	W		W	trace
27.76	Naphthalene, 1-methyl-	142	S	S		
27.89	Benzene,1-hexynyl-	158			W	
28.96	Naphthalene, 2-ethenyl-	154	S	S	M	W
29.17	Naphthalene, 1,2-dimethyl-	156	W	W		

Table II Continued

RT (min)	Library/ID	M_w	Pure PVC	PVC BaCl ₂	PVC ZnCl ₂	PVC CuCl ₂
29.23	Naphthalene, 2-ethyl-	156	W		M	W
29.28	1,1'-Biphenyl, 2-methyl-	168	M		W	W
29.32	Butane,1,1'-oxybis[4-chloro	198		W		
29.37	Benzene,1,5-cyclohexadien-1-yl-	156	W	W		
29.62	2,2'-Dimethylbiphenyl	182		M		
29.78	Diphenylmethane	168	W	W	W	W
29.56	Naphthalene, dimethyl-	156	W	W	W	W
30.02	Acenaphthylene	152	W	W		W
30.10	Naphthalene, 1-(2-propenyl)	168	W	W		W
30.19	Naphthalene, 1,2-dihydro-1,1,6- trimethyl-	172			W	
30.41	1,1'-Biphenyl, 2-methyl-	168	W			
30.51	Acenaphthene	154	W	W	W	W
30.63	1,1'-Biphenyl, 3-methyl-	168	W	W		W
30.68	Naphthalene, 2-[1-methylethyl]-	220			W	
30.75	2,5,8,11,14-Pentaoxahexadecan-16-ol	252		W		
30.88	Butylated Hydroxytoluene	220	W	W	M	W
30.99	Bibenzyl <i>o</i> -Hydroxybiphenyl	182	W	S		
31.03	Naphthalene,2,3,6-trimethyl	170			W	
31.04	Anthracene, 9,10-dihydro-	180	W			
31.12	2,2'-Dimethylbiphenyl Benzene,1-methyl-2-(phenylmethyl	182	W	W		W
31.23	Naphthalene,1,6,7-trimethyl	170			W	
31.68	1,1'-Biphenyl, 2-methyl-	168	W	M		M
31.75	Fluorene	166	S	S	S	S
31.88	Fluorene,2,4a-dihydro-	168			S	
32.32	1,1'-Biphenyl, 2-ethyl-	182			W	
32.73	Benzene, 1-methyl-3-(2-phenylethen	194	W			
32.78	Phenanthrene,9,10-dihydro	180	M			
32.80	9H-Fluorene, 2-methyl	180	M		S	S
32.91	1,2-Diphenylethylene	180	S	S		
33.04	9H-Fluorene, 1-methyl	180	M	S		
33.05	4,4'-Dimethylbiphenyl	182			M	
33.09	Naphthalene,2-(1-cyclopenten-1-yl)	194		S		
33.23	3,3'-Dimethylbiphenyl	182			S	S
33.34	1,2-Dihydrophenanthrene		S	S		
33.42	Phenanthrene	178			S	
33.48	Anthracene	178	S	S		M
33.55	Naphthalene,1,2-dihydro-1-phenyl-	206	S	S		
33.56	Naphthalene,2-(1-cyclopenten-1-yl)	194			S	
33.71	Cinnoline, 3-phenyl-	206	M			
34.00	Naphthalene, 1-phenyl-	204	S			
34.02	Phenyl,4-(1-methyl-1-phenylthyl)	212		S		
34.18	<i>o</i> -Terphenyl	230	M	M		
34.25	Anthracene,2-methyl-	210	S		S	
34.35	Phenanthrene,4-methyl	192			S	
34.41	Anthracene,1-methyl-	192	S			
34.47	1,2-Benzenedicarboxylic acid,butyl-2	334				S

Table II *Continued*

RT (min)	Library/ID	M_w	Pure PVC	PVC BaCl ₂	PVC ZnCl ₂	PVC CuCl ₂
34.49	5H-Dibenzo[a,b]-cyclohepten-5-one	210	M	S		
34.52	Dibutyl phthalate	278	M	M		
34.60	[1,1'-Biphenyl]-2-ol,5-(1,1-dimet	226	S			
34.69	2-Phenyl-naphthalene	204	S			
34.80	Naphthalene, 1-(phenylmethyl)-	218	M			
35.08	Octadecane,1-Chloro	288			M	
35.76	1,5-Diazacycloheptadecan-6-one,5-[3-ami	311			W	
37.50	Cyclopropanenonanoic acid,2[(2-butylyc	322		M		

were also considerably smaller when BaCl₂ and ZnCl₂ were added to PVC (Fig. 5 and Table II). The result suggests that metal chlorides may retard the aromatization reaction. The amounts of chlorinated hydrocarbons were very small. The addition of hydrogen during pyrolysis may enhance the hydrogenation reaction and therefore decrease the amount of solid residue.

CONCLUSION

The addition of metal chlorides, especially ZnCl₂ and BaCl₂ promoted the dehydrochlorination reaction of PVC during pyrolysis. On the other hand, pyrolysis in the presence of H₂ facilitated the further degradation of polyene at high temperature and decreased the amount of solid resi-

due. Product distributions in PVC pyrolysis in the different temperature regions indicated that it was possible to recover HCl and benzene as chemicals if pyrolysis was conducted below 350°C. High molecular weight of pyrolysis products was substantially reduced when ZnCl₂ and BaCl₂ were added to PVC.

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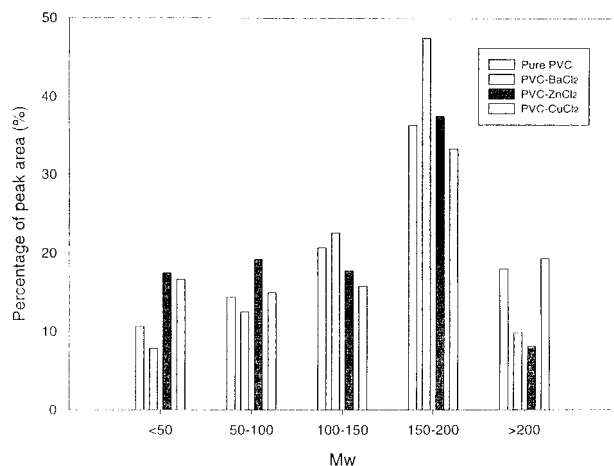


Figure 5 Molecular weight distribution of pyrolysis products for PVC with and without the addition of 0.5 mol % metal chlorides.

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