Char Formation in Polyvinyl Chloride. III. Mechanistic Aspects of Isothermal Degradation of PVC Containing Some Dehydrochlorination/Charring Agents

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Synopsis

We pyrolyzed PVC with and without the char-promoters iron (III) pyromellitate, zinc pyromellitate, and MoO_3 (1 phr) under isothermal conditions (207°C, nitrogen) and analyzed the soluble and insoluble residues to characterize the reactions important to charring. Both pyromellitates, apparently acting as their metal chlorides, catalyze dehydrochlorination and crosslinking that could lead to rapid charring; however, the zinc additive also catalyzes undesirable fragmentation. MoO_3, possibly acting as an oxychloride, has only a small effect on PVC degradation under the conditions used; however, it does suppress fragmentation. The relative rates of crosslinking to fragmentation are important in determining char yields.

INTRODUCTION

Previously, we reported that the SRI-developed materials, zinc pyromellitate and iron pyromellitate, and the commercial smoke suppressant MoO_3 all nearly doubled the char yield of rigid poly(vinyl chloride) (PVC) during radiant pyrolysis.[1] As part of our studies of condensed phase reactions that lead to charring in PVC,[2] we have used these three ostensibly equally effective charring agents [one part per hundred resin (1 phr)] in PVC to determine if the details of their charring reactions may vary. We wish to report isothermal pyrolysis results (207°C, nitrogen) of our mechanistic studies.

MATERIALS

The poly(vinyl chloride) used in these studies was a suspension-type blending resin (B. F. Goodrich, Geon 106-F2) stabilized with 2 wt % Ferro 5469 (Ferro Corp.), a liquid barium–cadmium stabilizer with organic inhibitor. The additives used were MoO_3 (Climax Molybdenum) and SRI-developed zinc pyromellitate and iron (III) pyromellitate.[1] Expressed in terms of the pyromellitate ion (C_{10} unit), the composition of the zinc pyromellitate is $C_{10}H_2O_8Zn_2 \cdot 2.0\ H_2O$, 0.2 ZnO and that of the iron pyromellitate is $C_{10}H_{4.6}O_{10.3}Fe_{1.7} \cdot 1.8\ H_2O$. The loading has always 1 phr. Samples were blended on a heated two-roll mill and then compression molded into 0.13-cm thick sheets.

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EXPERIMENTAL PROCEDURES

Isothermal Pyrolyses

Pyrolysis samples ($1 \times 3 \times 0.13$ cm; 0.7 g) cut from the compression-molded sheets were degraded isothermally at $207 \pm 1°C$ in nitrogen (150 cm/min) in a 2×4-cm Pyrex boat within a 30-cm long, 750-W tube furnace. The system was purged with nitrogen for 15 min each before and after pyrolysis with the sample in the cool zone. Pyrolysis residues, mostly separated into their soluble and insoluble portions, were variously analyzed for solubility (tetrahydrofuran, THF), infrared (IR), and ultraviolet (UV) absorptions, molecular weight, and elemental content.

Extreme care was taken to prevent polyene oxidation by peroxides in the THF.[3] The THF was purified by refluxing over sodium borohydride until no peroxides could be detected.[4] This THF was then stored over the sodium borohydride under nitrogen until needed. Just before use, the necessary THF was distilled under nitrogen from metallic sodium. Peroxides were detected by an iodometric method.[5] THF solutions, and pyrolysis residues, were stored and handled under nitrogen in a glove bag and their contact time with air during analysis was kept to a minimum. THF solutions were analyzed as soon as possible after preparation and were checked for peroxides just prior to any analysis. Only peroxide-free solutions were used.

The insoluble portions of the residues were characterized further using two different pyrolysis techniques. In one, we analyzed as before the nonvolatile products or residue formed during repyrolysis (207°C, nitrogen) of the insoluble residue. In the other, we analyzed the volatile products formed during flash pyrolysis of the insoluble residue.

Flash Pyrolysis/GLC Analysis

For flash pyrolysis/gas–liquid chromatography (GLC) analysis, we used 1.0–1.5-mg residue samples in a quartz sleeve (2 cm long, 0.20 cm i.d.) within the coil probe of a Pyroprobe 100 solids pyrolyzer (Chemical Data Systems, Inc.) attached to a Hewlett–Packard model 5750 gas chromatograph. Residue samples were pyrolyzed at 900°C for 10 sec. Only about 15% of each residue was volatilized. Volatile pyrolysis products were separated by a 4 ft $\times$ 1/8 in. Porapak QS (Waters Associates) column and detected by a flame ionization detector (FID). We also used a precolumn consisting of a 2 ft $\times$ 1/8 in. stainless-steel tube packed with 42- to 60-mesh 4Å molecular sieves to trap any HCl. The column was temperature programmed from 75 to 215°C at 30°C/min from the start of pyrolysis. Determinations were repeated four to six times. Peaks on the pyrograms were identified by comparing retention times with those of authentic compounds. Poor reproducibility results largely from sample inhomogeneity.

GRAVIMETRIC PYROLYSIS RESULTS

We used weight loss as a measure of the extent of dehydrochlorination of PVC. Weight loss for the four PVC samples as a function of pyrolysis time is shown in Figure 1. All three additives appear to produce an induction period to
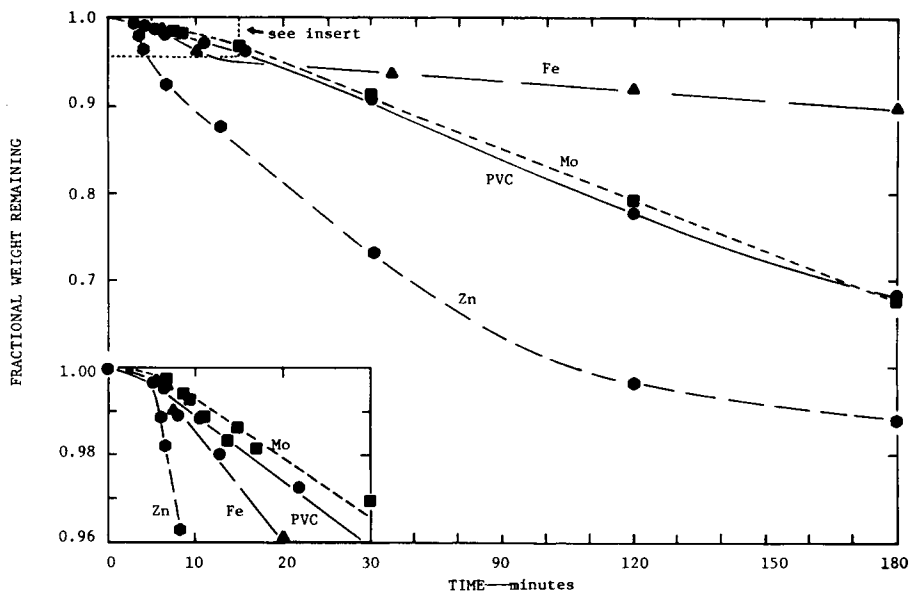
Fig. 1. Influence of pyrolysis on weight loss from PVC samples: PVC, ●; PVC/MoO₃, ■; PVC/Fe pyromellitate, ▲; and PVC/Zn pyromellitate, ⬤.   207°C Nitrogen.

dehydrochlorination as evidenced by brief retardation in the initial rates of weight loss as well as of development of unsaturation and discoloration. At 5 min or about 0.3% weight loss, only the PVC control is noticeably discolored; spectral analysis confirms that the additive systems are less unsaturated (see the following section). For PVC containing either pyromellitate salt, some of this initial weight loss could even be due to loss of water of hydration instead of HCl, as indicated by temperature-programmed thermogravimetric analysis of the salts.

For PVC/MoO₃, the induction period lasts about 11 min (1.2% volatilization). Thereafter, the rate of weight loss for PVC/MoO₃ becomes similar to that for PVC; both systems give brown final residues. The length of this induction period for PVC/MoO₃ is consistent with other results. At 11 min, unsaturation begins to increase rapidly and solubility to decrease (see the following). Furthermore, this 1% weight loss residue has only turned olive-brown, whereas, the 1% residues from the other three samples are all much darker brown; at 2% weight loss, the MoO₃ residue is also dark brown. The rate of volatilization from PVC/MoO₃ and PVC increases noticeably after the first 5% weight loss (30 min).

In contrast, after an induction period of only 6–7 min (1% volatilization), the rates of weight loss for PVC/Fe pyromellitate, and particularly PVC/Zn pyromellitate, become significantly faster than that for PVC alone. (The accelerating effect of Zn and Fe pyromellitates on early weight loss from degrading PVC has been noted previously.[6])   After an initial 5% weight loss (about 10 min for Zn pyromellitate, 25 min for Fe pyromellitate), however, the effect of the pyromellitates on subsequent decomposition on PVC changes. The zinc pyromellitate continues to accelerate weight loss but at a lesser rate, whereas, subsequent volatilization from PVC/Fe pyromellitate becomes considerably slower than that from the PVC control.

Some of the HCl lost initially from PVC probably reacts with the metal ad-

ditives and is retained in the residues most likely as the respective chloride or oxychloride. After 1 hr of heating, essentially all Mo, Zn, and Fe is still retained in the residues. HCl can promote degradation of PVC, and reaction of some HCl with the additives could account for the observed induction to dehydrochlorination when the additives are present.

The lengths of the observed induction periods are roughly proportional to the stoichiometric HCl requirements of the additives. At the additive loadings used (1 phr), conversion of Zn pyromellitate to $ZnCl_2$ would require 0.36% weight loss, as HCl from PVC alone, and conversion of Fe pyromellitate to $FeCl_3$, 0.45% weight loss. We find that by 1% weight loss, both pyromellitates are already very reactive reagents. By 1% weight loss (6–7 min), the starting material apparently has completely reacted. Thus, the salt absorption is gone from the infrared spectra and the extracts are no longer turbid (see the following). Pyromellitic acid and anhydride bands have also appeared in the infrared at this time, but conversion may not yet be complete. Pyromellitate features are not apparent in the UV of the soluble portion of the residues until 13 min for Zn pyromellitate and 20 min for Fe pyromellitate, or until about 5% weight loss for both. However, their appearance probably reflects a simple concentration effect, since they only appear after the polymer is extensively crosslinked. These results suggest that pyromellitate salt–HCl reaction products are the effective accelerating agents for weight loss.

The chloride of Mo(VI) is not known to exist, although oxychlorides do exist. Conversion of MoO_3 to oxychlorides would require from 0.50% (MoO_2Cl_2) to 0.75% ($Mo_2O_3Cl_6$) weight loss from PVC alone. The higher weight loss or HCl requirement for MoO_3 conversion could explain the slightly longer induction period with this additive. Unlike the pyromellitate salts, the lack of any major subsequent effect indicates that the MoO_3–HCl reaction products are ineffective catalysts.

CHARACTERIZATION OF COMPLETE RESIDUES

Infrared Analysis

Solid residues (KBr pellets), mostly from very low conversions, were analyzed by infrared spectroscopy for development of unsaturation and consumption of additive. For preparation of IR samples, brittle residues were first pulverized in a mortar, and plastic residues were shredded with a file, before being ground with KBr. After about 1% weight loss, minor development of unsaturation was apparent for all four samples in the 1650–1600-cm^{-1} double bond stretching region and the 970–965-cm^{-1} region characteristic of olefinic *trans* —CH=CH— absorption. Even at higher conversion (8%), these absorptions never become very intense.

The most distinct and noticeable change observed in the IR is the disappearance of the Zn and Fe pyromellitate salts (1560 cm^{-1}) and the appearance of pyromellitic acid (1725–1720 cm^{-1}) and pyromellitic anhydride (1805–1780 cm^{-1}, broad, and 1855 cm^{-1}) occurring between 0.3 and 1% weight loss for the PVC/Zn and Fe pyromellitate samples. At 1% weight loss, the zinc-containing sample gives relatively more anhydride-to-acid than does the iron-containing sample. At 8% weight loss, however, the situation is reversed and the iron sample gives relatively more of the anhydride.

THF Solubility

We used solubility in refluxing THF as a measure of the extent of crosslinking in the residues (Fig. 2). Both pyromellitates accelerate and enhance major crosslinking in PVC; they also promote major crosslinking at lower weight losses. After an apparent induction period, MoO_3 has only a small accelerating effect. In general, for PVC with and without additives, insolubility begins after about 1% weight loss and is nearly complete after about 8% weight loss. In all cases except possibly PVC/Zn pyromellitate, unsaturation (UV) is evident before insolubility; for PVC/Zn pyromellitate both processes are too fast to rank from present data.

For the metal-containing samples, turbidity in the THF extracts prior to filtration could relate to the presence of unreacted additive (see infrared results). Thus, with added MoO_3, the extracts are still turbid at 1% weight loss, but clear at 1.9% weight loss. With Zn or Fe pyromellitate, the extracts become clear between 0.3–1% weight loss.

CHARACTERIZATION OF SOLUBLE FRACTION OF RESIDUES

GPC Analysis

The THF extracts of residues were analyzed by gel-permeation chromatography (GPC) using tandem differential refractive index (DRI) and UV absorbance (254 nm) detectors. The UV detector is more sensitive to the development of unsaturation. GPC molecular weights are referenced to polystyrene standards.

Up to about 1% weight loss or while the residues are still mostly soluble, the GPC results provide evidence for development of unsaturation followed by
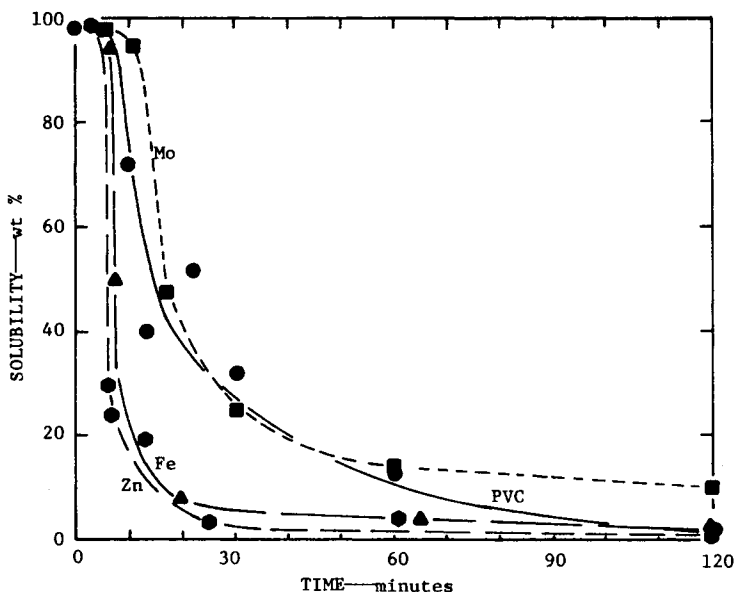

Fig. 2. Influence of pyrolysis on solubility in tetrahydrofuran of PVC samples: PVC, ●; PVC/MoO_3, ■; PVC/Fe pyromellitate, ▲; PVC/Zn pyromellitate, ◖. 207°C Nitrogen.
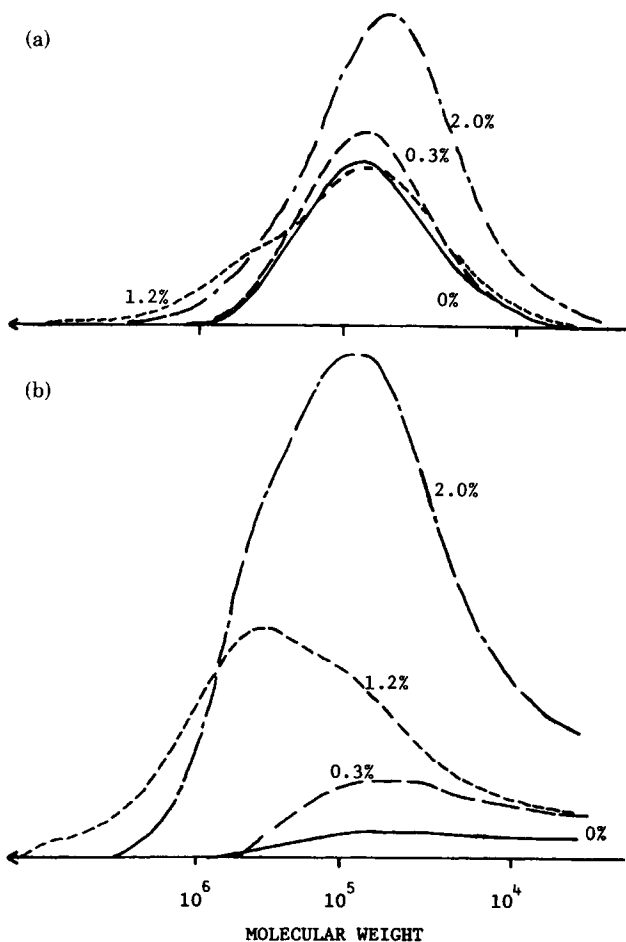
Fig. 3. Influence of pyrolysis on GPC chromatograms of PVC with (a) DRI detector; (b) UV detector (254 nm); numbers indicate weight loss. 207°C Nitrogen.

molecular enlargement (Figs. 3–6; the same weight of dissolved polymer was used in each chromatogram). By 0.3% weight loss (5 min; complete solubility), the UV results indicate that unsaturation presumably due to dehydrochlorination has developed in all samples but to a lesser degree in the additive systems. Apparently only dehydrochlorination has occurred, and the additives prolong the induction period to loss of HCl. Subsequently, unsaturation increases temporarily until crosslinking and insolubility that destroy or remove double bonds from the soluble fraction become competitive (Fig. 7). Between about 0.5 and 1% weight loss, the GPC of all four PVC samples broaden toward higher molecular weights indicative of molecular enlargement due to crosslinking. The results are unclear, but for PVC/Fe pyromellitate, some crosslinking might occur as early as 0.3% weight loss. In any case, all the enlarged species contain much unsaturation.

Once insolubilization becomes significant after about 1% weight loss, the molecular weight (DRI or UV) of the remaining soluble polymer in all four PVC samples decreases rapidly, particularly with Zn or Fe pyromellitate present (Fig.
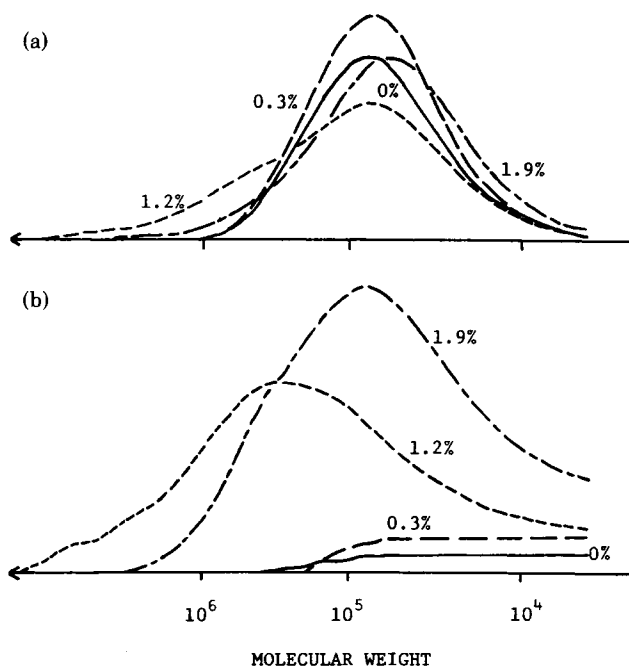
Fig. 4. Influence of pyrolysis on GPC chromatograms of PVC/MoO₃ with (a) DRI detector; (b) UV detector (254 nm); numbers indicate weight loss. 207°C Nitrogen.

8).   Crosslinking and the resulting insolubilization of high-molecular-weight material probably accounts for the early, rapid decrease in molecular weight, as well as a relative shift in unsaturation toward the low end of the molecular weight distribution (based on UV/DRI molecular weight ratios) observed at higher conversions for all PVC systems studied.   Consistent with the solubility results, these GPC results indicate that Zn and Fe pyromellitate accelerate crosslinking.   At low solubilities, where the decrease in molecular weight becomes more gradual, the decrease probably also results from fragmentation of both straight chain and crosslinked polymer.   Consistent with fragmentation, besides the polymer, unsaturated (UV) low-molecular-weight (<800) material eventually appears in the GPC chromatograms of all four PVC systems (Fig. 9, for a representative elution volume of 22.5 ml).   This material generally appears after initial rapid crosslinking and extensive insolubilization have occurred and the remaining soluble unsaturation, therefore, has leveled off or passed through a maximum.   Low-molecular-weight material is also obtained from pyrolysis of just the insoluble residues (see the following).   The relative time to appearance of this low-molecular-weight material should be an approximate measure of the relative rates of fragmentation.   Thus, zinc pyromellitate enhances fragmentation, whereas Fe pyromellitate and MoO₃ suppress it.   In all systems, crosslinking apparently occurs faster than fragmentation.

Ultraviolet Spectral Analysis

We followed the development of conjugated carbon–carbon double bonds and determined the length of the resulting polyene sequences $+CH=CH+_n$ in the THF extracts by UV spectroscopy.[7,8]   By UV analysis as by GPC analysis, we

(a)

0.3%

0.5%

1.0%

0%

(b)

1.0%

0.5%

0.3%

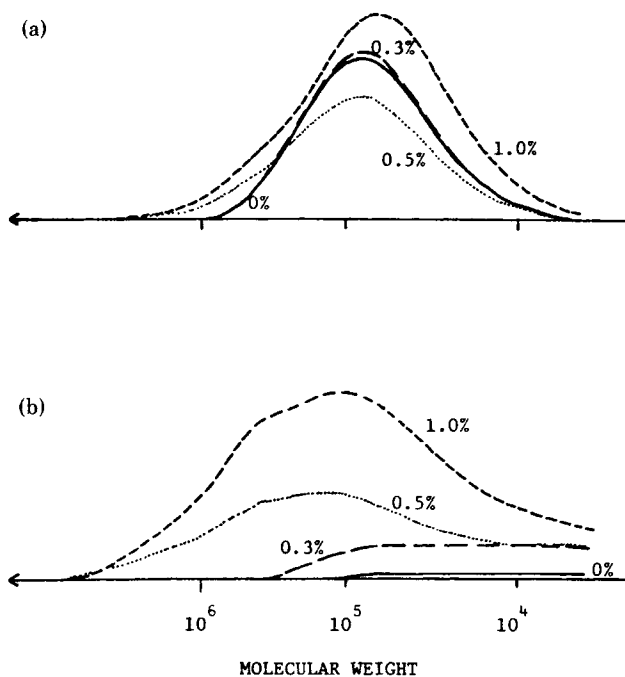0%

10^6 10^5 10^4

MOLECULAR WEIGHT

Fig. 5. Influence of pyrolysis on GPC chromatograms of PVC/Fe pyromellitate with (a) DRI detector; (b) UV detector (254 nm); numbers indicate weight loss. 207°C Nitrogen.

find that all three additives prolong the induction period to dehydrochlorination. Initially, the degree of unsaturation (optical density, O.D.) and polyene length do not increase as rapidly with the additives present (Figs. 10 and 11).

The change in optical density with time for the total extracts (Fig. 10 is representative) generally resembles that for the GPC polymer peak (Fig. 7) or

(a)

1.2%

1.8%

0,0.3%

(b)

1.8%

1.2%

0.3%

0%

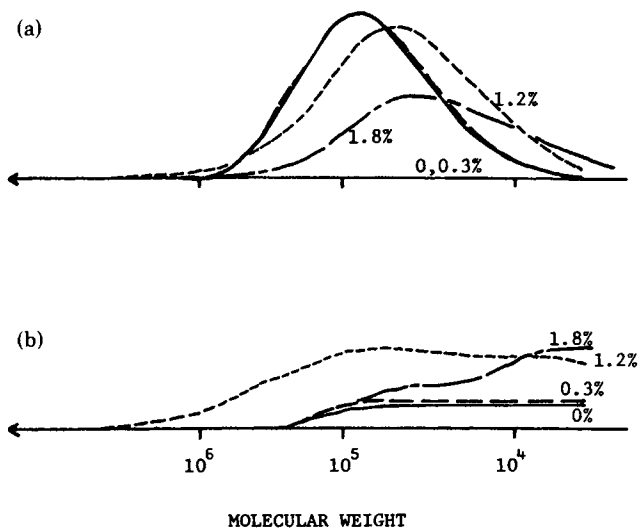10^6 10^5 10^4

MOLECULAR WEIGHT

Fig. 6. Influence of pyrolysis on GPC chromatograms of PVC/Zn pyromellitate with (a) DRI detector; (b) UV detector (254 nm); numbers indicate weight loss. 207°C Nitrogen.
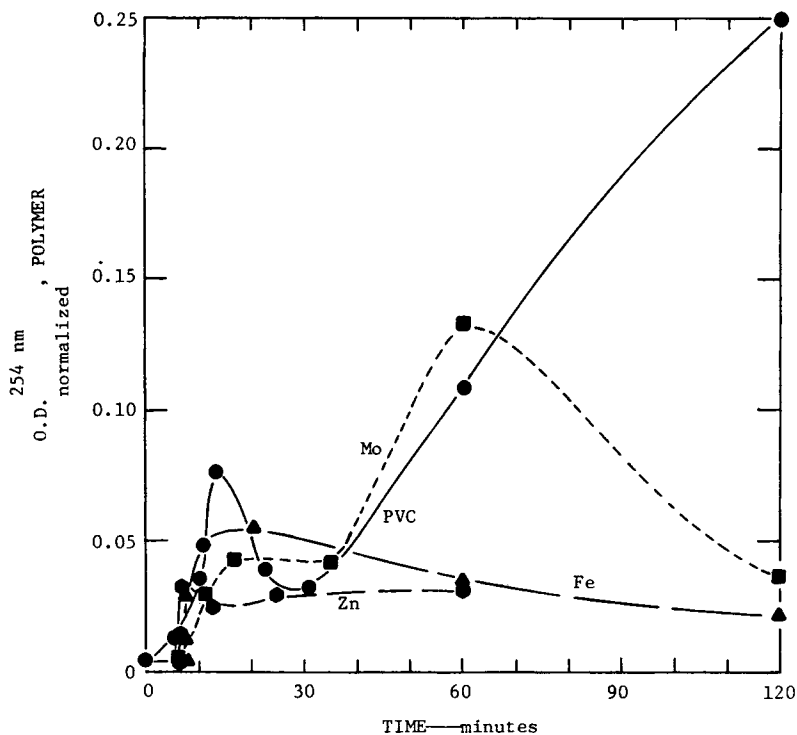
Fig. 7. Influence of pyrolysis on UV intensity (254 nm) of GPC polymer peak maximum for PVC samples: PVC, ●; PVC/MoO₃, ■; PVC/Fe pyromellitate, ▲; PVC/Zn pyromellitate, ●. 207°C Nitrogen.

low-molecular-weight material (Fig. 9) for PVC and PVC/MoO₃, but not for PVC/Zn pyromellitate and PVC/Fe pyromellitate. For the latter two systems, the early rapid increase in optical density must result from unsaturation present mostly in low molecular weight material, particularly additive residues. After 13 and 20 min, respectively, the zinc and iron pyromellitate samples exhibit benzenoid-type absorption in the 305–335-nm region that we tentatively attribute to additive residues; pyromellitic anhydride absorbs in this general region. The observed optical densities are not out of line with values calculated for the total amount of additive present as soluble pyromellitic anhydride.

Other benzenoid-type absorption also appears in the 260–270-nm region (indicated by open symbols in Fig. 10) for all systems except PVC/Fe pyromellitate. Degradation in the latter system may not have been carried far enough for this feature to appear. Aromatic structures have been found previously in partially dehydrochlorinated PVC residues.[9] All three additives retard significantly formation of this soluble aromatic material.

For the PVC control, the maximum length of the polyene sequence increases rapidly to $n = 11$ during the early stages of degradation (Fig. 11). All the additives, but especially both pyromellitate salts, decrease the maximum polyene length significantly, indicating that polyene destruction by crosslinking and fragmentation is more competitive with polyene formation. At long reaction times, the spectra of the pyromellitate salt systems are complicated by other absorption bands precluding the assignment of n. However, at low solubilities the polyene length appears to decrease for all four PVC systems.
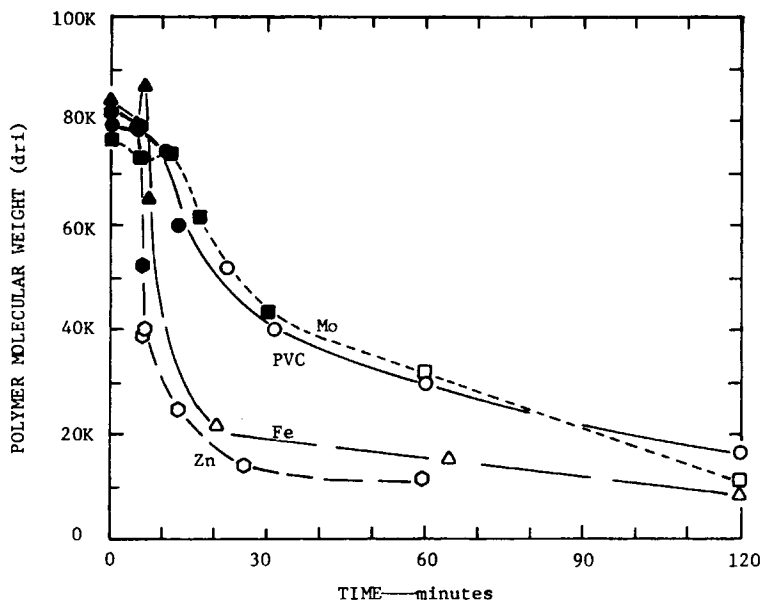
Fig. 8. Influence of pyrolysis on GPC (DRI) polymer peak molecular weight of PVC samples: PVC, ●; PVC/MoO₃, ■; PVC/Fe pyromellitate, ▲; PVC/Zn pyromellitate, ●. 207°C Nitrogen. △, ○, ○, □, indicate presence of low-molecular-weight material.

Infrared Analysis

The THF extracts of residues mostly from low conversions (1–2% weight loss) were analyzed by IR spectroscopy by evaporating several drops of solution directly on a NaCl IR plate. The results are similar to those for the unextracted residues; unsaturation develops, and Zn and Fe pyromellitates disappear with time, while pyromellitic anhydride and acid appear.

CHARACTERIZATION OF INSOLUBLE FRACTION OF RESIDUES

For these characterization studies, we used residues that had undergone the same extent of weight loss (8 ± 1 wt %) during pyrolysis at 207°C in nitrogen. Table I summarizes information on the initial pyrolysis conditions and the initial pyrolysis residues. Note that the different PVC systems require different pyrolysis times to reach the weight loss chosen for comparison, and the solubility of the PVC–Fe pyromellitate residue in particular is noticeably different (lower) from that of the other three. The insoluble portions of these residues were characterized further.

Isothermal Pyrolysis–Analysis of Nonvolatile Products

The insoluble portions of the initial residues were repyrolyzed (207°C, nitrogen) to 13 ± 1% weight loss. Interestingly, for PVC and PVC/MoO₃, the observed weight losses are in good agreement with calculated values for the respective time periods; however, for PVC/Zn pyromellitate the observed value is low and for PVC/Fe pyromellitate it is high (Table II). We compared the final residues from repyrolysis using the same analytical procedures outlined previously.
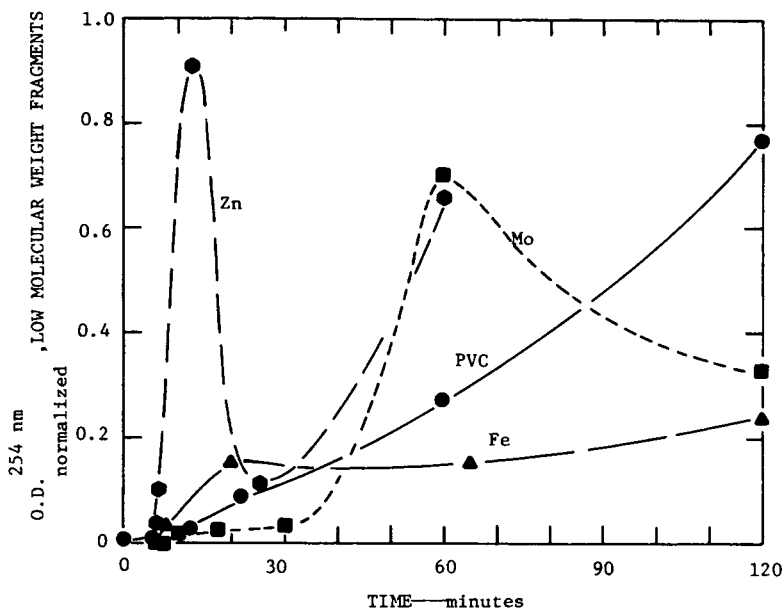
Fig. 9. Influence of pyrolysis on GPC maximum UV intensity (254 nm) of low-molecular-weight (<800) fragments from PVC samples: PVC, ●; PVC/MoO₃, ■; PVC/Fe pyromellitate, ▲; PVC/Zn pyromellitate, ◕.   207°C Nitrogen.

Fragmentation results for repyrolysis indicate that the initial residues from PVC with additives are more highly condensed or crosslinked than the PVC control residue (Table II).   Thus, PVC alone gives 22 wt % total fragmentation (volatiles plus soluble nonvolatiles), split about equally between volatiles and soluble nonvolatiles.   PVC with additives gives less total fragmentation (12–21%), mostly all as volatiles (67–93%).   Furthermore, these volatiles have higher chlorine contents and, therefore, lower organic contents than those for PVC alone. These differences in fragmentation suggest that more small, volatile fragments, probably including relatively more HCl, break off of the initial residues from PVC-containing additives.   Therefore, these residues could be more highly condensed or crosslinked than the PVC control residue.

The dominance, especially for additive systems, of very-low-molecular-weight material (≪800) in the soluble nonvolatile portions of all the repyrolyzed residues is also consistent with formation of small fragments from highly condensed or crosslinked structures.

For three of the systems, PVC, PVC/MoO₃, and PVC/Zn pyromellitate, the minor amounts of higher-molecular-weight material also present in the soluble nonvolatile portions further indicates some long uncrosslinked segments in the initial residues.   The length of these segments should relate to the average molecular weight between crosslinks, M_c.   In the PVC and PVC/Zn pyromellitate residues, these sequences are of about the same average length, but in the PVC/MoO₃ residue they are nearly 50% longer.   Not only the length, but also the number of these segments, depend on the particular residue.   Thus, in all three of these cases, but especially in the two with additives, this higher-molecular-weight material is a minor component of the extracts.   We conclude that the initial PVC control residue contains relatively more long uncrosslinked
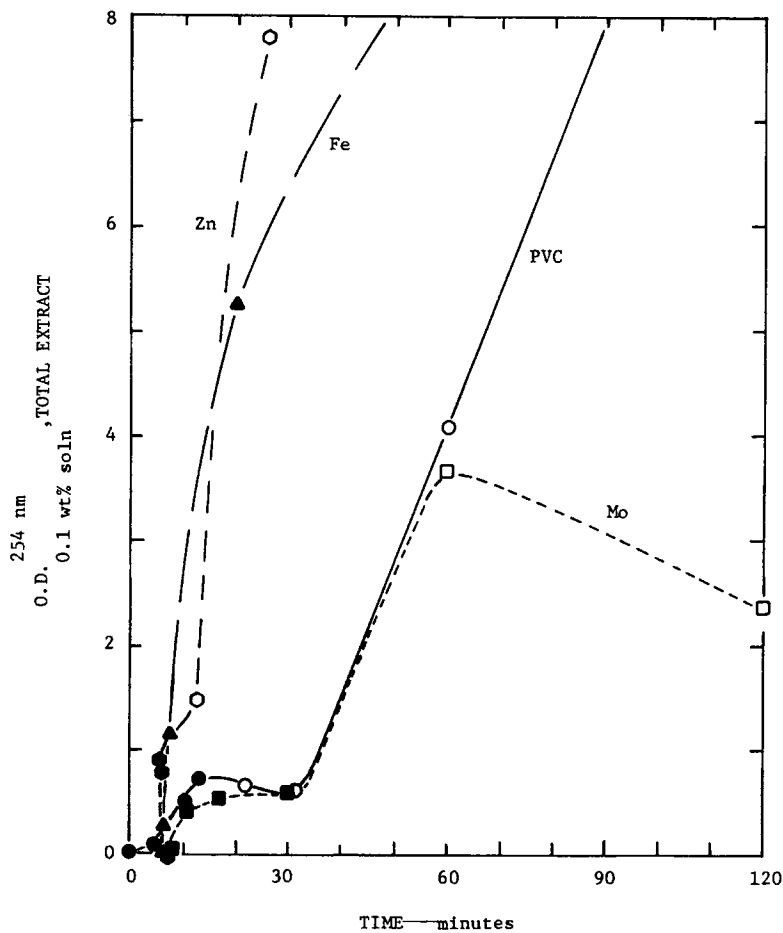
Fig. 10. Influence of pyrolysis on UV intensity at 254 nm of total extract of PVC samples;   PVC, ●; PVC/MoO₃, ■; PVC/Fe pyromellitate, ▲; PVC/Zn pyromellitate, ●.   207°C Nitrogen.   ○, ○, □, indicate presence of aromatic material.

segments than do the PVC/MoO₃ or PVC/Zn pyromellitate residues; the PVC/Fe pyromellitate residue contains none.

Perhaps reflecting the relative amounts of the high- and low-molecular-weight components, the nonvolatile fragments from pyrolysis of the initial PVC residue resemble partially unsaturated PVC, whereas those from residues of PVC with additives do not resemble PVC but possibly are aromatic.   (Because of low residue solubility, we could not obtain useful IR or UV spectra for the corresponding PVC/Zn pyromellitate extract.)

The IR spectra of the insoluble portions of all the repyrolyzed residues contain the features of PVC, some olefinic unsaturation, and, at least for PVC/Zn pyromellitate and PVC/Fe pyromellitate, some aromatic C—H.   Interestingly, from changes in the intensity ratio of the peaks for *trans*—CH=CH— to — CH₂—(965/1435), compared with the PVC control, for PVC with additives much more of the unsaturated material developed in the residue upon repyrolysis appears in the insoluble rather than in the soluble portion.
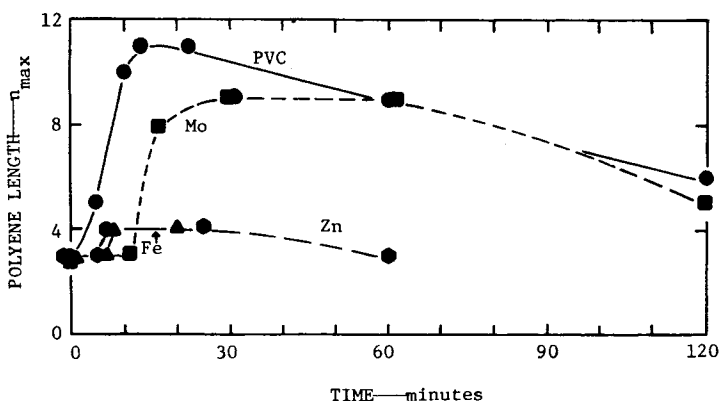
Fig. 11. Influence of pyrolysis on polyene length for PVC samples: PVC, ●; PVC/MoO₃, ■; PVC/Fe pyromellitate, ▲; PVC/Zn pyromellitate, ●.   207°C Nitrogen.

Flash Pyrolysis—Analysis of Volatile Products

The pyrogram of the PVC control residue contains two sets of peaks.   The first incompletely resolved set contains six major peaks, which are most probably C_1-C_6 hydrocarbons.   O'Mara identified a homologous series of saturated and olefinic hydrocarbons in this region when he flash-pyrolyzed PVC resin at 600°C.[10] The second set contains two major peaks followed by five minor peaks. The major peaks are benzene and toluene, respectively.   Following in order are chlorobenzene, two xylenes, indene (and/or o-dichlorobenzene), and an unresolved peak of unknown, probably aromatic, material.

Compared with the pyrogram for the PVC residue, pyrograms of the residues from PVC-containing additives showed that the kinds of volatile products were not affected, but that the distributions were different in two ways.   First, based

TABLE I
Results for Pyrolysis of PVC Systems and Characterization of their Initial Residues

Description	PVC	PVC/MoO₃	PVC/Zn pyromellitate	PVC/Fe pyromellitate
Starting material Cl content, wt%	56.10	55.70	55.26	55.05
Pyrolysis[a]				
weight loss, wt %[b]	9.2 (100)	7.9 (87)	7.3 (89)	8.2 (100)
time, min	60	60	13	120
Cl loss, wt %	17	12	12	17
metal loss, wt %	—	0	0[c]	1[c]
Residue, total				
Cl content, wt %	50.99	53.25	52.77	49.70
solubility, wt %	12 ± 4	14 ± 10	19 ± 12	3 ± 1
Soluble residue				
molecular weight	28,000	32,000	24,000	7400
polyene length, n_{max}	9	9	~4	~4
Insoluble residue (initial)				
Cl content, wt %	47.56	51.06	50.45	51.27
IR, 965/1435, T/T	0.93	0.87	0.76	0.87

[a] 207°C, nitrogen.
[b] % Cl loss calculated as HCl contributes to weight loss is in parentheses.
[c] Value at 60 min.

TABLE II
Results for Pyrolysis of PVC Residues

| | Initial insoluble residue[a] | | | |
Description	PVC	PVC/MoO$_3$	PVC/Zn pyromellitate	PVC/Fe pyromellitate
Pyrolysis[b]				
weight loss wt %[c]	12(13)	15(17)	13(25)	12(4)
time, min	60	90	60	120
Residue, total				
Cl content, wt %	50.87	48.67	—	50.02
solubility, wt %	12	7	≪1	~3
IR, 965/1435, T/T	1.03	0.86	0.64	0.91
Volatiles				
weight distribution, %	12	15	13	12
Cl content, wt %[d]	24	65	~77	61
Soluble residue				
weight distribution, %	10	6	≪1	2
molecular weight	9,000; <800	15,000; <800	8,000; <800	<800
IR, 965/1435, T/T	0.63	0, no max	—	0.25, no max
UV	$n_{max} = 5$	$\lambda_{max} = 268, 282, 322$	—	$\lambda_{max} = 320$ (benzenoid), 365
Insoluble residue				
weight distribution, wt %	78	79	87	86
Cl content, wt %	43.17	45.89	46.36	46.58
IR, 965/1435, T/T	0.86	0.90	0.85	0.90

[a] See Table I for origin of these residues.

[b] 207°C, nitrogen.

[c] Value in parentheses is weight loss calculated for insoluble residue alone for this pyrolysis period assuming contribution from insoluble residue to weight loss in Figure 1 is directly proportional to its concentration.

[d] Calculated by difference.

on peak areas, the relative amount of aliphatic (first set of GLC peaks) to aromatic (second set of peaks) material is shifted away from the aromatics to the aliphatics for the residues from additive systems (Table III). This shift is the greatest for the PVC/Fe pyromellitate residue and intermediate for the PVC/ MoO$_3$ and PVC/Zn pyromellitate residues.

Second, the distribution of aromatics is affected by the additives as shown in Table III. (With our GLC separation conditions, we could not detect changes in the aliphatics.) For the PVC residue, the major peaks, benzene and toluene, account for 54% of the total aromatic peak area. For the residues from the additive systems, the relative amount of benzene and toluene increases to 68–74% at the expense of the halo- and di-substituted, higher-molecular-weight aromatics. By reference to toluene, each of the other aromatic products is less abundant for the PVC-additive residues than for the PVC-control residue. The reduction in relative amounts of these other (nontoluene) aromatics is always smaller for the PVC/Zn pyromellitate residue and equally greater for the PVC/MoO$_3$ and PVC/Fe pyromellitate residues. The latter residue yields essentially no indene or higher aromatics.

The loss of relatively fewer aromatic fragments, especially higher molecular weight ones, suggest the initial PVC-additive residues are more tightly crosslinked than the PVC control residue. We cannot compare relative degrees of aromatization.

TABLE III
Flash Pyrolysis/GLC Results for Various PVC Residues

Sample	Volatilization, wt %	$\dfrac{\text{Aromatic}^a}{\text{aromatic + aliphatic}}$	$\dfrac{\phi H + \phi CH_3{}^a}{\text{total aromatic}}$	$\dfrac{\text{Benzene}^a}{\text{toluene}}$	$\dfrac{\text{Xylene} + \phi Cl^a}{\text{toluene}}$	$\dfrac{\text{Peaks after toluene}^a}{\text{toluene}}$
PVC residue	15 ± 4	0.49	0.54 ± 0.01	1.62 ± 0.05	1.07 ± 0.09	2.42 ± 0.50
PVC/Zn pyromellitate residue	16 ± 4	0.41 ± 0.02	0.68 ± 0.03	1.57 ± 0.12	0.82 ± 0.04	1.48 ± 0.50
PVC/MoO$_3$ residue	15 ± 2	0.38	0.70 ± 0.03	1.14 ± 0.04	0.71 ± 0.08	0.95 ± 0.13
PVC/Fe pyromellitate residue	15 ± 8	0.34	0.74 ± 0.02	1.20 ± 0.10	0.76 ± 0.06	0.77 ± 0.08

[a] Ratios are based on peak areas.

DISCUSSION

Volatilization behavior (Fig. 1) provides a good basis for describing the different effects of the three charring agents studied on the degradation of PVC. For PVC alone, major volatilization at 207°C in nitrogen begins after about 4–5% weight loss (about 30 min). Up to this point, dehydrochlorination accompanied by crosslinking and some fragmentation has occurred. Thus, by 5% weight loss, the residue is modestly crosslinked (32% soluble). The soluble portion of the residue contains polymer as well as some aromatic and low-molecular-weight materials (<800) probably resulting from fragmentation. The soluble polymer, which is modestly unsaturated and contains long polyene sequences ($n \simeq 10$), still has a moderately high molecular weight (50% decrease).

During subsequent major, rapid volatilization, fragmentation becomes noticeably more extensive relative to crosslinking. Thus, the intensity of the soluble low molecular weight material increases rapidly, while the rate of crosslinking (insolubility) slows down. Furthermore, the polyene length begins to decrease, indicating that polyene destruction by fragmentation and crosslinking is becoming more competitive with polyene formation by dehydrochlorination. Until insolubilization is complete, degradation of PVC must involve both the soluble and insoluble portions of the residue. Interestingly, the volatilization rate does not change when the residue becomes nearly insoluble around 15% weight loss. The absence of a rate change suggests that the crosslinked residue has a structure that can readily lose HCl, and fragment, too. Such a structure is confirmed by analysis of the crosslinked portion of a residue obtained after $8 \pm 1\%$ weight loss (12% solubility). The material contains some long uncrosslinked segments (M_c = 9000) that could easily dehydrochlorinate. Furthermore, the residue readily fragments to both nonvolatile low-molecular-weight (<800) and volatile organic material. The organic volatiles are approximately one-half aromatic and one-half aliphatic. Significantly, weight loss from the insoluble portion of the residue agrees well with the expected amount.

The three additives studied affect the degradation of PVC differently. Compared to the pyromellitates, MoO_3 has quite a small influence. After causing an induction period to dehydrochlorination, volatilization of PVC/MoO_3 becomes very similar to that or PVC. Major, rapid volatilization still begins after 4–5% weight loss (about 35 min). The most noticeable differences with the additive present are that crosslinking becomes more competitive with fragmentation (fragmentation is not apparent until well after major volatilization begins) and slightly more competitive with dehydrochlorination, at least during the early stage of weight loss. Thus, the 5% weight-loss residues for PVC with and without MoO_3 are comparably crosslinked (solubility), and except for the lack of low-molecular-weight material with MoO_3, the soluble portions of the two are also fairly similar. The insoluble residues have subtle differences. Like the insoluble residues from PVC after $8 \pm 1\%$ weight loss, the corresponding PVC/MoO_3 insoluble residue also can readily lose HCl; it contains relatively longer (M_c = 15,000) but apparently fewer uncrosslinked segments. More important, the PVC/MoO_3 insoluble residue fragments less readily to organic products, and the organic volatiles contain relatively more aliphatic than aromatic material compared to those from PVC, but the types of products are unchanged. As for PVC, weight loss from the PVC/MoO_3 insoluble residue agrees with its expected value.

The overall minor effect of MoO_3 in rigid PVC is in sharp contrast to its major effect in flexible PVC where MoO_3 reportedly lowers the temperature of major volatilization but not of onset of volatilization during temperature-programmed pyrolysis.[11] The plasticizer or other components in this fully formulated flexible sample could possibly account for this effect of MoO_3.

Both Zn and Fe pyromellitates have large effects on the isothermal pyrolysis of PVC. After causing a brief induction period to dehydrochlorination, both pyromellitates, but particularly the zinc salt, accelerate early volatilization of PVC. During this brief period, dehydrochlorination and crosslinking occur faster with the additives present. The zinc salt appears to be more effective at accelerating both processes; however, only this salt promotes fragmentation including production of aromatic material. Interestingly, after about 4–5% weight loss, when volatilization of PVC and PVC/MoO_3 increases, volatilization of the pyromellitate systems decreases: PVC/Zn pyromellitate is still slightly faster than PVC, but surprisingly, the iron system is now considerably slower.

After 4–5% weight loss (20–25 min), the iron-containing sample is nearly completely insoluble ($\sim$6%). Thus, subsequent degradation should involve largely the insoluble crosslinked residue. This residue could be the source of minor fragmentation to nonvolatile products (no aromatic ones) that first becomes apparent at this point. The insoluble portion of the PVC/Fe pyromellitate residue obtained after 8 ± 1% weight loss is more stable and more tightly crosslinked than any of the corresponding residues from the other three PVC systems. Consistent with the decrease in volatilization rate, this residue is less likely to dehydrochlorinate readily since it contains no long uncrosslinked segments (M_c <800). However, volatilization of this iron residue is still due mostly to loss of chlorine. Fragmentation of the residue, which is minor, gives primarily volatile organics. Compared to the other three PVC systems studied, these volatiles contain more aliphatic material and fewer types of aromatic material. Interestingly, although still very stable, this insoluble PVC/Fe pyromellitate residue loses much more weight upon pyrolysis than expected. Therefore, extraction appears to destabilize this residue; possibly the Fe agent stabilizes the insoluble residue.

After 4–5% weight loss (8–10 min) when volatilization of PVC/Zn pyromellitate slows down, the solubility of the residue (20% solubility) is roughly intermediate between those for PVC and PVC/Fe pyromellitate at the same weight loss. In this case, however, this ranking does not reflect an intermediate degree of crosslinking. The soluble portion of this residue appears to contain mostly low-molecular-weight polymer fragments and very little high-molecular-weight polymer, undoubtedly a consequence of the early enhanced fragmentation. Furthermore, these fragments probably become an eventual source of weight loss (see the temporary drop in intensity in Fig. 9 after 13 min). This insoluble residue is moderately crosslinked, but it still can dehydrochlorinate and fragment readily. After 8 ± 1% weight loss, the insoluble PVC/Zn pyromellitate residue contains some, but fewer, uncrosslinked segments (M_c = 8000) that are nearly as long as those found in the PVC residue. Upon pyrolysis, this PVC/Zn pyromellitate insoluble residue volatilizes about as readily as the corresponding PVC residue, but chlorine loss is a bigger contributor in the former case. Compared to PVC, the organic volatiles from this PVC/Zn pyromellitate residue are shifted away from aromatics to aliphatics and among the aromatics away from higher-

to lower-molecular-weight components. However, compared to the other additives, Zn pyromellitate gives the smallest shifts. Interestingly, weight loss for this insoluble zinc residue upon pyrolysis is less than that expected. In this case, extraction seems to stabilize the residue; removal of the zinc agent could be beneficial.

We can now comment on the requirements for a fire retardant to function effectively as a condensed-phase charring agent in PVC. Since crosslinking apparently involves the polyene, a fast-acting catalyst should accelerate both dehydrochlorination and crosslinking; to actually increase char yields, an effective catalyst should also increase the rate of crosslinking relative to fragmentation. Of the additives studied, only Fe pyromellitate seems to meet both criteria. (However, under more severe thermal conditions, the effective species, $FeCl_3$, is volatile, so the influence of the additive could be different[6]). Zn pyromellitate meets the first but not the second criterion; it accelerates both crosslinking and fragmentation. MoO_3 meets only the second criterion; it is largely ineffective under the conditions used, but it does suppress fragmentation somewhat.

The ability of Fe pyromellitate and MoO_3 to reduce fragmentation of PVC to organics including volatile and nonvolatile aromatic material is relevant to smoke suppression. Aliphatic fuels are generally less smoky than aromatic ones. It has been proposed that benzene results from intramolecular cyclization of polyene sequences of at least three double bonds.[12-14] Besides limiting the polyene lengths, thereby possibly restricting intramolecular cyclization, we speculate that these additives might promote formation of trans polyene sequences that cannot undergo intramolecular cyclization but that can crosslink. Such a condensed phase mechanism has recently been proposed for the fire retardant and smoke suppressant action of MoO_3 in PVC.[14]

For the three additives studied, the metal chlorides of Zn and Fe and possibly oxychlorides of Mo appear to be the probable effective catalysts for the various degradation processes in PVC. The chloride of Mo(VI) is not known to exist, but oxychlorides are known. Furthermore, $MoO_2Cl_2(g)$ can result from pyrolysis of $MoO_3(s)$ and HCl.[11] The initial induction to degradation of PVC with the additives present is consistent with reaction of the additives with HCl. We do not know exactly when this reaction is complete, but the induction periods do generally correspond to the stoichiometric requirements for reaction with HCl, and to the disappearance of the Zn and Fe pyromellitates salts and the appearance of pyromellitic anhydride and acid in the IR. Although some intermediate additive–HCl reaction products might be effective catalysts, their contribution is probably unimportant since they should be readily converted to the final metal chloride or oxychloride under these conditions. In each case, the same metal species would appear to affect dehydrochlorination, crosslinking, and fragmentation, but to different degrees.

The product metal chlorides and oxychloride can act as Lewis acids.[15] $ZnCl_2$ reportedly catalyzes initial dehydrochlorination,[4,16] subsequent polyene formation,[17] and crosslinking in PVC.[18,19] $FeCl_3$[19,20] and ferric ions generally[18] are known to catalyze dehydrochlorination and crosslinking to PVC. Molybdenum oxychlorides are not very strong Lewis acids and accordingly appear to be fairly ineffective in PVC under our conditions.

Other sources of Lewis acids should also be good char formers.[1,6,18,21] The organic portion of the pyromellitates regulates the initial reactivity of the metal

but apparently does not participate directly in the charring process.   However, details of the charring reactions for other precursors to Lewis acids may vary. The smoke suppression properties of such additives may depend on how effectively crosslinking competes with cyclization, aromatization, and fragmentation in the condensed phase.   The nature and concentration of the additive as well as the reaction conditions could alter these relative rates.[2,6,20]

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