In three recent publications,[4-6] workers from Bell Laboratories have proposed a "Lewis acid" scheme to explain the role of MoO_3 as a smoke and fire retarder additive in plasticized PVC. This mechanism is based on the formation of trans polyene chains which cannot cyclize to form benzene. The Bell Labortories Lewis acid scheme is not consistent with our reductive coupling scheme of early crosslinking.

The fourth report presented the results of our studies of MoO_3 in rigid PVC using our recently developed deuterium labeling methods.[7] It also extended our study of SS-50 and MoO_3 to syndiotactic PVC. These experiments were designed to show that metal smoke retarders in PVC predominantly function by means of our reductive coupling scheme, not by means of the Bell Laboratories Lewis acid scheme.

The fifth report in this series reviewed the literature publications which have been aimed at understanding the functional role of smoke retarders in PVC during either pyrolysis or burning.[8] In it we critically evaluated the Lewis Acid mechanism proposed by Bell Laboratories workers. We showed that the primary role of metal-based smoke retarders in PVC is best understood in terms of our proposed reductive coupling mechanism.[3,7]

This report (Part VI) presents the results of our studies of head-to-head (H-H) PVC, including H-H PVC compositions containing MoO_3 and SS-50 smoke retarders. The results of our experiments provide additional evidence to support our conclusion that the primary functional role of the smoke retarder is to promote early crosslinking of the PVC chains during thermal degradation. Our results also suggest that H-H PVC has superior combustibility characteristics compared to both heterotactic head-to-tail (H-T) and syndiotactic H-T PVC.

This report also provides a detailed review of the published studies concerning the structure and thermal degradation of H-H PVC. Our results are discussed in light of these published studies. It is intended that this review also will be useful in determining the direction of our current H-H PVC synthesis and evaluation program.

EXPERIMENTAL PART

Pyrolysis - flame ionzation-gas chromatography (PY-FID-GC) experiments were carried out as described previously.[3] The CDS 100 pyroprobe was used with a Varian 3700/CDS 111 GC system (Porapak PS column). Quantitative determinations for benzene and toluene pyrolyzates were made on the following samples:

(1) PVC (103EP-F76)
(2) H-H PVC (4025F-79-451)
(3) 10 parts - MoO_3 + 100 parts - PVC
(4) 10 parts - MoO_3 + 100 parts - H-H PVC
(5) 10 parts - SS-50 + 100 parts - PVC
(6) 10 parts - SS-50 + 100 parts - H-H PVC

The H-H PVC sample, 4025F-79-451, was prepared by R.G. Parker (Corporate Research). It was made by passing gaseous chlorine through a methylene chloride solution of cis-1,4-polybutadiene (CB-221). The reaction was run in subdued light. Air was not purged from the solution prior to adding the chlorine - this should minimize free radical chlorination. The recovered H-H PVC contained 56.3% Cl and had T_g = 79°C.

Pyrolyses were carried out in a helium atmosphere at 550°C for 20 seconds. Response factors for benzene and toluene were determined (external standard method) by injection of standard solutions (n-pentane solvent.). Samples (3-6) were mixed with an agate mortar and pestle. About 1-2 mg of a particular sample was pyrolyzed in each run; triplicate runs were made on all samples.

Qualitative PY-GC-mass spectroscopy runs were made on the H-H polymer (4025F-79-451) to identify the volatile pyrolyzates. Chromatograms using a Porapak QS GC column (Figure 1) and an SP-2100 GC column (Figure 2) are included.

Smoke-char analyses were made on the above six compositions using the Goodrich Smoke-Char Test.[9] The liquid N_2-pelletizing technique, described in reference 9, was used.

BFG-8783-B

BIC
03/29/80 9:00:00
SAMPLE:
RANGE: G 20. 682 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: MS1013AS #1
ENHANCED (S 38B 2N 0T)

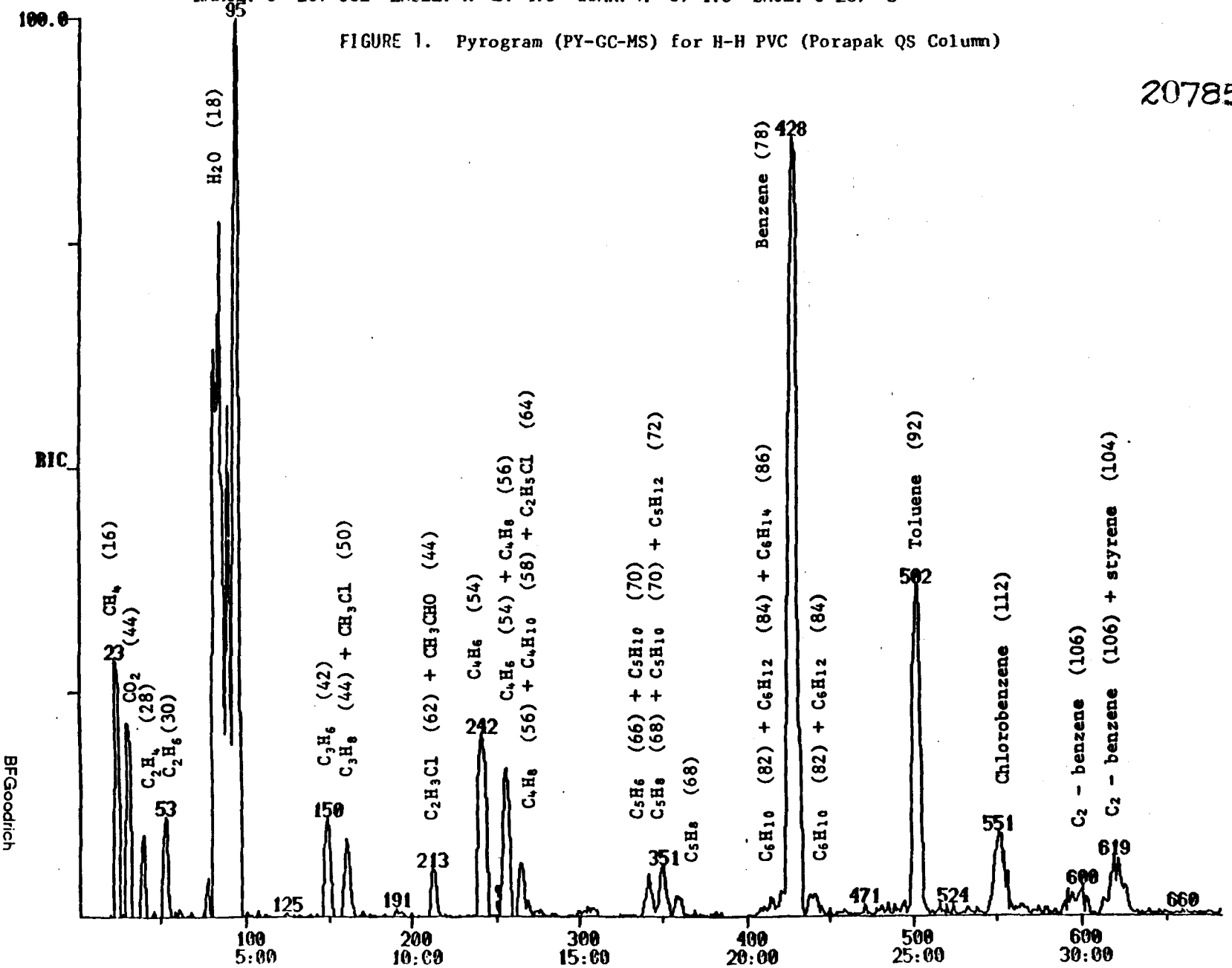
SCANS 1 TO 682

287744.

FIGURE 1. Pyrogram (PY-GC-MS) for H-H PVC (Porapak QS Column)

20785011

BFG06495



BFGoodrich
Research and Development Center

10

Corporate Research, 4008F-80
Corp. Tech. Support, 9101-80
RR, March 31, 1980

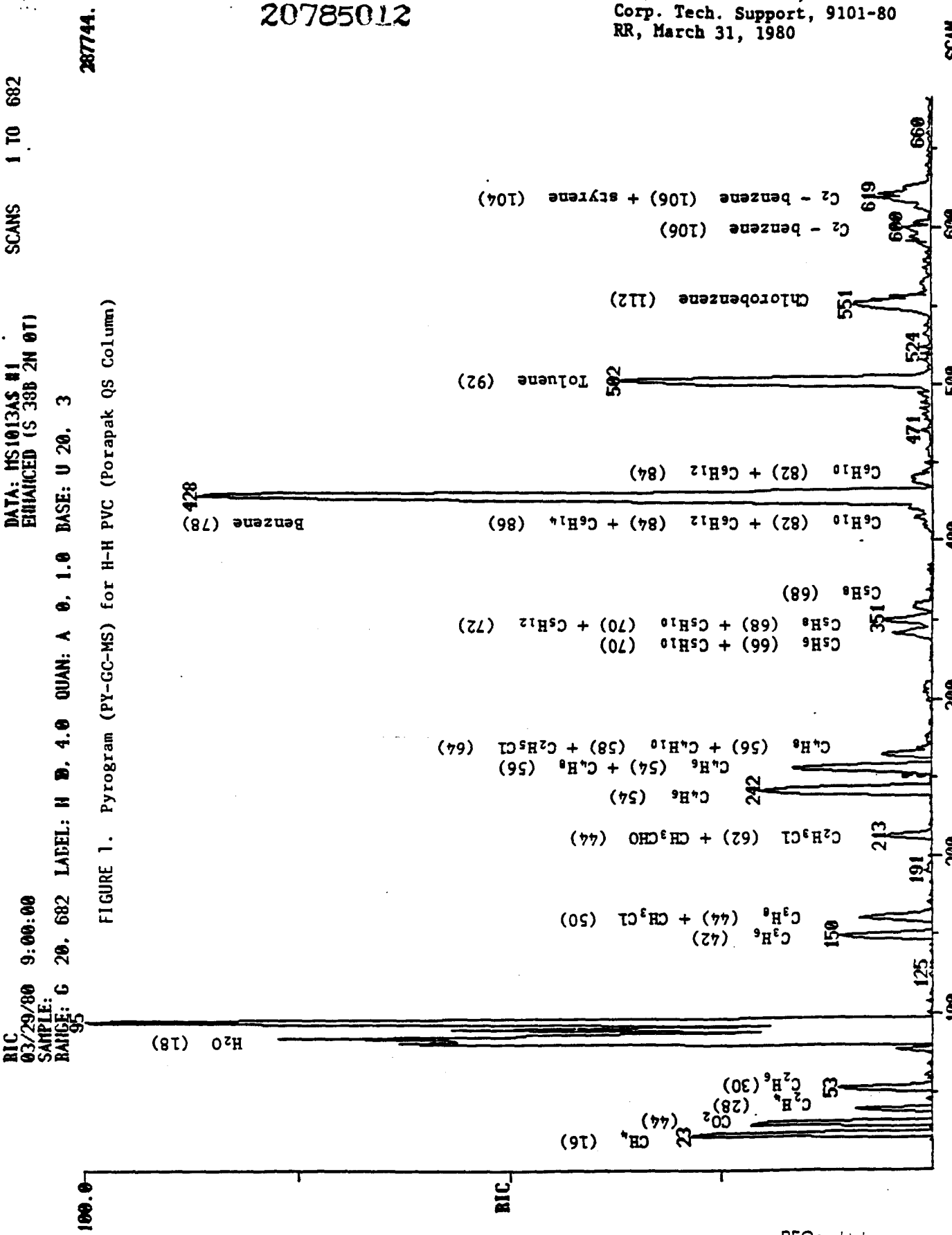


FIGURE 1. Pyrogram (PY-GC-MS) for H-H PVC (Porapak QS Column)

BFG-8783-B

BFG06496

BFGoodrich
Research and Development Center

RIC
04/05/80 11:10:00
SAMPLE:
RANGE: G 21. 831 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: MS1013CS #1
ENHANCED (S 40B 2H 0T)

SCANS 1 TO 800

287072.

FIGURE 2. Pyrogram (PY-GC-MS) for H-H PVC (SP2100 Column).

LITERATURE REVIEW: STRUCTURE AND THERMAL DEGRADATION OF HEAD-TO-HEAD PVC

In 1966, Murayama and Amagi compared the thermal degradation of H-H PVC to that of head-to-tail, H-T, (heterotactic) PVC using thermogravimetric analysis (TGA) in argon.[10] The H-H PVC was made by reacting a 99% 1,4-trans PB with Cl_2. The reaction was carried out in the dark in CCl_4 at 50°C, and produced a polymer containing 56.3% Cl.

Murayama and Amagi found that H-T PVC starts to dehydrochlorinate at 230°C, while H-H PVC begins to lose HCl around 200°C. However, H-H PVC loses HCl at a slower rate, and at 300°C retains more than 15% of the available HCl. In contrast, H-T PVC only retains about 3% of the available HCl at 300°C. They suggest that the 1,2-Cl arrangement in H-H PVC is less stable than the 1,3-Cl arrangement in H-T PVC. They further suggest that the chlorine in the degraded product, formed in the early stages of dehydrochlorination of H-H PVC, is more stable than its H-T counterpart; i.e., the chlorine attached to an unsaturated carbon should be more stable:

$$-CH_2-CH=\underset{\underset{\text{(vinylic)}}{Cl}}{C}-CH_2- \quad \text{more stable than} \quad -CH_2-CH=CH-\underset{\underset{\text{(allylic)}}{Cl}}{CH}-$$

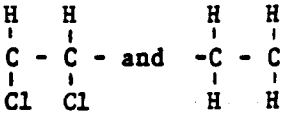
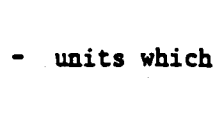
In the same paper,[10] Murayama and Amagi also showed that while H-T poly(vinylidene chloride), PVDC, rapidly dehydrochlorinates between 200 and 250°C, H-H PVDC is stable to about 280°C. H-T PVDC loses ~40% of its weight by 240°C. In comparison, H-H PVDC does not reach 40% weight loss until ~330°C. They suggest the higher stability of H-H PVDC may be due to freedom from a zipper-like decomposition reaction, and fewer adjacent hydrogen atoms to one chlorine atom relative to H-T PVDC.

Sobajima et al. in 1968 reported an NMR spectroscopy study of the structure of a chlorinated polybutadiene (ClPB) which had the H-H PVC stoichiometry.[11] The starting PB was 35% cis-1,4, 57% trans-1,4 and 7% 1,2 structures. Chlorination was performed in a mixture of $CHCl_3$ and CCl_4. Besides confirming the H-H structure, the broad character of the proton resonances was interpreted to indicate that segmental motions are restricted by chlorination, and that many types of $-CH_2-$ groups exist in the polymer. The suggestion of the restricted segmental motions is interesting in light of a recent note written by M.H. Lehr (Corporate Research).[12] In it Lehr describes a possibility to explain our observation (see Results and Discussion section) that H-H PVC gives off less benzene than heterotactic H-T PVC during inert atmosphere pyrolysis. Lehr suggests that the substitution of the more rigid 1,2-dichloroethylene group for a vinyl chloride group at the end of a conjugated olefin sequence results in increased chain stiffness which makes intramolecular cyclization to form benzene during the early stages of dehydrochlorination less likely.

The most detailed study of the thermal degradation of ClPB was reported by Ito et al. in 1970.[13] They used PY-GC to study the pyrolysis of a series of ClPB of different degrees of chlorination. Pyrolyses

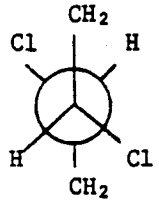
were carried out at 493°C. The starting polybutadiene polymers were 99.6% cis-1,4 and 0.4% 1,2 and 3.9% cis-1,4, 94.6% trans - 1,4 and 1.4% 1,2. The polymers were chlorinated in $CHCl_3$ by chlorine gas under the illumination of a mercury lamp.

Ito et al. found that the cis- and trans- PB gave almost identical pyrograms. Two main peaks were observed - one from C_1 - C_4 hydrocarbons and the other from C_8 butadiene dimer. They defined the degree of chlorination, DC, to be the number of Cl atoms contained per four C atoms in the ClPB. DC = 2 represents the stoichiometry of H-H PVC which would be formed if the chlorination were exclusively by addition of Cl_2 to double bonds.

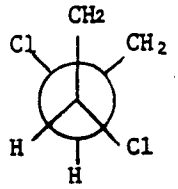
Benzene and small amounts of ethylbenzene, styrene, and naphthalene appear in the pyrograms when the cis-PB is chlorinated. When DC = 1.5, chlorobenzene appears, and at DC = 2.0, vinylidenechloride is reported in the pyrograms. Also at DC = 2.0 the ClPB corresponds to H-H PVC and contains both  and  units which make chain scission more favorable than in H-T PVC. This feature is used to explain why the yield of benzene from H-H PVC is lower than from H-T PVC.

Ito et al. report that the yield of benzene from Cl-trans-PB increases more rapidly (compared to Cl-cis-PB) as the degree of chlorination increases. They interpret this to mean that the addition of Cl_2 to double bonds in cis - PB proceeds more locally than in trans - PB.

Finally, Ito et al. draw on the suggestions of Hörhold et al.[14] to conclude that the Cl-trans-PB probably has the erythro-configuration with the trans-1 conformer dominating:



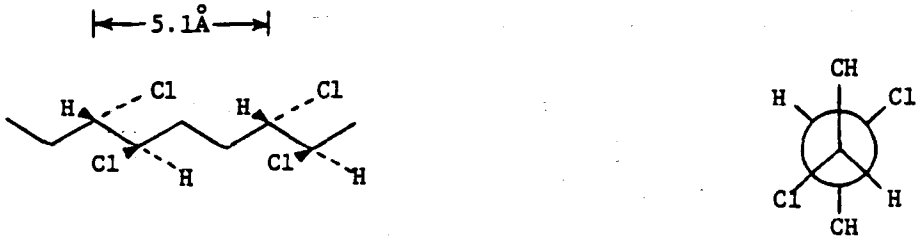
They also conclude that the Cl-cis-PB probably has the threo-configuration with the trans-2 conformer dominating:



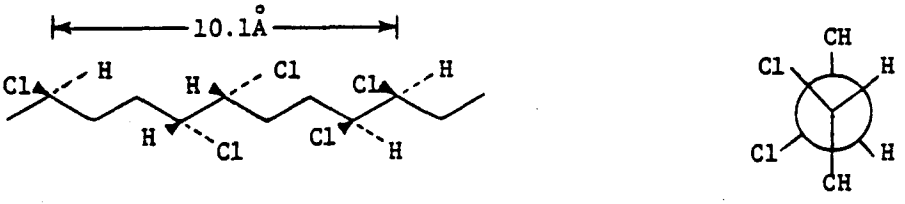
It is unfortunate that Ito et al. did not use PY-GC-mass spectroscopy to identify the pyrolyzates. Thus, some of their identifications (based apparently on GC retention times) are questionable. For example, toluene was not reported as a pyrolyzate, while we know from our experiments that toluene is a rather prominent pyrolyzate from H-H PVC (see Figures 1-2). Their poor resolution of lower-boiling pyrolyzates also makes the identification of vinylidene chloride subject to question. Furthermore, some of the mechanistic interpretations of Ito et al. seem speculative at best. Nevertheless, the observations and conclusions made by these authors seem generally valid.

In their 1973 paper, Dall'Asta et al. also suggest that if stereoregular trans- and cis-1,4 PB are chlorinated the resultant H-H polymers should be poly(1,2-erythro-dichlorobutamer) and poly(1,2-threo-dichlorobutamer), respectively.[15] They also report that pure addition chlorination in CH_2Cl_2 leads to H-H polymers which are partially (10-15%) crystalline. This is interpreted in terms of a stereospecific Cl_2 addition over rather long sequences of the monomeric units. Finally, crystallinity is accounted for by invoking stereoregularity over sufficiently long chain segments.

Bassi and Scordamaglia reported in 1973 the structure of the crystalline regions of the cis- and trans- H-H polymers.[16] They confirmed the prediction of Dall'Asta et al.[15] that the crystalline chain segments in trans-H-H PVC are isotactic, while the crystalline chain segments in cis-H-H PVC are syndiotactic.



diisotactic poly(erythro-1,2-dichlorobutamer)

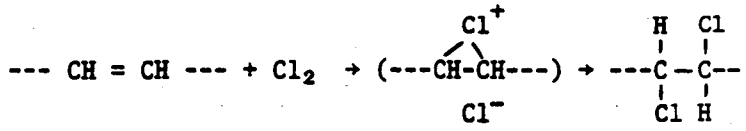


disyndiotactic poly(threo-1,2-dichlorobutamer)

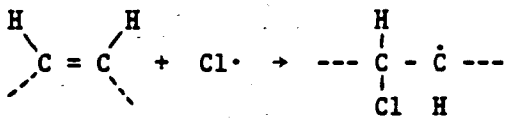
Also in 1973, Royo et al. reported a study of the addition of Cl_2 to linear cis- and trans- PB.[17] They found that the greater the cis- content, the more gel formation (crosslinking) became a problem, especially in nonpolar solvents. In addition, the IR spectra of the crosslinked products showed a significant cis- trans isomerization had occured during reaction.

Royo et al. interpreted their results in terms of two competing chlorination mechanisms: a primary ionic one, and a secondary free radical one.

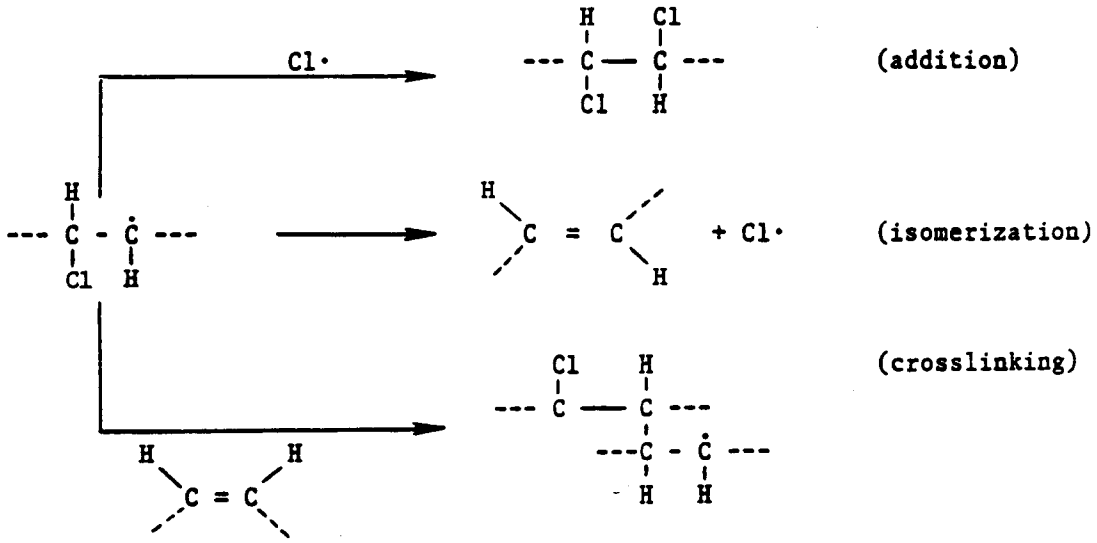
Primary:



Secondary:



They used the free radical mechanism as a way to explain their observations of isomerization and crosslinking.



Royo et al. also studied the addition of NO_2 to cis-1,4 PB.[17] This type of reaction is generally accepted as being of a radical character.

When THF was used as the solvent, isomerized soluble addition products - with THF taking part in the reaction - were obtained. This is an interesting observation, since M.P. Dreyfuss (Corporate Research) has reported a similar finding for chlorinating cis-1,4 PB in a mixed CH_2Cl_2 -THF solvent system.[18] Perhaps this indicates the presence of a secondary free radical mechanism for chlorinating cis-1,4 PB, at least in the CH_2Cl_2 - THF solvent system.

In 1974 Iida et al. reported that the isolated methylene linkages along the polyene chain are the most likely positions for the scission of the polymer backbone during the thermal decomposition of PVC.[19] They also concluded that recombination of hydrogen chloride and/or chlorine atoms with the double bonds in the polymer backbone occurs.

In a later paper (1975), Iida et al. reported a detailed study of the pyrolysis of chlorinated polybutadienes, and reaffirmed their early conclusions which are listed in the preceeding paragraph.[20] The important results of their pyrolysis (200-800°C) studies are listed below:

1. Lower aliphatics are more easily released from H-H PVC than from H-T PVC.
2. In ClPB, lower aliphatics are more easily released from polymers of lower chlorine content.
3. H-H PVC always releases less pure conjugated aromatics than H-T PVC.
4. More alkyl-substituted aromatics are released from H-H PVC than from H-T PVC.
5. Alkyl-substituted aromatics are released more easily from ClPB of lower chlorine contents.
6. ClPB releases more chlorine-containing aromatics as the chlorine content increases.
7. The release of chlorine-containing aromatics from a ClPB of any chlorine concentration, and at any pyrolysis temperature is greater than that from H-T PVC.

Mitani et al. reported in 1975 the results of their study of the thermal and radiation induced dehydrochlorination of H-H PVC.[21] The H-H PVC was made by the dark chlorination of a PB containing 96.6% cis-1,4, 1.8% trans-1,4, and 1.6% 1,2 units in $CHCl_3$ at 20°C. The H-H product contained 55.1% Cl (56.7% theoretical wt. %) with a T_g of 74°C.

Mitani et al. reported that H-H PVC starts to decompose in N_2 ~30°C lower than H-T PVC. The ratio of the extent of dehydrochlorination of H-H to that of H-T PVC at 180°C in N_2 is ~1.5. The activation energies between 150 and 190°C in N_2 are:

E_{ACT} H-H = 22.9 kcal/mole
E_{ACT} H-T = 28.7 kcal/mole

The mechanism assumed to explain their results follows:

$$\{ CH_2 - CHCl - CHCl - CH_2 \}_n \xrightarrow{k_1} \{ CH = CH - CHCl - CH_2 \}_n + HCl$$

$$\{ CH_2 - CHCl - CHCl - CH_2 \}_n \xrightarrow{k_2} \{ CH_2 - CH = CCl - CH_2 \}_n + HCl$$

$$\{ CH = CH - CHCl - CH_2 \} \xrightarrow{k_3} \{ CH = CH - CH = CH \}_n + HCl$$

Mitani et al. supplement their dehydrochlorination studies with a PY-GC study of 2,3-dichlorobutane.[21] They conclude that a conjugated polyene chain can be formed from the thermal decomposition of H-H PVC. However, they also used UV spectroscopy to study the length of the polyene chains formed when both H-H PVC and H-T PVC undergo thermal dehydrochlorination. H-T PVC gave long polyene segments, and the average polyene length increased with temperature. In contrast, H-H PVC gave shorter polyene chain segments, and the segment length was independent of temperature. Some comparative data for n, the average length of a polyene chain segment, follow:

H-T (140 - 180°C)	$n_{polyene} \cong 11\text{-}17$
H-H (140-180°C)	$n_{polyene} \cong 4$

In order to account for the restricted polyene formation from H-H PVC, Mitani et al. assumed that k_1 and k_2 are of the same order of magnitude.

The most current paper which discusses the degradation of H-H PVC was published in 1978 by Crawley and McNeill.[22] Unfortunately it was rather short on facts and long on conjecture. The H-H PVCs were made by chlorinating Ameripol CB-221 in various solvent systems. The CB-221 contained 98.5% cis-1,4, 1% trans-1,4, and 0.5% 1,2 vinyl units. Chlorinations in vacuum, air, and N_2 gave similar results. When CCl_4 and $CHCl_3$ were used, overchlorination readily occurred. In CH_2Cl_2 the reaction was complete in 30 min. (55.7% Cl found vs. 56.7% Cl theoretical). According to Crawley and McNeill some cyclization of unsaturated units occurs in CH_2Cl_2.

The TGA data of Crawley and McNeill show that H-H and H-T PVC give about the same average weight loss during the first stage of thermal decomposition (~375°C). However, the ultimate weight of residue at 500°C is significantly greater for H-H PVC.

RESULTS AND DISCUSSION

Quantitative determinations of benzene and toluene from both H-H and H-T PVC are given in Table I. The H-H PVC shows about 50% reduction in benzene formation compared to the H-T PVC. In contrast, the toluene yields are essentially identical.

The H-H PVC also forms significantly less benzene than syndiotactic (SYN) PVC under the same conditions of inert atmosphere pyrolysis.[4] For example, SYN PVC only gave about 25% reduction in benzene formation relative to H-T PVC.[4]

TABLE I

Quantitative Determination of Benzene and Toluene Produced from Pyrolyzing H-H and H-T PVC

Sample[a]	Pyrolysis Yields (mg/g - PVC) Benzene	Toluene
1. H-T PVC	40.9 ± 2.4[b]	5.7 ± 0.4
2. H-H PVC	19.0 ± 1.1	6.4 ± 1.0
3. H-T + MoO_3	17.6 ± 2.1	3.6 ± 0.6
4. H-H + MoO_3	1.9 ± 0.3	1.6 ± 0.1
5. H-T + SS-50	8.4 ± 1.2	2.8 ± 0.3
6. H-H + SS-50	1.5 ± 0.3	1.3 ± 0.3

[a] Completely described in the Experimental Part.
[b] Standard deviations were determined from triplicate pyrolysis runs.

The addition of smoke retarders to either H-H or H-T PVC effectively reduces the amount of benzene and toluene formed during inert atmosphere pyrolysis (Table I). But the reduction is much greater in the case of H-H PVC. For example, the addition of 10 phr of MoO_3 to H-T PVC reduced benzene by ~57%. In contrast, the addition of 10 phr of MoO_3 to H-H PVC gave ~90% reduction in benzene. The data in Table I also show that while our best smoke retarder system, SS-50, was twice as effective as MoO_3 in reducing benzene from H-T PVC, it was not more effective in H-H PVC, within the accuracy of the experiments.

The relative amounts of aliphatic hydrocarbons produced from H-H and H-T PVC during the inert atmosphere pyrolyses are shown in Table II. Compared to H-T PVC, H-H PVC gave ~60% more aliphatic hydrocarbons. When 10 phr of MoO_3 was added, the MoO_3-H-H PVC mixture again gave about 60% more aliphatics than the MoO_3-H-T PVC. In the case of SS-50, the SS-50-H-H PVC mixture gave even less aliphatics than the SS-50-H-T PVC mixture.

TABLE II

Relative Yields of Aliphatic Hydrocarbons Produced from Pyrolyzing H-H and H-T PVC

Sample	Total Aliphatics[a]
1. H-T PVC	100
2. H-H PVC	160
3. H-T + MoO_3	110
4. H-H + MoO_3	190
5. H-T + SS-50	140
6. H-H + SS-50	120

[a] Sum of C_1 - C_6 aliphatic hydrocarbon peaks (Porapak PS GC column).

Furthermore, the addition of either smoke retarder system, to either H-H or H-T PVC, did not significantly change the actual yield of aliphatics. We did not determine if the actual yield of aliphatic pyrolyzates from H-H PVC is small relative to the yield of aromatic pyrolyzates. However, the aliphatic pyrolyzate yield from H-T PVC at 550°C is about 10-15% of the total yield of volatile pyrolyzates.[3] The observed large decreases in benzene and toluene formation in smoke retarded H-H and H-T compounds are not accompanied by corresponding large increases in the formation of aliphatics.

Table III summarizes the results of the Smoke-Char Test evaluation of H-H PVC compared to H-T PVC. Because of a limited supply of H-H PVC, the samples for the Smoke-Char Test were prepared by grinding the ingredients together at liquid nitrogen temperature, and pressing them into small pellets at room temperature. This is similar to the technique used to prepare samples for the PY-GC studies. When compared to the benzene and toluene yields from the PY-GC studies (Table I), the data in Table III clearly show a direct correlation between smoke formation (in the Smoke-Char Test) and benzene formation during inert atmosphere pyrolysis; when benzene decreases, smoke decreases in a corresponding fashion.

TABLE III

Smoke-Char Evaluation of H-H PVC

4016 F-79-182 Sample No.	PVC	Additive	Level(phr)	S_{PVC}	% BC
4	H-T	-	-	64.1 ± 5.1	9.4 ± 0.3
1	H-H	-	-	36.7 ± 5.1	30.3 ± 0.6
5	H-T	MoO_3	10.09	30.5 ± 0.6	39.0 ± 4.6
2	H-H	MoO_3	10.07	4.8 ± 4.1	42.5 ± 2.8
6	H-T	SS-50	10.02	7.2 ± 0.4	50.3 ± 10.2
3	H-H	SS-50	10.03	5.8 ± 1.9	50.4 ± 4.9

Since benzene and toluene account for most of the total aromatic pyrolyzates, we have combined their yields (Table I) for each compound to approximate the total aromatic pyrolyzate (AP) yield. A linear plot of aromatic pyrolyzates versus smoke is shown as Figure 3. The datum points in Figure 3 represent the average smoke and pyrolyzate values for each of the six different PVC compounds. A linear regression analysis was used to determine the best straight line fit to the experimental data. This line is shown in Figure 3. All of the individual datum points, in the form of systematically selected matched pairs, were used in the linear regression analysis. The poorer degree of fit in the low smoke - low pyrolyzate region results from an increased uncertainty in the experimental data (see Tables I and II) as the "limiting" value of smoke and/or pyrolyzate formation is approached.

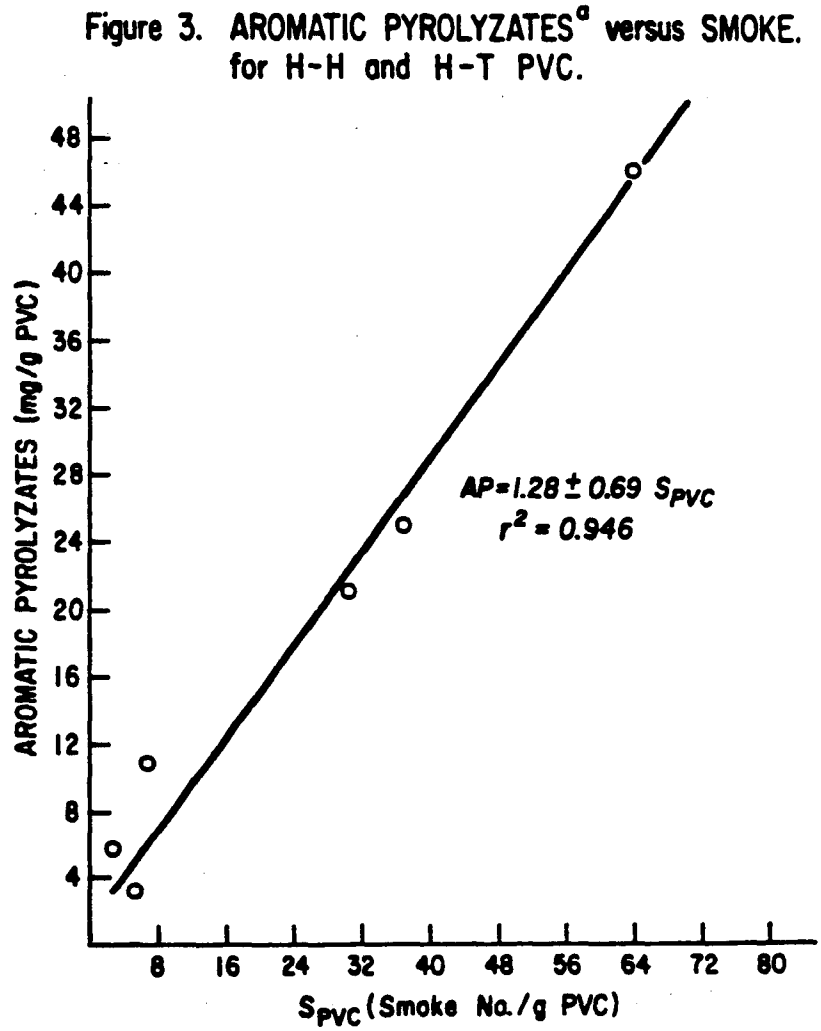
It is surprising to find such a good fit considering that the data are from six very different rigid PVC compounds. These results strongly support our initial contention[2] (and that of Starnes and Edelson[6]) that smoke primarily results from the combustion of aromatic pyrolyzates, and that metal smoke retarders act to reduce the formation of aromatic hydrocarbons from thermally degrading PVC. The data in Figure 3 also suggest that metal smoke retarders have the same general functional role in H-H PVC as in H-T PVC; i.e., they act to promote early crosslinking of PVC via a reductive coupling mechanism.[3,7]

Finally, our results show that MoO_3 and SS-50 smoke retarders are even more efficient in reducing aromatic pyrolyzate formation from H-H PVC compared to H-T PVC. This is illustrated in Table IV where the total aromatic pyrolyzates represent the combined yields of benzene and toluene.

Corporate Research, 4008F-80
Corp. Tech. Support, 9101-80
RR, March 31, 1980

Figure 3

Aromatic Pyrolyzates[a] Versus Smoke
for H-H and H-T PVC



[a] Approximated as the sum of benzene plus toluene.

TABLE IV

Effectiveness of MoO_3 and SS-50 in Reducing Total Aromatic Pyrolyzates During Pyrolysis

Smoke Retarder (10phr)	Aromatic Pyrolyzate Reduction (%) H-T PVC	H-H PVC
MoO_3	54.	86.
SS-50	76.	89.

The increased efficiency in H-H PVC is impressive, considering that H-H PVC by itself produces ~46% less aromatic pyrolyzate than H-T PVC.

The increased efficiency of smoke retarders in H-H PVC compared to H-T PVC also holds for smoke reduction during combustion. The data in Table III show that MoO_3, which is an average performing smoke retarder in H-T PVC, performs very effectively in H-H PVC. In H-H PVC, 10 phr of MoO_3 gave ~87% reduction in smoke compared to ~52% reduction in H-T PVC.

We concluded that the performance of smoke retarders in H-H PVC provides additional evidence to support the "reductive coupling" mechanism[3,7] which we believe explains the primary functional role of metal smoke retarders in rigid PVC. The H-H PVC data are consistent with the smoke retarder promoting crosslinking during the early stages of thermal degradation, and not with the predictions of the "Lewis acid" mechanism[5,6,8] reported in the literature.

Although our experimental data on the thermal degradation of H-H PVC are limited, it is instructive to compare our results with those in the literature as reviewed in a previous section of this report.

The literature shows that H-H PVC starts to decompose at a lower temperature than H-T PVC.[10,21,22] However, it is also reported that the rate of dehydrochlorination of H-H PVC is slower compared to H-T PVC.[10,21,22] In fact, one paper reports that the ultimate weight of residue at 500°C in a TGA experiment is significantly less for H-H PVC relative to H-T PVC.[22] Without invoking proposed mechanisms, the literature data on thermal decomposition of H-H PVC would suggest that it would form less aromatic pyrolyzates (and hence less smoke) and more char during combustion. This prediction is consistent with our experimental results.

A number of mechanisms (explanations) have been offered in the literature to explain the observed differences in the thermal decomposition of H-H and H-T PVC. Interestingly, they all are consistent with H-H PVC forming less aromatic pyrolyzate compared to H-T PVC, as experimentally quantified in our studies. One explanation is that the chlorine remaining in the H-H polymer after the initial phase of dehydrochlorination is more stable (partially vinylic) compared to its H-T counterpart (allylic), or to the original H-H PVC.[10] Another explanation is that restricted segmental motions in H-H PVC make it more difficult for

it to cyclize intramolecularly during the initial stages of dehydrochlorination.[11] One author has suggested that it is the presence of the 1,2-dichloroethylene group in H-H PVC which increases chain stiffness and restricts segmental motions.[12] Retardation of intramolecular cyclization will permit other thermally induced processes, such as chain scission and crosslinking, to occur and further reduce the possibility of forming benzene and other aromatic hydrocarbons. In fact, one paper reports that the polyene chains from H-H PVC are short relative to those from H-T PVC.[19] This could imply that chain scission and/or crosslinking is taking place in H-H PVC. However, the short segment length may simply result from a less favorable mechanism for formation. Another paper suggests that it is the presence of both $-\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}-$ and $-\overset{H}{\overset{|}{C}}-\overset{Cl}{\overset{|}{C}}-$ groups in H-H PVC which makes chain scission more favorable.[13] Another, related report claims that isolated methylene linkages along the polyene chains (formed during dehydrochlorination and rehydrochlorination of H-H PVC) are the most likely positions for chain scission.[19]

One of the pertinent literature reports also compared the thermal stabilities of H-H poly(vinylidene chloride), PVDC, and H-T PVDC.[10] The H-H PVDC was much more stable. It had no weight loss up to 280°C. In contrast, by 240°C H-T PVDC had experienced a 40% weight loss. These results imply to us that overchlorination (substitution chlorination) of H-H PVC could lead to H-H type polymers with improved thermal stabilities and combustibility characteristics compared to H-H PVC.

Only two pryolysis studies of H-H PVC are reported in the literature.[13,20] The most recent report[20] makes two conclusions which are consistent with our experimental results: One conclusion is that H-H PVC releases less pure conjugated aromatics than H-T PVC. The other is that more alkyl-substituted aromatics are released from H-H PVC compared to H-T PVC. However, we find that when smoke retarded versions of H-H and H-T PVC are compared, the H-H compound gives less pure conjugated aromatics and less alkyl substituted aromatics.

William J. Kroenke

William J. Kroenke

Robert P. Lattimer

Robert P. Lattimer

lk

20785025

ACKNOWLEDGEMENTS

Betty Starkey assisted in the preparation of the samples and conducted the combustibility experiments. Ilmars Sockis assisted with the PY-GC experiments, and Ed Harris assisted with the mass spectroscopy. Ruth Spindler provided valuable assistance with the literature review, as did Pete Dreyfuss. Dick Parker provided the H-H PVC sample. We also wish to acknowledge helpful discussions with Pete Dreyfuss and Dick Parker. Andy Fairlie helped with the statistical analysis of the data.

REFERENCES

1. R. P. Lattimer and W. J. Kroenke, "Smoke Reduction Mechanisms in PVC. I. Preparation, Pyrolysis, and Smoke Testing of PVC Model Compounds", Research Report, Project 4007F-77, September 1, 1977.

2. R. P. Lattimer and W. J. Kroenke, "Smoke Reduction Mechanisms in PVC. II. Aromatic Pyrolyzate Reduction, Smoke Formation, and Char Formation in SS-50 Compounds", Research Report, Project 4007F-78, March 15, 1978.

3. R. P. Lattimer and W. J. Kroenke, "Smoke Reduction Mechanisms in PVC. III. The Functional Role of Smoke Retarders During Burning and Pyrolysis", Research Report, Projects 4007F-78 and 9101-79, June 30, 1979.

4. R. M. Lum, J. Appl. Polym. Sci., 23, 1247 (1979).

5. D. Edelson, V. J. Kuck, R. M. Lum, E. Scalco, W. H. Starnes, Jr. and S. Kaufman, Spring Technical Meeting of the Combustion Institute, Canadian Section, Kingston, Ontario, May, 1979; Combustion and Flame, in press.

6. W. H. Starnes, Jr., and D. Edelson, Macromolecules, 12, 797 (1979).

7. R. P. Lattimer and W. J. Kroenke, "Smoke Reduction Mechanisms in PVC. IV. Further Investigation of the Functional Role of Smoke Retarders in PVC", Projects 9101-79 and 4007F-78, September 7, 1979.

8. W. J. Kroenke and R. P. Lattimer, "Smoke Reduction Mechanisms in PVC. V. Critical Review of the Functional Role of Smoke Retarders in Rigid PVC", Projects 4007F-78 and 9101-79, September 15, 1979.

9. E. D. Dickens, Jr., R. E. Evans, and W. J. Kroenke, "The Smoke/Char Test", Research Report, Projects 4007-74 and 4016-74, January 23, 1974.

10. N. Murayama and Y. Amagi, Polym. Letters, 4, 115 (1966).

11. S. Sobajima, N. Takagi, and H. Watase, J. Polym. Sci.: Part A-2, 6, 223 (1968).

12. M. H. Lehr, "Pyrolysis of CPVC Powders: Yields of Benzene Versus Residual PVC", IOC to Distribution List, Project 4025F-79, December 3, 1979.

13. H. Ito, S. Tsuge, T. Okumoto, and T. Takeuchi, Makromol. Chem., 138, 111 (1970).

14. H. H. Hörhold, R. Kuhmstedt, R. Hindersin, H. Dawczynski, and G. Drefahl, Makromol. Chem., 122, 145 (1969).

15. G. Dall'Asta, P. Meneghini, I. W. Bassi, and U. Gennaro, Makromol. Chem., 165, 83 (1973).

16. I. W. Bassi and R. Scordamaglia, Makromol. Chem., 166, 283 (1973).

17. J. Royo, L. Gonzalez, L. Ibarra, and M. Barbero, Makromol. Chem., 168, 41 (1973).

18. M. P. Dreyfuss, Private Communication, January, 1980.

19. T. Iida, M. Nakanishi, and K. Goto, J. Polym. Sci.: Polym. Chem. Ed., 12, 737 (1974).

20. ibid., 13, 1381 (1975).

21. K. Mitani, T. Ogata, H. Awaya, and Y. Tomari, J. Polym. Sci.: Polym. Chem. Ed., 13, 2813 (1975).

22. S. Crawley and I. C. McNeill, J. Polym. Sci.: Polym. Chem. Ed., 16, 2593 (1978).

1k
35A