Pyrolysis Studies of Chlorinated Poly(vinyl chloride)

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ABSTRACT: The thermal decomposition of chlorinated poly(vinyl chloride), CPVC, has been studied by pyrolysis–gas chromatography (Py–GC), Py–GC–mass spectrometry (Py–GC–MS), and Curie-point pyrolysis–mass spectrometry (Py–MS). It was found that the yield of chlorobenzene pyrolyzate as determined by Py–GC correlates well with the weight percent chlorine in the polymer or with microstructural parameters determined by ^{13}C NMR. Py–MS data for several CPVC samples were studied by computerized pattern recognition techniques (factor analysis and canonical variate analysis). It was found that numerous Py–MS fragments (namely, a number of aromatic and chloroaromatic hydrocarbons) are strongly correlated with increases in the chlorine content of the polymer. Aliphatics and aromatics with more aliphatic character are negatively correlated with increasing chlorine level in the polymer. Py–MS with computerized statistical analysis holds considerable potential for characterizing the composition and studying thermal decomposition mechanisms in synthetic polymers.

Introduction

The thermal decomposition behavior of chlorinated poly(vinyl chloride), CPVC, has been the subject of several studies. Berticat prepared CPVC with a high chlorine level (73.2 wt % Cl) and found that CPVC was more thermally stable than PVC and that the principal volatile pyrolyzate was hydrogen chloride.[1] In later work Berticat reported thermogravimetric (TGA) results that showed a two-phase thermal decomposition for CPVC (73–74% Cl).[2] The first phase (~270–300 °C) was mostly dehydrochlorination, and the second phase at higher temperatures was characterized by the evolution of chlorine-containing hydrocarbons. The greater thermal stability observed for CPVC as compared to PVC was attributed in part to cross-linking reactions.[2] Tsuge et al. studied a series of CPVC's with chlorine contents up to 73.2% by pyrolysis–gas chromatography (Py–GC).[3] The volatile pyrolyzates detected at 460 °C were benzene, toluene, naphthalene, chlorobenzene, dichlorobenzenes (three isomers), trichlorobenzenes (three isomers), and tetrachlorobenzenes (three isomers). Tsuge et al. investigated the *relative* yields of these pyrolyzates as a function of the degree of chlorination. At "low" chlorine levels (up to ~62%), the relative benzene concentration decreased, while the chlorobenzene increased. The chlorobenzene concentration reached a maximum at ~64% chlorine and then decreased as di- and trichloro compounds became dominant. The Py–GC results were used to deduce microstructural information regarding the CPVC samples.

In 1971 Liebman et al. studied the thermal decomposition and smoke evolution of PVC and CPVC. Electron spin resonance measurements demonstrated that free radicals are present during dehydrochlorination.[4] It was suggested that the greater stability of CPVC compared to that of PVC was due to long sequences of –CHCl– units in the polymer.[5] The better cross-linking (char forming) properties of CPVC as compared to those of PVC were also noted.[5] Liebman et al. also studied the evolution of smoke from burning PVC and CPVC.[6] A steady decrease in smoke evolution was observed as the chlorine level was increased. It was concluded that smoke was high in low-chlorine polymers because these materials evolved larger quantities of benzene and chlorobenzene—both of which burn with a smoky flame. More highly chlorinated PVC's evolve di-, tri-, and tetrachlorobenzenes upon pyrolysis; these aromatics yield less smoke upon burning.[6] This earlier work suggested that certain pyrolysis fragments (specifically chlorobenzene) could provide further details of PVC and CPVC microstructure.[7]

Table I
Chlorobenzene Pyrolyzate Yield and Other Characterization Data for Chlorinated PVC's

sample no.	% Cl[a]	% Cl[b] (NMR)	mol %[b] (111)	mol %[b] (020)	wt %[c] chlorobenzene
1	56.2	56.8	0.0	0.0	~0[d]
2	56.7	57.3	1.1	0.0	0.081 ± 0.012
3	57.8	57.7	1.7	0.0	0.15 ± 0.04
4	58.3	58.7	3.3	0.5	nd[e]
5	58.0	59.5	4.0	0.5	nd
6	57.9	60.1	5.6	0.6	0.48 ± 0.07
7	59.4	60.6	7.1	1.4	0.69 ± 0.07

[a] Schöniger oxygen flask method (data repeated from ref 10). [b] ^{13}C NMR (from ref 10). [c] Pyrolyzate yield (based on weight of polymer). Standard deviations are given from multiple runs. [d] Trace of chlorobenzene observed by Py-GC-MS. [e] Not determined.

Interpretation of results from earlier pyrolysis/combustion experiments[3,6] was somewhat hampered by the lack of definitive microstructural data for the CPVC samples studied. ^{13}C NMR has recently made great progress in defining the microstructural units in CPVC and related polymers.[8-10] We have examined by Py–GC and Py–MS a series of chlorinated PVC's that have also been characterized by ^{13}C NMR.[10] Our primary objective was to determine if correlations could be made between the NMR and pyrolysis data. A secondary objective was to determine if Curie-point Py–MS in combination with pattern recognition techniques could differentiate CPVC samples with varying chlorine contents. This report describes our preliminary results and conclusions.

Experimental Section

CPVC Samples. The chlorinated PVC's (≲61 wt % Cl) were prepared by solution photochlorination of Geon 103EP PVC (The BFGoodrich Co.) in tetrachloroethane at 80 °C. The samples and numbering system are the same as described in the NMR study.[10]

Py–GC and Py–GC–MS. In our study five of the seven NMR samples[10] were analyzed by pyrolysis–gas chromatography (Py–GC). NMR characterization data along with chlorobenzene pyrolyzate yields are given in Table I. Forty micrograms of polymer was deposited on the ribbon pyrolysis probe from tetrahydrofuran solution. After evaporation of the solvent, the samples were pyrolyzed at 600 °C for 20 s (temperature rise time ~8 ms) in

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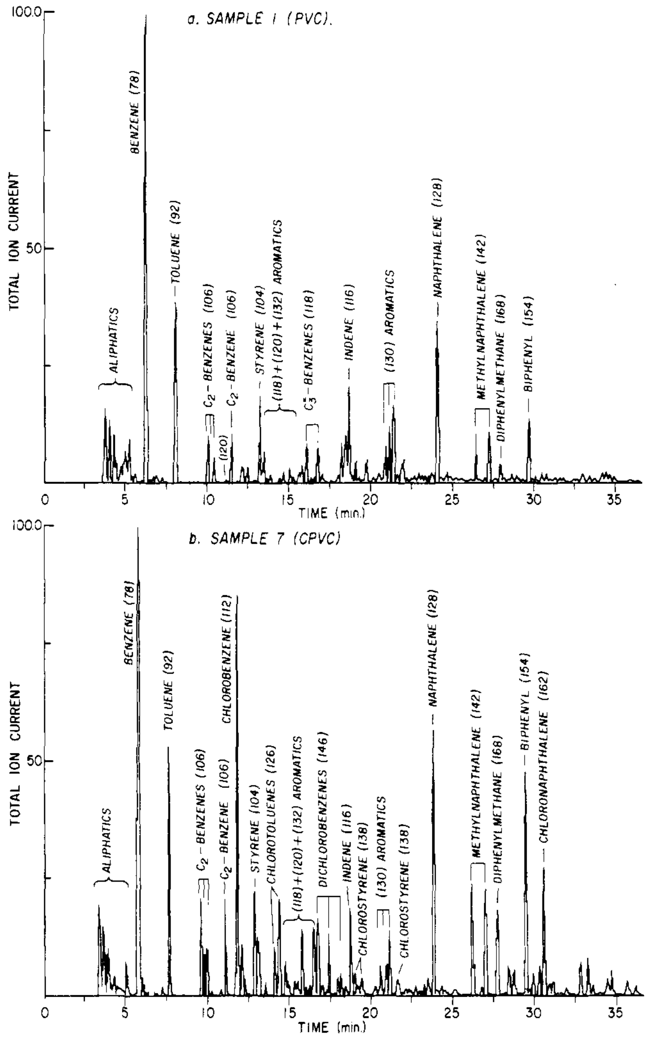


Figure 1. Capillary mass pyrograms: (a) sample 1 (PVC); (b) sample 7 (CPVC).

a helium atmosphere using a Chemical Data Systems Model 100 Pyroprobe. The pyrolyzates were separated with a 40-m Carbowax 20M fused-silica capillary column. A Varian 3700/CDS 111 GC-microprocessor system (The BFGoodrich Co.) was used with a flame ionization detector. The capillary injector split ratio was 50/1. Calibration for quantitative analysis was achieved by using injections of chlorobenzene in *n*-pentane solution (external standard method). A Varian 3700/Finnigan MAT 311A/Finnigan Incos 2400 GC-MS-DS (The BFGoodrich Co.) was used for qualitative identification of the pyrolyzates. Figure 1a shows the mass pyrogram for sample 1 (PVC), and Figure 1b shows that for sample 7 (CPVC). A trace of chlorobenzene appeared in sample 1, while several chloroaromatics appeared in sample 7 (chlorobenzene is the most abundant).

Py-MS. Six of the NMR samples[10] were also analyzed by Curie-point Py-MS using an Extranuclear 5000-1 system (University of Utah). About 4 μg of polymer was applied by microsyringe to the pyrolysis wire from tetrahydrofuran solution and air-dried under gentle rotation of the wire. Each sample was analyzed in triplicate. Py-MS conditions were as follows: Curie-point temperature 610 °C, temperature rise time 5 s, total heating time 10 s, reaction tube directly in front of the ion source (no expansion chamber used), electron energy setting 11 eV, mass range scanned m/z 20–260, scan rate 2000 amu/s, total scan time ~25 s. Approximately 200 spectra were obtained for each sample, and the results are reported as a single spectrum that is the integration of these individual spectra. Spectra for sample 1 (PVC, Figure 2a) and sample 7 (CPVC, Figure 2b) are included.

Py-MS Data Processing. Computerized processing of the Py-MS data involved the use of spectrum calibration and normalization procedures described elsewhere,[11] as well as multivariate statistical analysis routines available in the Statistical Package for the Social Sciences (SPSS).[12] Multivariate analysis consisted of principal component analysis of the complete Py-MS data matrix followed by canonical variate analysis of the correlations between the nine most significant (eigenvalues >1.0) principal components (factors) and the chlorine content of the CPVC samples as determined by ^{13}C NMR.[10] Finally, the canonical variate "spectrum" was calculated according to a procedure described by Windig et al.[13]

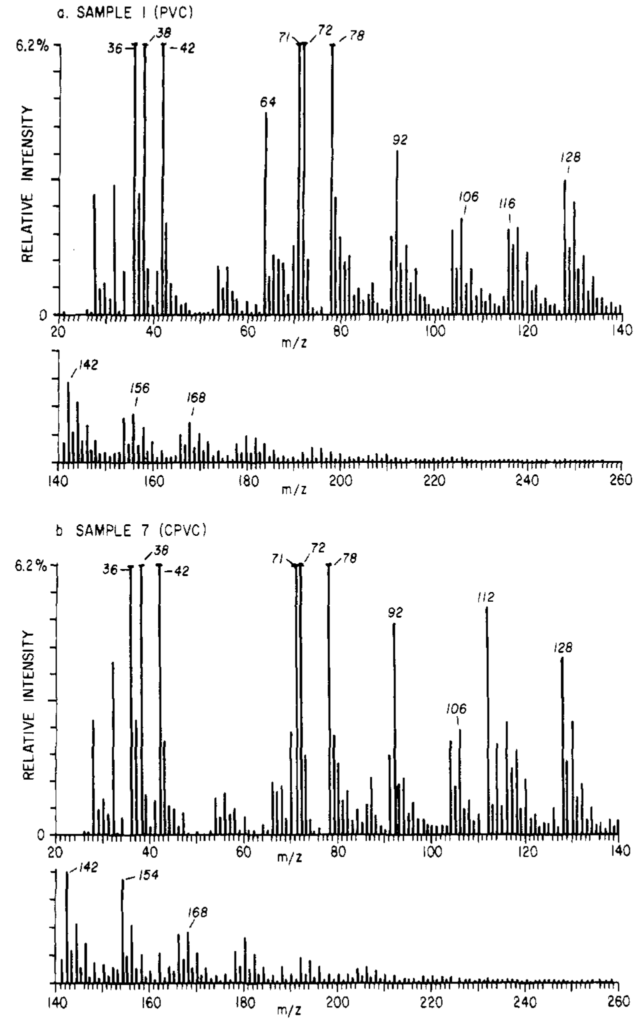


Figure 2. Curie-point pyrolysis mass spectra: (a) sample 1 (PVC); (b) sample 7 (CPVC).

Results and Discussion

Chlorobenzene Pyrolyzate Yield. It was of interest to determine whether the yield of chlorobenzene as a pyrolyzate could be used as an indicator of the level of chlorine in CPVC. Only a trace of chlorobenzene is observed as a pyrolyzate in pyrolysis gas chromatography of PVC itself (Figure 1 and Table I). As the amount of chlorine in CPVC increases, the yield of chlorobenzene pyrolyzate, as detected by Py-GC, increases in a regular manner (Table I). The correlation of chlorobenzene pyrolyzate yield with Schöniger percent chlorine is not at all good (correlation coefficient 0.925), since the Schöniger method is only accurate to ~±0.5%. Chlorobenzene correlation with percent chlorine by ^{13}C NMR is nearly linear (Figure 3, correlation coefficient 0.988), but a better linear correlation is obtained by plotting chlorobenzene yield vs. mole percent (111) + (020) structures from NMR (Figure 4, correlation coefficient 0.999). This linear correlation is consistent with established PVC decomposition pathways,[14-16] since either (111) or (020) structures can lead to chlorobenzene formation (see Scheme I). We would expect this linear relationship to hold up to the point at

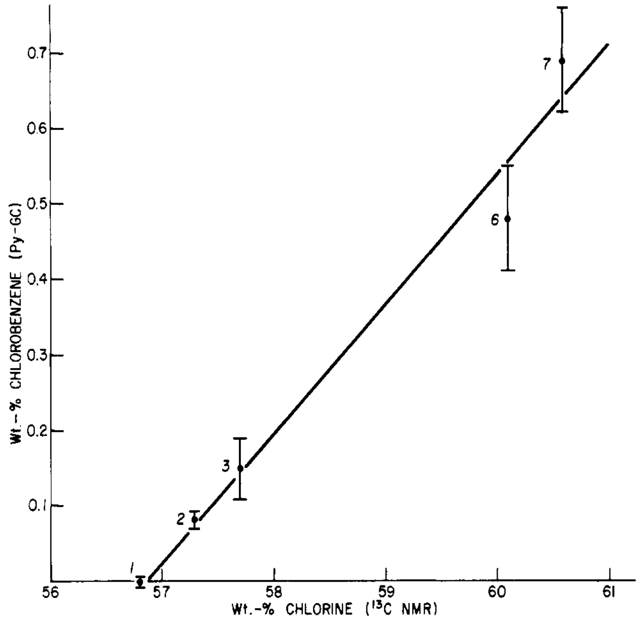


Figure 3. Chlorobenzene pyrolyzate yield (Py-GC) vs. percent chlorine.

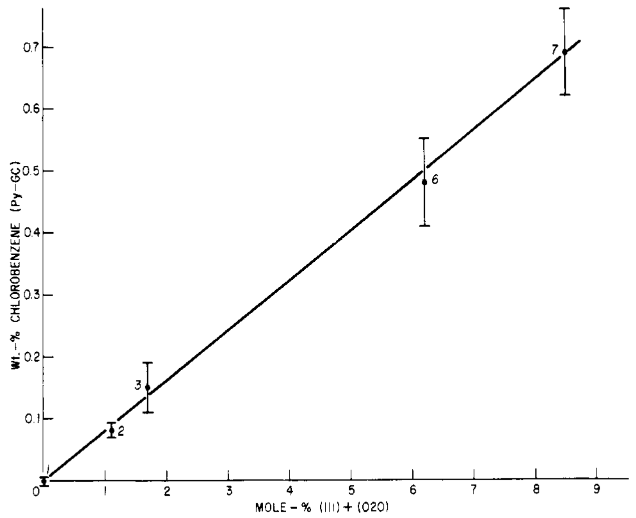


Figure 4. Chlorobenzene pyrolyzate yield (Py-GC) vs. mole percent (111) + (020).

which dichlorobenzene formation starts to become important compared to chlorobenzene. This transition is apparently ~61-62% Cl.[3]

Py-MS Correlations. The largest pyrolyzate peaks in the Curie-point pyrolysis mass spectra (Figure 2a,b) were *m/z* 36-38 $[HCl]^{+\cdot}$ and *m/z* 78 $[C_6H_6]^{+\cdot}$. Ions from residual tetrahydrofuran solvent (*m/z* 72-71-42) were also prominent in most samples; these peaks were ignored in the pattern recognition analyses. Some samples also showed appreciable $[SO_2]^{+\cdot}$ (*m/z* 64) from an unknown source.

The regular increase of chlorobenzene yield with increasing percent chlorine is quite apparent in the Curie-point Py-MS data. A bivariate plot of *m/z* 112 $[C_6H_5{}^{35}Cl]^{+\cdot}$ vs. *m/z* 114 $[C_6H_5{}^{37}Cl]^{+\cdot}$ is given in Figure 5 (correlation coefficient 0.995). Note that appreciable intensities of *m/z* 112 and 114 were observed even for sample 1 (PVC), which yields only a trace of chlorobenzene pyrolyzate. These "base line" intensities are due mainly to small amounts of hydrocarbon pyrolyzates (C_8H_{16} and C_8H_{18}).

A plot of mole percent (111) + (020) vs. the relative intensity of (*m/z* 112 + *m/z* 114) is shown in Figure 6.

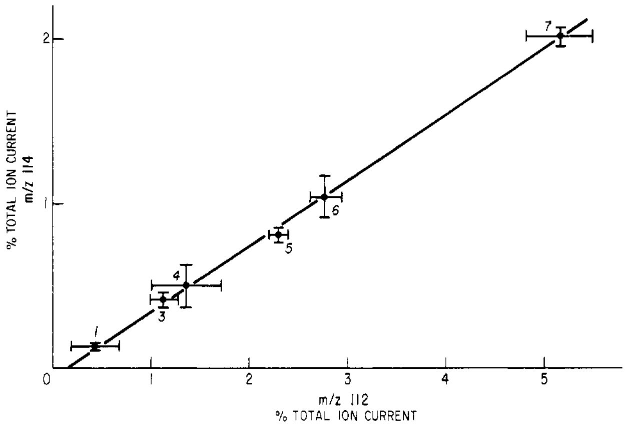
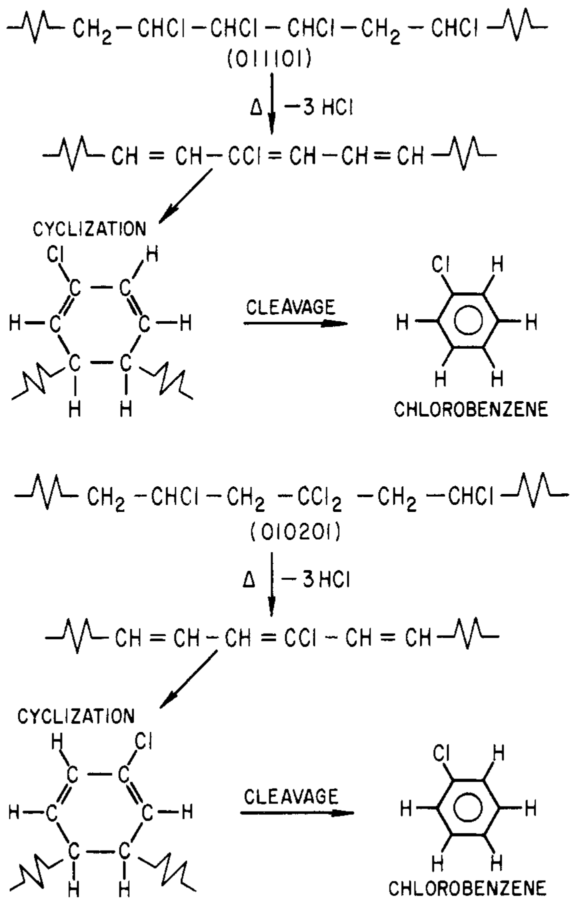


Figure 5. Bivariate plot (Py-MS) of *m/z* 112 and *m/z* 114.

Scheme I



The graph shows some curvature (correlation coefficient 0.943). We have shown that the *absolute* yield of chlorobenzene is a linear function of the mole percent (111) and (020) structures (Figure 4). The nonlinearity of Figure 6 is due to the fact that *relative*, rather than absolute, intensities of (*m/z* 112 + 114) have been plotted. Figure 6 would be linear only if the *overall* yield of volatile pyrolyzates were independent of the chlorine content of the polymer. Since the overall yield of volatile pyrolyzates in CPVC is known to decrease as the chlorine level increases,[6] the data in Figure 6 do not give a good linear correlation.

As known from the literature[3] as well as evidenced by the chromatogram in Figure 1b, several chloroaromatic compounds in addition to chlorobenzene can be found as CPVC pyrolyzates. Since the intensities of such chloroaromatic species in the pyrolysis mass spectra of CPVC samples may be expected to correlate more or less strongly with chlorine content (as shown in Figures 5 and 6 for

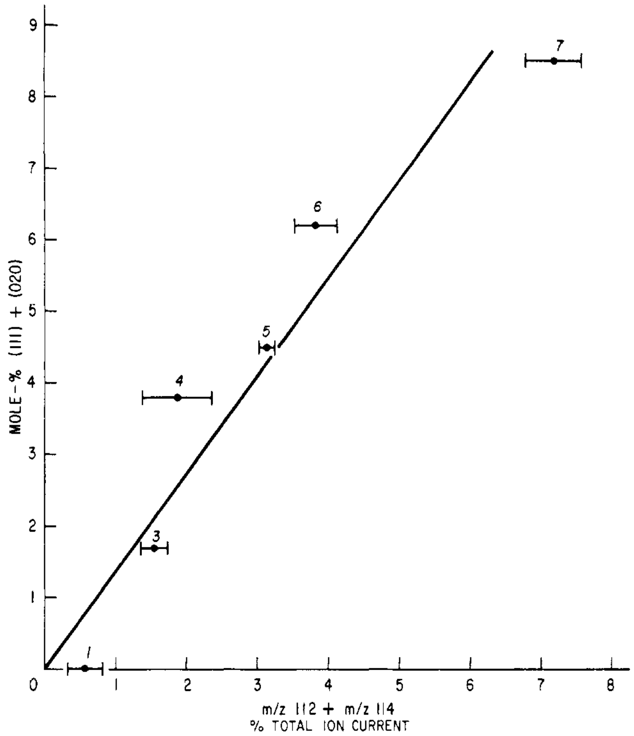


Figure 6. Mole percent (111) + (020) vs. (m/z 112 + m/z 114).

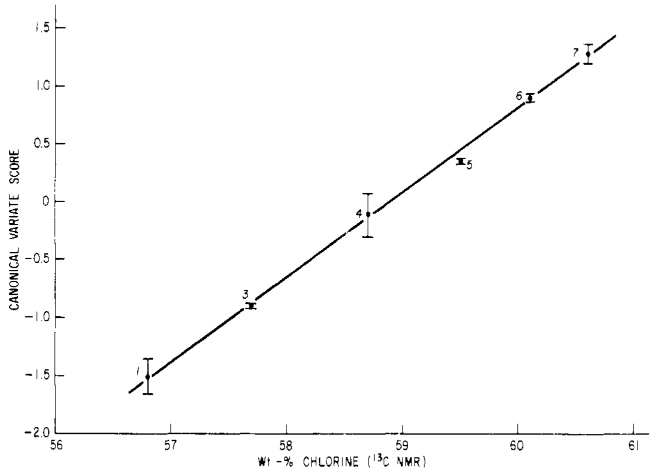


Figure 7. Canonical variate score vs. percent chlorine.

chlorobenzene), multivariate statistical analysis methods[11-13] can be used to identify these correlated peak series. Figure 7 shows the correlation between the canonical variate function calculated from the Py–MS data and the chlorine content values derived from NMR data.[10] As described in the Experimental Section, this canonical variate function was calculated in the space described by the nine most significant principal coordinates (factors) of the Py–MS data using the canonical variate routine in the SPSS program.[12,13] Only peaks in the range m/z 78–177 were included in this calculation because of limitations in the size of the data matrix that can be handled by the program. The high correlation coefficient (0.995) and the sizable fraction (34.0%) of total variance in the Py–MS data set explained by the canonical variate function demonstrate that differences in chlorine content are among the most pronounced tendencies in the spectral patterns.

Because of the very limited size of the present set of samples, no attempt was made to test the reliability of the canonical variate function for indicating the chlorine content of unknown samples. However, apart from its potential usefulness as a quantitative tool, the canonical variate function also enables the visualization of ion signals most strongly correlating with changes in chlorine content. Figure 8 shows a canonical variate spectrum calculated according to Windig et al.[13] The spectrum is dominated by chlorobenzene signals (m/z 112–114), but several other chloroaromatic signals are apparent at m/z 126–128 (chlorotoluene), m/z 138–140 (chlorostyrene), m/z 150–152 (chloroindene), and m/z 162–164 (chloronaphthalene); most of these were also observed by Py-GC–MS (Figure 1b). In addition, a pronounced series of nonchlorinated aromatic pyrolyzates is also present—m/z 78 (benzene), m/z 92 (toluene), m/z 104 (styrene), m/z 106 (C_2 alkylbenzenes), m/z 116 (indene), m/z 128 (naphthalene), m/z 142 (methylnaphthalenes), m/z 154 (biphenyl/acenaphthene), m/z 156 (C_2 alkylnaphthalenes), m/z 166 (fluorene), and m/z 168 (methylbiphenyls/methylacenaphthenes). A final peak that shows a positive correlation is m/z 87, which we believe is an artifact due to degraded (oligomerized) tetrahydrofuran solvent.

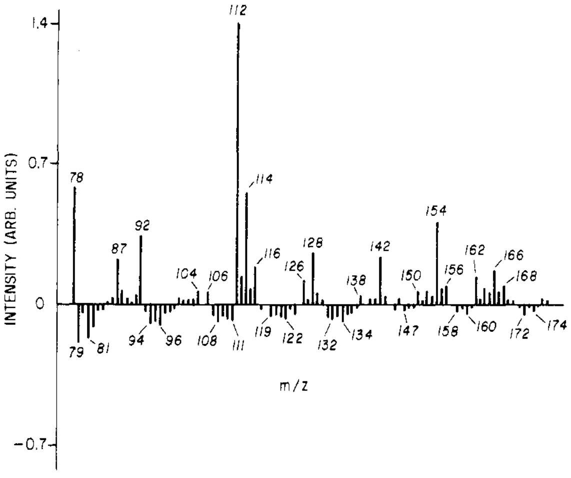


Figure 8. Canonical variate spectrum.

Several hydrocarbon peaks are also observed on the negative side of the canonical variate spectrum (Figure 8). These compounds are either unsaturated aliphatics or else aromatics with appreciable aliphatic character. It is probable that lower molecular weight aliphatic hydrocarbons would also appear on the negative side of the spectrum, but the canonical variate analysis did not include mass numbers less than m/z 78.

Conclusions

Overall our results suggest that the CPVC pyrolyzates can be divided into three categories with respect to their formation tendencies:

1. Chloroaromatic compounds increase in both relative and absolute abundance as the chlorine level in the polymer increases. This was documented in earlier work[3,6] and has been confirmed in our studies.

2. Pure conjugated aromatic hydrocarbons and aromatics with small (C_1–C_2) aliphatic side groups increase in *relative* abundance as the chlorine level increases. Other work shows that in *absolute* abundance these compounds actually decrease with increasing chlorine level.[3,17]

3. Aliphatics and aromatics with more aliphatic character decrease in both relative and absolute abundance with increasing chlorine level in the polymer.

Our results show that as the chlorine level in the polymer increases, the volatile hydrocarbon pyrolyzates exhibit an overall decrease in hydrogen-to-carbon ratio. There are two explanations for this decrease in hydrogen in the volatile pyrolyzates. First, there is less hydrogen available in the polymer, since for every chlorine atom added to the polymer, one hydrogen atom is lost. Second, more hydrogen is consumed in producing HCl. That is, presumably more HCl is formed from the polymer during pyrolysis as the chlorine level increases. The HCl pyrolyzate yield as a function of polymer chlorine level has apparently not been the subject of careful study, however. A third possible explanation would be that more hydrogen remains in the polymer residue as char as the chlorine level increases. This is probably not a factor, since chars are generally very deficient in hydrogen.

While PVC itself produces little char during thermal decomposition, addition of chlorine to the polymer results in a steady increase in char residue.[6,18] This implies that cross-linking mechanisms not significant in PVC become important as more chlorine is added to the polymer. These mechanisms may involve intermolecular HCl elimination, Diels–Alder reactions, and various free radical processes.

These preliminary results suggest that Py–MS with computerized statistical analysis holds considerable potential for characterizing the composition and studying thermal decomposition mechanisms in chlorine-containing polymers. Further studies are in progress that should help to elucidate the thermal decomposition behavior of CPVC in more detail.

Acknowledgment. Appreciation is expressed to The BFGoodrich Co. for support of this work. W. Windig and A. M. Harper (University of Utah) assisted with the computerized statistical analysis, and W. H. McClennen (University of Utah) performed the Curie-point Py–MS experiments. I. Sockis and R. E. Harris (The BFGoodrich Co.) assisted with the Py–GC and Py–GC–MS experiments. Helpful discussions with E. D. Dickens, Jr., G. S. Huvard, R. A. Komoroski, W. J. Kroenke, M. H. Lehr, and R. G. Parker (The BFGoodrich Co.) are appreciated. S. A. Liebman (Chemical Data Systems, Inc.) is also acknowledged for encouraging us to work on this project.

Registry No. Chlorobenzene, 108-90-7.

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Study of the Low-Frequency Acoustic Modes of Oriented Poly(ethylene) with a Multipass Fabry–Perot Interferometer

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Received December 7, 1982

ABSTRACT: The low-frequency spectra of high-density polycrystalline poly(ethylene) films are studied with a Fabry–Perot interferometer. The sound velocities and associated elastic constants are determined as a function of stretch ratio (R_s). In contrast to the results of other polymer films, the spectral line associated with the longitudinal acoustic phonon propagating along the stretch axis shows increased broadening as the film is gradually stretched. For films stretched to $R_s = 7.0$ or above, the longitudinal acoustic phonon spectrum broadens considerably and finally merges with the background noise. This unusual feature is attributed to the interaction between the localized LAM associated with the lamellae stems and the long-wavelength longitudinal acoustic wave propagating along the orientation axis. This hypothesis is corroborated by the observation of the angular independence of the low-frequency spectrum of a high-pressure crystallized poly(ethylene) with large lamellar thickness ($\approx$7000 Å). The effects of annealing and quenching on the Brillouin frequencies of the oriented film are also investigated.

Introduction

The poly(ethylene) (PE) chain has the simplest repeat unit of all synthetic high polymers. The structural simplicity of this polymer has promoted many theoretical and experimental studies that have the aim of characterizing its physical properties. One area of current research interest is the vibrational spectroscopy of the PE chain in the solid state. Calculations of the normal modes of vibration in the PE crystal[1,2] have shown that the interchain interactions between adjacent chains in the unit cell affect the vibrational modes of the crystal significantly. The low-frequency acoustic modes are strongly affected by the crystal field and thus deserve to be studied in more detail.

A considerable amount of information regarding the morphology of semicrystalline PE has been obtained from the Raman scattering study of the longitudinal acoustic mode, or LAM. In the crystalline n-paraffins[3] and in PE single crystals,[4-6] the frequency of the LAM is found to be inversely proportional to the straight chain length. In semicrystalline PE, the microstructure is composed of

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