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Degradation Mechanisms of Poly(vinyl fluoride) Films

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ABSTRACT: The mechanism of degradation of poly(vinyl fluoride) films in both oxidative and nonoxidative environments has been examined. In nonoxidative environments, the homogeneous pyrolysis of related small molecules like 2-fluoropropane or 2-fluoropentane constitutes a useful model for both the product distributions and the rates. The oxidative chemistry, however, occurs at much lower temperatures and will dominate the degradation mechanism at even small partial pressures of oxygen. It is a radical chain process leading to oxygen incorporation in the polymer, main chain cleavage, and formation of new acyl fluoride chain ends. HF is formed in both mechanisms. In the oxidative chemistry, a plausible route to HF is the hydrolysis of acyl fluorides by water vapor generated in situ.

Introduction

It has been known from the earliest studies of poly(vinyl fluoride) (PVF) decomposition that HF can be a principal degradation product.[1] However, the mechanism and rate expressions for HF formation have never been adequately examined. Although both oxidative and nonoxidative routes for PVF degradation have been suggested, the relative importance of these routes in the formation of HF and the loss of polymer physical properties has not been addressed.[2-6] In this paper we report a comprehensive study of the early stages of degradation of PVF films and powders under a variety of atmospheres, using a combination of thermal analysis and spectroscopy to follow the course of the chemistry. We have demonstrated the following: 1. Both oxidative and direct pyrolytic degradation can lead to HF. 2. The direct pyrolysis forms HF as a primary product, and its rate can be adequately predicted using activation parameters from corresponding small-molecule pyrolysis chemistry. 3. The oxidative chemistry occurs at much lower temperatures and involves cleavage of the polymer backbone as a primary degradative event. 4. A likely route to HF in oxidative environments is via hydrolysis of intermediate acyl fluorides.

Experimental Section

Most of the work reported in this paper was carried out on films of poly(vinyl fluoride) cast from dispersions (33 wt %) of commercial PVF powder (DuPont PV-116) in propylene carbonate (Aldrich).[7] Dispersions were applied to glass slides using a doctor blade to control thickness. Typical film thicknesses were 20–100 μm. Films were dried in an oven at 200 °C for 7 min. In addition to films prepared in this way, in a few experiments, the powder was examined directly, and in a few other cases, films made from polymer prepared under specially controlled conditions to alter the molecular weight or backbone branching (vide infra) were used.

Weight loss data under controlled atmospheres were obtained using a combined vacuum microbalance/mass spectroscopy apparatus that has been described in detail previously.[8] Typical background pressures were 1×10^{-8} Torr. Degradation atmospheres were controlled by addition of gases through a variable leak valve from an attached manifold. Baratron capacitance manometers were used to measure the partial pressures of added gases in the microbalance chamber. Infrared (Nicolet 60SX) and UV–vis (Varian Cary 5) spectra were run in transmission mode on films degraded under these controlled conditions. Samples were handled under ambient conditions during transport from the microbalance chamber and spectroscopic characterization.

Results

Inert Atmospheres. As shown in Figure 1, when PVF is heated in vacuum at 5–10 °C/min, no significant weight loss occurs until temperatures above 350 °C are reached.[3] HF is (by far) the principal product observed by mass spectroscopy on the effluent gas stream. A small amount of vinyl fluoride may also be evolved. At 350 °C in a dynamic vacuum of $<10^{-6}$ Torr, a pseudo-zero-order phenomenological rate of weight loss of 1.75 μg/(g s) can adequately describe the first 5% of the degradative weight loss. The UV–vis spectrum of a polymer film degraded to ~0.5% weight loss at 350–400 °C under vacuum is shown in Figure 2a. Well-defined new features between 200 and 300 nm are observed as well as a diffuse absorbance tail extending out to about 500 nm. The UV features appear at the wavelengths and in the sequence expected for double bonds with increasing degrees of conjugation (i.e. 230 nm, $n = 2$; 270 nm, $n = 3$; 305 nm, $n = 4$).[10] Partially vacuum-degraded films have also been examined by infrared spectroscopy (Figure 3B). Unfortunately, these spectra are not especially useful in characterizing the details of the olefin formation chemistry. The strong infrared absorbance below 1500 cm^{-1} in the starting PVF film obscures the C–H bending regions that would be most helpful in distinguishing among different isomers and substitution patterns that could be formed. Nevertheless, as is clear from Figure 3, infrared spectroscopy does show that films degraded to equivalent extents in vacuum and in the presence of O_2 are quite different in structure. A film degraded to <1% in vacuum (Figure 3B) shows no new features in the carbonyl region 1700–1900 cm^{-1}. Although weak, there do appear to be new features in a region characteristic of C=C stretching, 1500–1700 cm^{-1}.

This chemistry and these rates are in agreement with what one might expect from corresponding homogeneous pyrolysis studies on fluorine-containing hydrocarbons. For example, the homogeneous pyrolysis of 2-fluoropropane leads to propene and HF in the same way that the products of the PVF degradation in inert atmospheres are principally HF in the vapor and olefin formation along the polymer chain. Furthermore, the Arrhenius parameters for the gas-phase pyrolysis of 2-fluoropropane are log *A*

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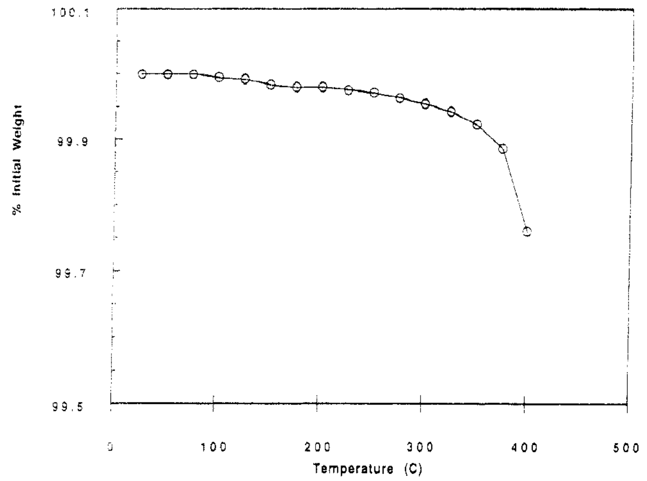


Figure 1. Weight loss vs temperature for PVF film heated at 5 °C/min in vacuum ($P_{\mathrm{background}} < 10^{-6}$ Torr).

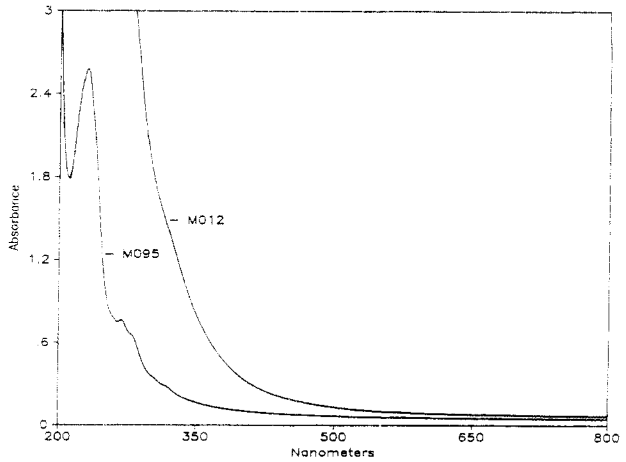


Figure 2. Difference UV–vis spectra in transmission mode for PVF films degraded to ~0.5% weight loss (a) in vacuum at 350 °C (M095) and (b) in 10 Torr of O_2 at 250 °C (M012).

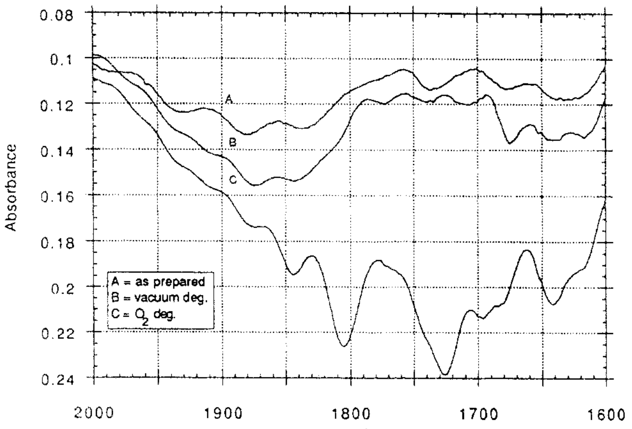


Figure 3. Infrared spectra in transmission mode for PVF films (A) as prepared, (B) degraded to ~0.5% weight loss in vacuum, and (C) degraded to ~0.5% weight loss in 10 Torr of O_2.

= 13.3 and E_a = 225.5 kJ/mol.[9] Assuming that this same chemistry occurs at random along the polymer chain, these parameters predict a rate of initial weight loss of ~1 μg/(g s) at 350 °C, in reasonable agreement with the observed value.

Using the known film thickness and a molar absorptivity for diene units estimated from small molecules (hexadienes)[11] and assuming that the measured absorbance at 230 nm arises from conjugated dienes along the polymer backbone, we may estimate the concentration of diene functional units in this partially degraded film using Beer's law.[12] We may compare this concentration with the statistical probability of diene formation if unsaturation were created randomly along the chain. For example, 0.5% weight loss corresponds to a conversion of 1.15% of the monomer units to olefins if it is assumed that all of the weight loss is due to HF evolution and one C=C is produced for each HF evolved. If the olefins are generated randomly along the chain, then the concentration of dienes would be expected to be ~0.01% of the monomer concentration. The concentration of dienes determined from the absorbance calculation is within a factor of 3 of this value, good agreement for this rough estimate. The appearance of the UV spectrum (Figure 2a) is also consistent with this picture, showing almost no evidence for conjugated olefins with more than 3 units of unsaturation at these early stages. When the PVF degradation is followed over several hours (>3 half-lives), at 350 °C under N_2 flow, the weight loss can be fit very well by a first-order process leading to complete dehydrofluorination of the polymer. The first-order rate constant is approximately ×20 greater than that observed for the initial 1% of inert-atmosphere degradation. This increase in rate constant may reflect the magnitude of the allylic activation effect that has been shown to be important in poly(vinyl chloride) (PVC) degradation.[13] The implication is that the *rates* of the allylic-activated HF loss and the random HF loss become competitive under these conditions at about 5% degradation.

Oxygen-Containing Atmospheres. Both the degradation kinetics and product distribution are completely different when even low partial pressures of oxygen are present in the pyrolysis atmosphere. While the polymer is essentially unaffected by prolonged heating at 250 °C in vacuum, in 1 h in air, several % weight loss, accompanied by severe discoloration, occurs. The fractional weight loss after heating for 1 h at 250 °C has been measured at four different oxygen partial pressures. At $<10^{-6}$, 1, 10, and 500 Torr, film samples lost <0.02%, 0.1%, 0.52%, and 6.0% of their mass respectively. The rate of weight loss at 250 °C in air is at least 10^4 greater than would be predicted from extrapolating the rate parameters derived from the data at 350 °C in vacuum to these lower temperatures. The true difference is even larger, because the weight loss underestimates the oxidative degradation rate, since oxygen is being incorporated into the sample as it degrades (vide infra).

The oxygen-mediated degradation process displays the characteristics expected for a hydroperoxide-based radical chain process of the type that is well established for hydrocarbon polymers like polyethylene and polypropylene.[13] (1) As described above, there is a strong oxygen partial pressure dependence to the rate. (2) The mass loss is preceded by a period of weight gain (Figure 4) as oxygen is incorporated into the polymer. (3) The kinetics are markedly affected by the addition of radical trapping agents either to the vapor as shown in Table I or to the film during casting. (4) The degradation rate is sensitive to the degree of branching along the polymer chain, with increased branching leading to more rapid degradation (Table I).

The IR spectra of films degraded in the presence of oxygen are especially informative in mapping out this mechanism. Figure 3C indicates that, at low extents of degradation, a variety of new carbonyl functionalities have already been formed. Overlapping absorbance features are observed throughout the 1500–2000-cm^{-1} range. Particularly noteworthy are strong bands at 1840, 1805, 1725,

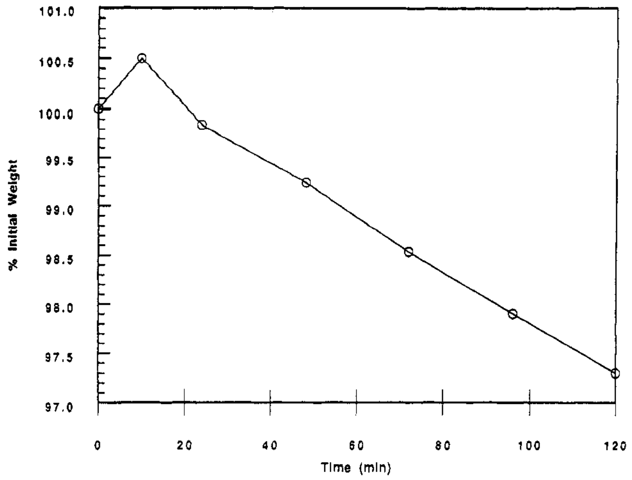


Figure 4. TGA in air for PVF powder at 240 °C.

Table I. Relative Rates of Weight Loss of PVF Films at 250 °C[a]

% branching[b]	atmosphere	relative rate
0.80	10 Torr of O_2	1.00
1.93	10 Torr of O_2	1.31
0.46	10 Torr of O_2	0.72
0.80	10 Torr of O_2 + 1 Torr of CHD[c]	0.70
0.80	10 Torr of O_2 + 1 Torr of TEP[d]	0.17

[a] Static conditions, pseudo-zero-order rates, total weight loss in all cases less than 2%. [b] Determined from F-NMR on the basis of the integral of tertiary F.[14] In the oxidation reactions, branching at tertiary C–H, rather than tertiary C–F, probably has a more significant impact on the rates. We assume that the relative % branching of this kind falls in the same sequence. For details of sample preparation, see ref 15. [c] 1,4-Cyclohexadiene. [d] triethyl phosphite—relative rate not corrected for possibility of incorporation of TEP into polymer.

and 1700 cm^{-1}. On the basis of a comparison with model compounds, and some observations on the reactivity of the functionalities that give rise to these bands, we believe that the 1840- and 1805-cm^{-1} bands are due to acyl fluorides and α,β-unsaturated acyl fluorides. The 1725- and 1700-cm^{-1} bands are consistent with aldehydes and α,β-unsaturated aldehydes, respectively, although the breadth of the bands and the prominent shoulders in this spectral region suggest that this is not a complete description of the carbonyl population.[16] These types of functionalities can only be formed if the early stages of oxidative degradation are accompanied by chain cleavage. As the degradation proceeds, these four IR bands do not grow progressively, but rather the IR spectrum broadens and the spectral density shifts toward lower cm^{-1}. This is consistent with a picture in which the growth of conjugation adjacent to the carbonyl groups competes with new carbonyl formation as the degradation proceeds. Once carbonyl chain ends are formed, the adjacent C–H bonds are activated toward radical abstraction, and extending the conjugation becomes increasingly favored relative to creating isolated olefins or new chain ends.

Figure 2 compares the UV–vis absorbance spectra for films degraded to equivalent extents as measured by weight loss, in vacuum at 350 °C and in 10 Torr of oxygen at 250 °C. As one might expect from these spectra, the vacuum-degraded sample shows only a slight yellowing; the air-degraded sample is strongly colored. The progress of the oxidative degradation is manifested in the UV–vis spectra by a progressive growth of an essentially featureless absorption that tails strongly into the visible (Figure 5). The UV–vis spectra can be understood on the basis of the evolution of functionalities observed in the infrared. At low extents of conversion, the spectra should be characteristic of a mixture of essentially isolated saturated and α,β-unsaturated aldehydes and acyl fluorides. All of these functional groups should show n,π^* absorption maxima ranging from 220 to 320 nm. The α,β-unsaturated carbonyls, in addition, will have strong π,π^* bands at 200–230 nm. The resulting absorption spectrum after short exposures should be a convolution of bands from these functionalities and is likely to be the type of featureless absorption shifted toward the visible from the vacuum-degraded material that is shown in Figure 2b. As the degree of conjugation and the inhomogeneity of the carbonyl distribution increases with increasing degradation, new stronger π,π^* absorptions appear first at shorter wavelengths but progressively toward longer wavelengths as the conjugation length increases. This is consistent with the spectral changes accompanying the progressive oxidation as shown in Figure 5.

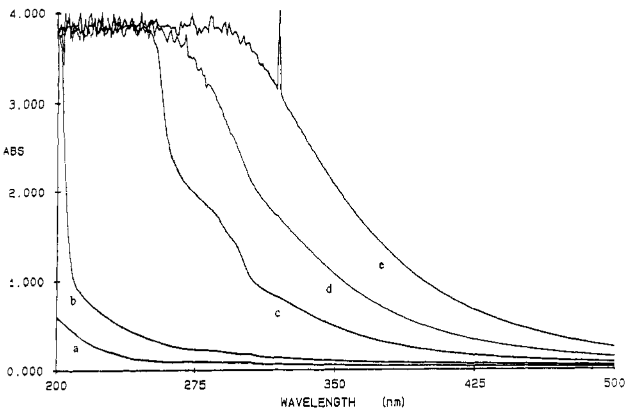


Figure 5. Changes in UV–vis absorbance with time for PVF film degrading in 10 Torr of O_2 at 250 °C (a) as prepared and after (b) 5 min, (c) 30 min, (d) 60 min, and (e) 90 min.

HF is produced under these conditions.[3] If the pyrolysis is carried out in a side arm attached to a vapor IR cell, the line spectrum of HF can be clearly observed after a few minutes at 250 °C in 50 Torr of O_2.[17] Because we have shown that the rate of formation of HF by a direct 1,2-elimination from the polymer backbone is negligible at these temperatures, there must be an additional mechanism for HF formation in the presence of oxygen. We believe that an important route to HF is via the hydrolysis of acyl fluorides. Evidence for this conclusion is shown in Figure 6. Figure 6a shows the transmission IR spectrum of a film degraded to 0.4% weight loss at 250 °C in 10 Torr of O_2. The bands due to acyl fluoride groups described above are clearly resolved. Figure 6b shows this same film after exposure to 1 Torr of water vapor at 250 °C for 1 h. The acyl fluoride and α,β-unsaturated acyl fluoride stretching features are essentially gone, and shoulders at 1765 and 1740 cm^{-1} have newly appeared. These frequencies are consistent with the carboxylic acid and α,β-unsaturated carboxylic acid groups that would be formed via hydrolysis of the acyl fluoride end groups. The 1725- and 1700-cm^{-1} bands associated with aldehydes, and therefore insensitive to hydrolysis, are unchanged.

Discussion

This work demonstrates that there are two distinctly different mechanisms for the early stages of poly(vinyl fluoride) degradation. One route, which dominates at high temperatures and very low oxygen partial pressures, can be described as a direct 1,2-elimination of HF at random along the polymer backbone. The second route, which dominates at lower temperatures and even modest oxygen partial pressures, is radical-initiated and involves oxygen

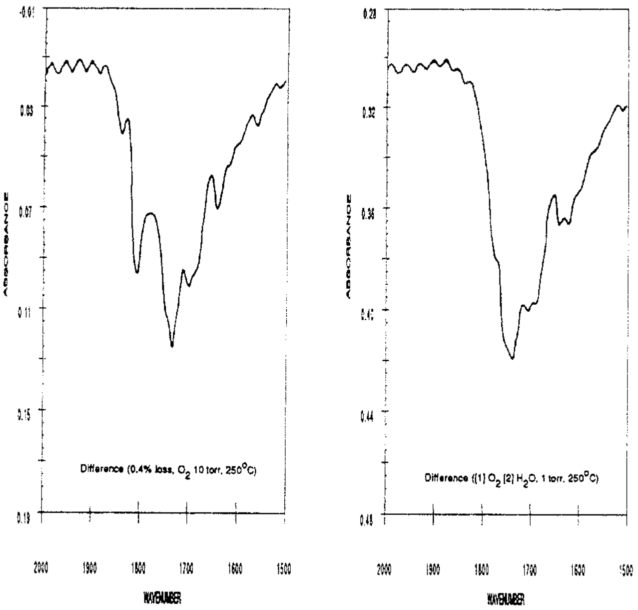
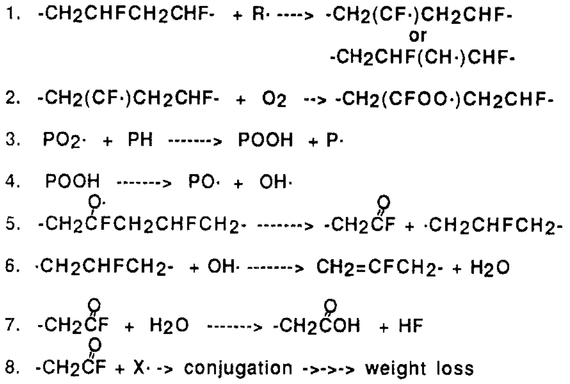


Figure 6. Difference IR spectra for PVF film (a, left) degraded to 0.4% weight loss in 10 Torr of O_2 and (b, right) same film after exposure to 1 Torr of H_2O at 250 °C for 1 h.

Scheme I

1. $-CH_2CHFCH_2CHF- \longrightarrow -CH_2CH{=}CHCHF- + HF$

Scheme II



1. $-CH_2CHFCH_2CHF- + R\cdot \longrightarrow -CH_2(CF\cdot)CH_2CHF-$ or $-CH_2CHF(CH\cdot)CHF-$
2. $-CH_2(CF\cdot)CH_2CHF- + O_2 \longrightarrow -CH_2(CFOO\cdot)CH_2CHF-$
3. $PO_2\cdot + PH \longrightarrow POOH + P\cdot$
4. $POOH \longrightarrow PO\cdot + OH\cdot$
5. $-CH_2\overset{O\cdot}{C}FCH_2CHFCH_2- \longrightarrow -CH_2\overset{O}{C}F + \cdot CH_2CHFCH_2-$
6. $\cdot CH_2CHFCH_2- + OH\cdot \longrightarrow CH_2{=}CFCH_2- + H_2O$
7. $-CH_2\overset{O}{C}F + H_2O \longrightarrow -CH_2\overset{O}{C}OH + HF$
8. $-CH_2\overset{O}{C}F + X\cdot \rightarrow$ conjugation $\rightarrow\rightarrow\rightarrow$ weight loss

incorporation into the polymer chain. These mechanisms are detailed in Schemes I and II. Scheme II is by no means a complete description of the oxidative degradation. But it provides a satisfying explanation for all of our major observations. Several aspects of Scheme II are noteworthy.

1. As in most radical chain processes, the initial source of radicals is difficult to determine and will vary with subtle aspects of the ambient environment.

2. Because the bond dissociation energies of the C–H bonds in –CHF and $-CH_2-$ units along the polymer backbone should not be very different,[18] it seems likely that the radical products of step 1 are produced in comparable quantities. The presence of IR bands for both acyl fluorides and aldehydes which result from initial hydrogen abstraction at –CHF– and $-CH_2-$ groups, respectively (vide infra), is consistent with this expectation.

3. The cleavage of the O–O bond in the hydroperoxide shown in step 4 leads to the mobile hydroxyl radical, which can carry the chain, and an alkoxy radical bound to the polymer chain. Because the C–C backbone bond is considerably weaker than the C–F bond at the carbon adjacent to the oxygen-centered radical, it seems likely that the lowest energy unimolecular reaction of this radical is the cleavage to produce the acyl fluoride as shown in step 5. The corresponding chemistry for the radical derived from abstraction at the $-CH_2-$ unit will lead to the formation of new aldehyde chain ends.

4. $OH^\bullet$ continues the chain by hydrogen abstraction and formation of H_2O. One possible abstraction reaction of $OH^\bullet$ is the disproportionation and chain termination step shown in step 6. In any case, whether $OH^\bullet$ abstracts H from radicals in a termination step or saturated polymer segments in a propagation step, water is being produced in situ. Since we have shown above that water vapor will react readily with acyl fluorides at the degradation temperature, reaction of the in situ generated water with acyl fluoride provides a logical route to HF as shown in step 7.

5. If the alkoxy radical bound to the polymer chain that is formed in step 4 abstracts hydrogen instead of cleaving a C–C bond in the backbone, an α-F alcohol is formed. This functional group should be thermally unstable to HF loss and formation of a ketone along the chain. This chemistry may be responsible for some of the additional carbonyl functionality shown in the infrared spectra.

Conclusions

The mechanism of degradation of poly(vinyl fluoride) has been shown to be a sensitive function of oxygen partial pressure. In the absence of oxygen the homogeneous pyrolysis of related small molecules like 2-fluoropropane or 3-fluoropentane[19] constitutes a useful model for the initial stages of the polymer degradation chemistry. In the presence of oxygen, the poly(vinyl fluoride) degradation chemistry is more closely related to the oxidative decomposition of hydrocarbon polymers like polyethylene or polypropylene. It is a radical chain reaction leading to oxygen incorporation, main chain cleavage, and formation of carbonyl-containing chain ends. HF is formed by an indirect route via oxygen-containing intermediates. It is interesting that poly(vinyl chloride) (PVC), on which much more work has been done, does not seem to be a very good model for the PVF degradation chemistry. PVC undergoes rapid thermal degradation even at 200 °C. As a result, addition of O_2 to the degradation atmosphere has only a modest effect on the overall rate. The absence of chain cleavage early in the reaction pathway and the domination of HCl in the oxidative product distribution are also different.[20] This is probably the result of the huge difference in C–Cl and C–F bond dissociation energies, allowing $Cl^\bullet$ to be an effective chain carrier in an oxidative environment while $F^\bullet$ is not.

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