The Thermal Degradation of Hydrofluoro Polymers

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Synopsis

The evolution of hydrogen fluoride (or other degradation products giving rise to F⁻ ions in aqueous solution) from a number of hydrofluoro polymers has been studied in nitrogen or air over a range of temperatures using a fluoride ion selective electrode to monitor the process. The results in an inert atmosphere illustrate the effect of chemical structure upon the relative ease of hydrogen fluoride elimination.

INTRODUCTION

Most of the elastomers that have been developed for high temperature applications contain both hydrogen and fluorine in their structures, and hence the elimination of hydrogen fluoride (HF) at elevated temperatures is possible. Although the degradation of a number of these polymers has been studied in detail and the volatile products of decomposition analyzed, relatively little has been reported on the quantitative determination of the HF evolved. Wall and Straus[1] studied the copolymers of vinylidene fluoride with chlorotrifluoroethylene or hexafluoropropylene, by heating them in vacuo for 30 min at various temperatures and measuring mass spectrometrically the silicon tetrafluoride formed by reaction of the HF produced with the glass of the apparatus. This, although comparing the polymers under standard conditions, gave no indication of the temperature at which HF evolution first occurred, of the rate of evolution at any particular temperature, or of the final total yield which could be obtained. Clearly such data are important for hydrofluoropolymers, as they indicate possible maximum-use temperatures and also whether in certain circumstances corrosion is likely to occur. Furthermore, a correlation of the ease, or otherwise, of HF evolution with chemical structure could help in formulating a more thermally stable elastomer of the hydrofluoro type.

An intensive study of the degradation of elastomers based on vinylidene fluoride and chlorotrifluoroethylene[2–5] and a less detailed one of the copolymer of vinylidene fluoride and hexafluoropropylene[6] have been made by Degteva et al. In these studies they trapped the volatile degradation products and subsequently analyzed them for halide by conventional methods. This gave a measure of the rate of evolution of HCl and HF with time and temperature; but, being a single-point method, it was rather laborious.

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In the present work, the thermal degradation of a number of available hydrofluoro polymers was studied in inert or oxidizing atmospheres, and the evolution of breakdown products giving rise to F^- ions when dissolved in aqueous solution was monitored continuously using a fluoride ion-specific electrode. Results on hydrofluoroethylene polymers have been reported previously,[7] but some of the data will be included for comparison purposes.

EXPERIMENTAL

Polymers Examined

The polymers examined were as follows:

Addition Homopolymers. Poly(pentafluorostyrene), $[CH_2CH(C_6F_5)]_n$, prepared by addition of 0.0015 g azobiscyanocyclohexane to 1 ml pentafluorostyrene followed by heating in an evacuated, sealed ampoule at 63°C for 63 hr. Poly(3-methylene octafluorocyclohexene), $[CH_2C_6F_8]_n$, prepared by thermal polymerization of the pure monomer at 60°C in an evacuated, sealed ampoule.

Addition Copolymers. These copolymers of vinylidene fluoride and hexafluoropropylene, $[CF_2CH_2-CF_3CFCF_2]$, were proprietary materials supplied by du Pont. They were designated as Viton A, which analyzed as a 61 weight % CF_2CH_2, 39 weight % C_3F_6 copolymer; Viton A-HV of higher molecular weight than Viton A, but with the same elemental analysis and Viton LD-234, which analyzed as a 49 weight % CF_2CH_2, 51 weight % C_3F_6 copolymer. A crosslinked sample of Viton A was prepared by addition of 3% DIAK 3 to the gumstock, followed by a press cure of 30 min at 150°C.

Condensation Polymers. Poly(fluoroethers), $[OCH_2(CF_2)_3CH_2OCH_2-mC_6H_4CH_2]$, $[OCH_2(CF_2)_3CH_2OCH_2pC_6H_4CH_2]$, $[OCH_2(CF_2)_3CH_2OCH_2-pC_6H_4OpC_6H_4CH_2]$, $[OCH_2(CF_2)_3CH_2OpC_6F_4pC_6F_4]$, and $[OCH_2(CF_2)_3-CH_2O(C_5NF_3)]$, were prepared by the Williamson reaction of hexafluoropentane-1,6-diol with the appropriate dihalo compound.[8] $[OCH_2pC_6F_4-CH_2OpC_6F_4pC_6F_4]$ was prepared by polycondensation of $BrCH_2C_6F_4CH_2Br$ and $NaOC_6F_4C_6F_4ONa$.[9] $[OCF_2pC_6H_4]$ was prepared by polymerization of p-trifluoromethylphenol in cold, dilute alkali.[10] One further polymer, $[(CF_2)_3mC_6H_4]$, was synthesized by reaction of $IC_6H_4(CF_2)_3I$ with copper in a mixture of dimethyl sulfoxide and benzotrifluoride.[11]

Apparatus and Experimental Technique

Polymer samples (approximately 5 mg) were pyrolyzed in a stream of nitrogen or air (50 ml/min), and the effluent gas was monitored for species giving rise to F^- ions in aqueous solution. The apparatus and experimental technique have been described in detail elsewhere,[7] but essentially the method consisted of heating the sample contained in a platinum crucible in a calcium fluoride tube at a constant rate of temperature rise (2°C/min). The gas stream, which only came into contact with calcium fluoride or poly(tetrafluoroethylene), was passed into a buffer solution containing

initially 10^{-5} mole of F^- ion per liter, and the change in F^- ion concentration was monitored with a fluoride ion-specific electrode manufactured by Orion Research Ltd. The output of the electrode was fed via a pH meter to the y-axis of an x-y recorder, the x-axis being connected to a thermocouple placed inside the furnace tube. In this way, a plot was obtained of pF versus temperature which could be transposed to a plot of the percentage of available F released versus temperature. It had been shown previously[7] that platinum did not catalyze the breakdown reaction.

Thermogravimetry in a flow of nitrogen or air (50 ml/min) was done on all the polymer samples (approximately 5 mg) at a heating rate of 4°C/min using a du Pont 950 thermogravimetric analyzer.

RESULTS AND DISCUSSION

Addition Homopolymers

Data for poly(pentafluorostyrene) and poly(3-methylene octafluorocyclohexene) are given in Figure 1. The percentage yield of available F rather than that of available HF is plotted against temperature to allow for the formation of other products in air which also give F^- ions when dissolved in aqueous solution. The curves are the averages of three experiments. Also included on the graphs are plots of total weight loss versus temperature
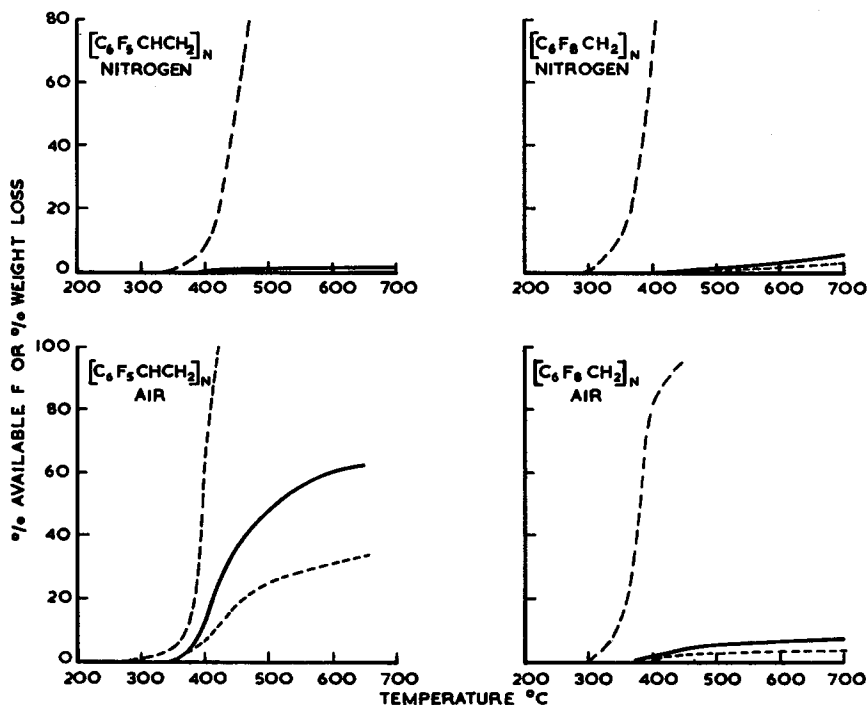

Fig. 1. Comparison of results for addition homopolymers: (—) yield of F; (—-) total weight loss; (- - -) yield of F as % weight loss.
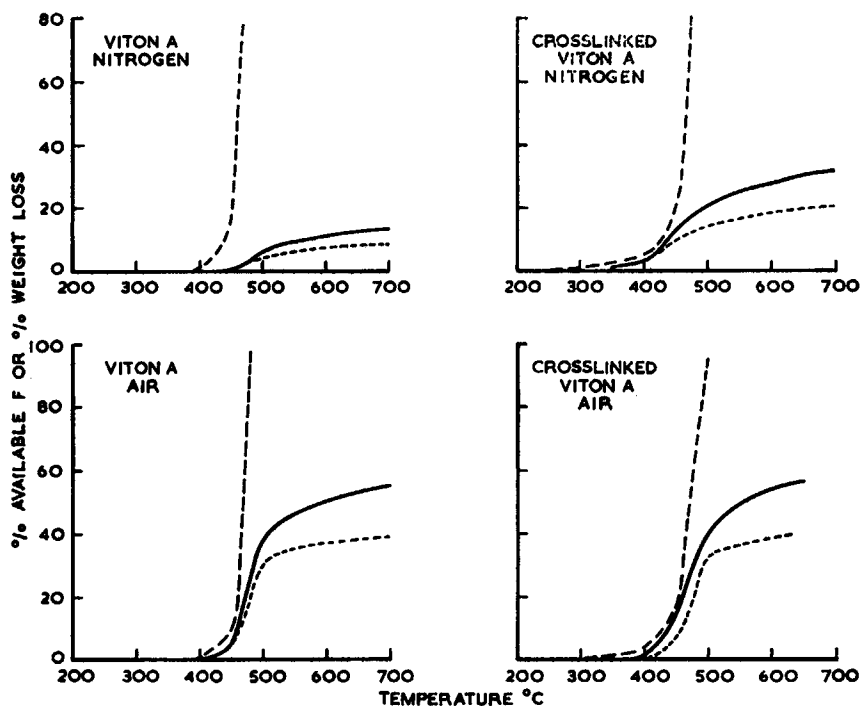
Fig. 2. Comparison of results for Viton A, crosslinked and uncrosslinked: (—) yield of
F; (—·—) total weight loss (---) yield of F as weight loss.

derived from the thermogravimetry experiments and of the yield of F ex-
pressed as a percentage weight loss versus temperature.

It should be noted that differences between the curves of total weight loss
and total F yield may be partly a consequence of the different experimental
techniques.   In the thermogravimetric experiments, total weight loss from
the sample boat is recorded.   In the F yield experiments, volatile degrada-
tion products may condense in the cooler parts of the furnace tube, only to
be further degraded as the temperature of this part of the tube rises with the
programmed heating cycle.

The type of curves obtained for F yield are formally analogous to thermo-
gravimetric analysis plots, and it would be perfectly feasible to utilize any
of the many theoretical treatments that have been proposed for analysis of
such data to give orders of reaction and overall activation energies for
degradation.   This was not done, as it is considered that many of the treat-
ments are of questionable value, and quite widely differing values for the
activation energy can be obtained depending on the weight a particular
treatment gives to different stages of the reaction.

In nitrogen, very little F was obtained from either polymer, even as a
secondary reaction.   For poly(pentafluorostyrene), this is in accord with
the results of Wall et al.,[12] which indicated that the major volatile decom-

position product was probably monomer. The results for poly(3-methylene octafluorocyclohexene), although confirming the report of Sayers et al.[13] that sudden decomposition occurred at about 320°C, does not support their supposition that this was associated with pyrolytic dehydrofluorination occurring between the methylene group and the adjacent tertiary fluorine atom. Whatever species was eliminated leading to conjugation and a black coloration, it was certainly not HF.

The presence of air had apparently relatively little effect on the degradation of the poly(3-methylene octafluorocyclohexene). With the styrene polymer, however, the overall stability was reduced, and there was quite a large yield of F due to reaction of oxygen with the fluorine of the perfluoro aromatic ring.

Addition Copolymers

In Figures 2 and 3 are given the results for Viton A in gumstock form or crosslinked with 3% of Diak 3, and for Viton A-HV and Viton LD-234, both in gumstock form. The results for the three gumstocks in nitrogen are virtually identical both with respect to weight loss and F yield, indicating that the changes in molecular weight and overall composition had little ef-
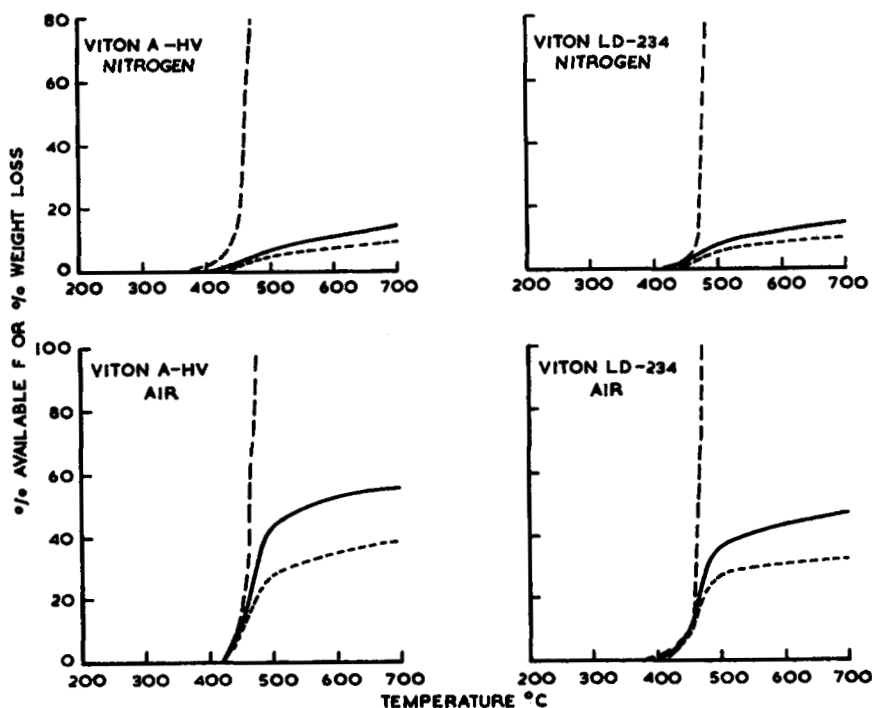

Fig. 3. Comparison of results for Viton A-HV and LD-234: (−) yield of F; (–) total weight loss; (--) yield of F as % weight loss.

fect.   This illustrates once again the dangers inherent in dynamic measurements of this type, as earlier isothermal work had shown that the higher molecular weight Viton A-HV was of somewhat lower stability than the other two materials.[14]   In air, the results for Viton A and Viton A-HV were similar, with higher F yields than in nitrogen; but Viton LD-234, although giving much the same weight loss curve, had a lower total yield of F.   This reflects the lower proportion of vinylidene fluoride in this copolymer.

The crosslinked sample of Viton A gave considerably more F in nitrogen than the uncrosslinked analog, although there was little difference in air. It would appear that the action of the crosslinking agent led to structures that favored dehydrofluorination in an inert atmosphere.   Later work with fully compounded material, however, has shown that more F is obtained from the compounded material than from the gumstock in both nitrogen and air.

For all the polymer samples the start of weight loss and F yield was approximately the same, but it is apparent from the curves that about 50% of the final total yield of F was accounted for by secondary breakdown of volatile degradation products.

Wall and Straus,[1] in their study of the degradation of Viton A under vacuum, cited a total HF yield of 24%.   This is in reasonable agreement with the average figure of 29% obtained from the three experiments performed in nitrogen in this investigation, especially considering the difference in experimental techniques.

Condensation Polymers Containing [OCH₂(CF₂)₃CH₂O] and [OCH₂C₆F₄CH₂O] Units

Results for polymers containing the [$OCH_2(CF_2)_3CH_2O$] grouping and no other fluorine-containing groups are shown in Figure 4.   In nitrogen, there was essentially no yield of F, the polymers breaking down completely by another mechanism.   The stabilities of the three polymers examined were low and practically the same.   In air, there was an appreciable yield of F, and again the behavior of all three polymers was similar.   If, however, perfluoroaromatic or heterocyclic groups were also present in the polymer, then the pattern changed.   As can be seen from Figure 5, the inclusion of such units, (C_6F_4, C_5HF_3), resulted in superior thermal stability, but also in the production of large amounts of F, even in nitrogen.   The inference is that this must have arisen from the perfluoro ring structures. Further confirmation for this is given by the data obtained for the polymer where [$OCH_2C_6F_4CH_2O$] was substituted for [$OCH_2(CF_2)_3CH_2O$].   This gave the largest yield in nitrogen of the available F of any of the polymers studied, and the weight loss and F yield curves were nearly superimposable both in nitrogen and in air.   This observation led to the study of the yield of F from perfluoro polymers, which will form the subject of a separate paper.
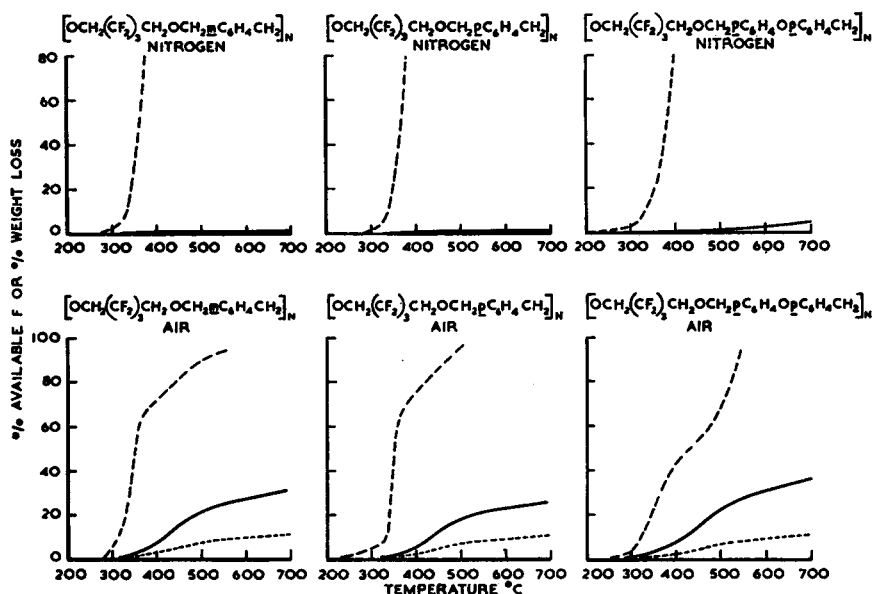
Fig. 4. Comparison of results for [OCH$_2$(CF$_2$)$_3$CH$_2$O]-linked polymers: (−) yield of F; (—) total weight loss; (---) yield of F as % weight loss.
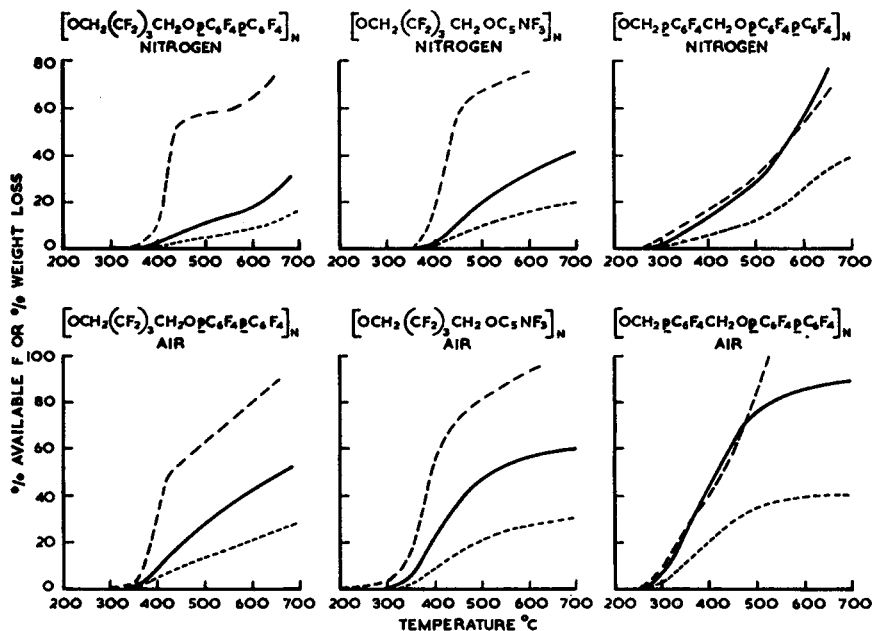
Fig. 5. Comparison of results for [OCH$_2$(CF$_2$)$_3$CH$_2$O]- and [OCH$_2$C$_6$F$_4$CH$_2$O]-linked polymers: (−) yield of F;   (—) total weight loss;   (---) yield of F as % weight loss.

Condensation Polymers Containing [OCF₂] and [CF₂]₃ Units

The final pair of polymers studied comprised phenylene rings linked by either [OCF₂] or [CF₂]₃ groups. Figure 6 shows that the latter polymer was of considerably higher thermal stability both in inert and oxidizing atmospheres. From both polymers, however, in contrast to the analogous [OCH₂(CF₂)₃CH₂O]-linked materials discussed above, appreciable quantities of F were obtained. It is suggested that the difference arises because of an alternative low-temperature decomposition route open to the [OCH₂(CF₂)₃CH₂O]-linked polymers.
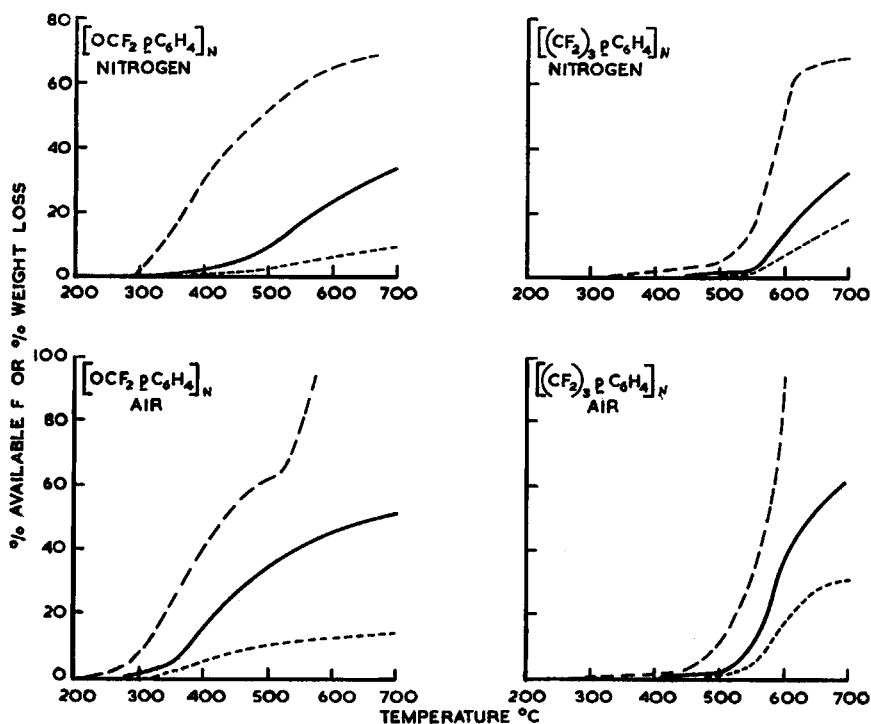
Fig. 6.   Comparison of results for [OCF₂]- and [CF₂]₃-linked polymers: (−) yield of
F;   (--) total weight loss;   (---) yield of F as % weight loss.

Overall Comparison of Results

It was stated above that previous investigations on hydrofluoro polymers had given no indication of the temperatures at which HF evolution first occurred, or of the rate of evolution at any particular temperature, or of the final total yield which might be obtained. The present study gives direct information on the first and the last of these three quantities and indirect evidence of a comparative nature on the second. (Absolute rate data depend upon isothermal experiments, which are now in progress on selected polymers.) Tables I and II give the following information for all

TABLE I
Summary of Results in Nitrogen

Polymer structure	Temperature, °C, for				Final total yield of F, %
	Initial weight loss	1% weight loss	Initial F yield	1% F yield	
ɟCHFCH₂ɟ	240	320	177	337	70.8
ɟCF₂CH₂ɟ	240	320	284	396	70.5
ɟCF₂CFHɟ	320	390	329	475	8.5
ɟCH₂CH(C₆F₅)ɟ	340	365	413	—	0.9
ɟCH₂C₆F₈ɟ	290	305	312	492	4.8
[CF₂CH₂/CF₂CF(CF₃)] Viton A	270	350	136	457	12.9
Viton A-HV	350	410	141	430	13.2
Viton LD-234	400	440	271	442	13.5
Viton A crosslinked	170	320	188	361	28.5
ɟOCH₂(CF₂)₃CH₂OCH₂mC₆H₄CH₂ɟ	250	305	292	>600	1.1
ɟOCH₂(CF₂)₃CH₂OCH₂pC₆H₄CH₂ɟ	270	295	337	>600	1.7
ɟOCH₂(CF₂)₃CH₂OCH₂pC₆H₄OpC₆H₄CH₂ɟ	220	270	254	494	4.8
ɟOCH₂(CF₂)₃CH₂OpC₆F₄ɟ	340	375	192	366	35.3
ɟOCH₂(CF₂)₃CH₂O(C₅NF₃)ɟ	340	365	244	368	41.0
ɟOCH₂pC₆F₄CH₂OpC₆F₄pC₆F₄ɟ	213	255	205	260	87.6
ɟOCF₂pC₆H₄ɟ	250	280	244	329	33.7
ɟ(CF₂)₃pC₆H₄ɟ	270	350	437	499	32.9

TABLE II
Summary of Results in Air

Polymer structure	Temperature, °C, for				Final total yield of F, %
	Initial weight loss	1% weight loss	Initial F yield	1% F yield	
ɟCHFCH₂ɟ	190	250	153	276	93.7
ɟCF₂CH₂ɟ	250	320	214	386	75.4
ɟCF₂CFHɟ	300	330	311	373	36.0
ɟCH₂CH(C₆F₅)ɟ	290	325	294	359	63.4
ɟCH₂C₆F₈ɟ	300	320	294	387	6.9
[CF₂CH₂/CF₂CF(CF₃)] Viton A	340	395	143	431	54.2
Viton A-HV	380	420	195	417	54.7
Viton LD-234	370	425	259	420	46.5
Viton A crosslinked	200	360	220	383	56.2
ɟOCH₂(CF₂)₃CH₂OCH₂mC₆H₄CH₂ɟ	200	250	199	334	31.7
ɟOCH₂(CF₂)₃CH₂OCH₂pC₆H₄CH₂ɟ	240	270	243	348	25.9
ɟOCH₂(CF₂)₃CH₂OCH₂pC₆H₄OpC₆H₄CH₂ɟ	260	290	269	333	36.3
ɟOCH₂(CF₂)₃CH₂OpC₆F₄pC₆F₄ɟ	250	360	175	361	54.0
ɟOCH₂(CF₂)₃CH₂O(C₅NF₃)ɟ	180	250	186	327	59.7
ɟOCH₂pC₆F₄CH₂OpC₆F₄pC₆F₄ɟ	190	255	153	266	91.2
ɟOCF₂pC₆H₄ɟ	240	260	221	296	51.7
ɟ(CF₂)₃pC₆H₄ɟ	295	380	280	420	61.3

the polymers examined, together with data for hydrofluoroethylene poly-
mers for comparison purposes: the temperature for initial loss in weight,
the temperature for 1% weight loss, the temperature for initial yield of F
(the lowest figure obtained in three experiments), the temperature for 1%
yield of F (the average figure for the three experiments), and the final total
yield of F expressed as a percentage of that available (again the average of
three results). The reason for including the 1% levels was that variations
were observed in the electrode response at the 10^{-5} molar concentration,
and this led to apparent variations in the temperature at which F was first
evolved. This objection does not apply to the temperatures for 1% F
yield, and hence these should give a more accurate comparison of the
polymers. The figures for the lowest temperature for the initial detection
of F are nevertheless important from a practical point of view.

From the tables it can be seen that although the temperatures for initial
weight loss and initial F yield were approximately the same in many cases,
especially in an oxidizing atmosphere, there were numerous examples of F
being detected at temperatures much lower than weight loss. These in-
cluded the important commercial products poly(vinyl fluoride), poly-
(vinylidene fluoride), and the Viton gumstocks. The one exception in the
Viton series was the crosslinked Viton A, but it should be noted here that
the overall stability had been considerably reduced by the crosslinking
process. One would expect F yield at even lower temperatures if the
experiments were carried out isothermally.

In air, all the polymers examined, with the exception of poly(3-methylene
octafluorocyclohexene), gave an F yield of at least 25% of that possible, the
yield rising to greater than 90% in two cases.

It is noticeable too that in nitrogen the polymers containing perfluoro
aromatic rings in the chain gave lower temperatures for initial yield of F
and higher final yields of F than most of the polymers containing only
fluorine attached to aliphatic structures.

CONCLUSIONS

The data obtained show that there were quite considerable differences in
the ease of evolution of HF (or other species giving rise to F ions in aqueous
solution) with differences in chemical structure. It would obviously be
preferable from this point of view, in the hydrofluoroethylene series, to have
trifluoroethylene in a copolymer rather than vinylidene or vinyl fluoride.
There are important practical implications of the low temperatures for
initial yield of F, which in some cases were appreciably lower than the
temperature at which weight loss was first detected. Another important
consideration is the reduced thermal stability brought about by cross-
linking in the Viton gumstock. Comparative isothermal studies are now
in progress on gumstocks and fully compounded materials.

The relative ease of elimination of F from polymers containing perfluoro
aromatic rings in the chain was somewhat unexpected and has been the
subject of a more detailed study, which will be reported separately.

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