MECHANISMS OF PYROLYSIS OF FLUOROPOLYMERS

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SUMMARY

  A systematic study of the mechanisms of the pyrolysis of fluoropolymers was made by means of pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) and direct Py-MS. For perfluoropolymers and chlorine-containing fluoropolymers the depolymerization reaction predominates during pyrolysis. However, the introduction of OCF3 groups into pernuoro-polymers in place of F atoms brings about significant changes in their mode of degradation. The OCF3 groups activate the F atoms attached to the same carbon atoms and make them easier to transfer. Therefore, random chain cleavage accompanied by the F transfer becomes predominant in the course of the pyrolysis. When the F atoms of perfluoropolymers are partly replaced by H atoms, elimination of hydrogen nuoride arid chain cleavage. accompanied by H transfer would occur with great ease. For fluoropolymers containing H, Cl and OCF3 as side groups, the depolymerization, the elimination of hydrogen chloride and hydrogen fluoride and the random chain cleavage accompanied by H and F transfer would occur simultaneously and compete with each other.

INTRODUCTION

  Fluoropolymers characterized by superior physico-chemical properties can meet a variety of severe requirements presented by modern engineering, so they have become important artificial materials in science and industry.
  For the structural analysis of fluoropolymers, routine spectrometric methods are restricted to some extent owing to difficulties in sample handling. Recently, pyrolysis-gas chromatography (Py-GC) has rapidly grown into a powerful tool for the identification of fluoropolymers [1,2]. A systematic study of the mechanisms of the pyrolysis of fluoropolymers would be helpful in the investigation of their structures and in the identification or unknown fluoropolymers [3-5].
  In this work, some common fluoropolymers were investigated by means of Curie-point Py-GC-mass spectrometry (Py-GC-MS) and direct Py-MS. The mechanisms of the pyrolysis of the polymers are discussed in relation to their major pyrolysis products.

EXPERIMENTAL

Experiments were carried out using a MAT 44-S GC-MS system and a JHP-2 Curie-pbint pyrolyser. The outlet of the pyrolyser was directly coupled with a GC column, thus constituting a Py-GC-MS combined system. The experimental conditions for Py-GC-MS were Curie-point temperature 590°C, pyrolysis time 5 s, column A for volatile fluoro compounds, 2 m x 2 mm I.D., packed with Porapak Q (80-100 mesh), column temperature 90°C, column B for fluoro compounds containing more than four carbon atoms, 2 m x 2 mm I.D., packed with 10% dioctyl phthalate (DOP), column temperature 60°C. For Py-MS the electron impact mode ion source was maintained at 150°C. A small piece of sample was placed on the 0.1 mm spiral platinum wire, which was inserted into the ion source by a direct sample probe. The wire temperature, controlled by a microprocessor, was increased to the pyrolysis temperature of the polymer at a rate of about 100°C/min.

RESULTS AND DISCUSSION

Table 1 shows the analysis results for various fluoropolymers. There are some differences between the results obtained by Py-GC-MS and Py-MS. These might be caused by the fact that Py-MS involves almost all the products formed during pyrolysis, whereas Py-GC-MS is restricted to the volatile pyrolysis products that can be eluted through the column.

Mechanisms of pyrolysis of fluoropolymers

Figs. 1 and 2 show the pyrogram and the pyrolysis-mass spectrum of F46, respectively.

The thermal degradation mode of perfluoropolymers is different to that of polyolefins. For perfluoropolymers such as polytetrafluoroethylene and tetrafluoroethylene-hexafluoropropylene copolymer, the depolymerization reaction predominates during pyrolysis. When they are decomposed, the main carbon chains are first cleaved, forming free radicals at the end carbon atoms of the broken chains, which consecutively initiate a-cleavage of the neighbouring C-C bonds, producing large amounts of monomers (see Figs. 1 and 2). If Cl atoms partly replace the F atoms in perfluoropolymers, the degradation mode remains almost the same as that for F3.

However, the introduction of OCF_3 groups into perfluoropolymers in place of F atoms causes significant changes in their degradation mode. Perfluoromethoxy groups activate the F atoms attached to the same carbon atoms and make them easier to transfer. Therefore, random chain cleavage accompanied by F transfer becomes predominant in the course of the pyrolysis, forming large amounts of perfluoroalkanes and perfluoroolefins
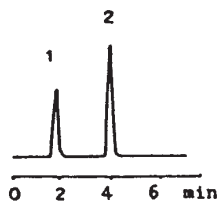
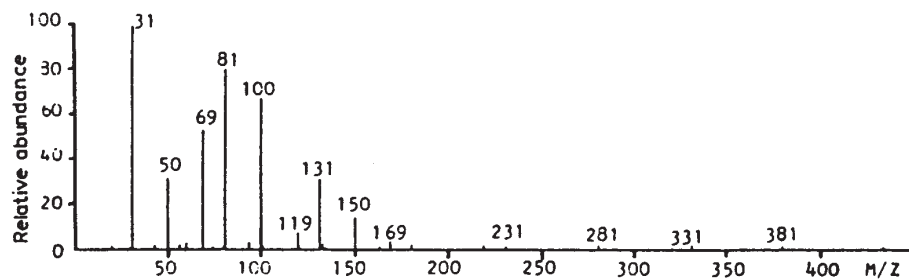Fig. 1. Pyrogram of F46. Peaks: $1 = C_2F_4$; $2 = C_3F_6$.
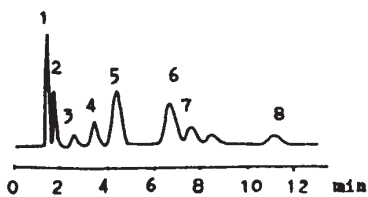

Fig. 2. Pyrolysis–mass spectrum of F46.

Fig. 3. Pyrogram of F40. Peaks: $1 = C_2F_6$; $2 = C_2F_4$; $3 = C_3F_8$; $4 = C_3F_6$; $5 = CF_3OC_2F_3$; $6 = C_4F_{10}$; $7 = C_4F_8$; $8 = CF_3OC_3F_5$.
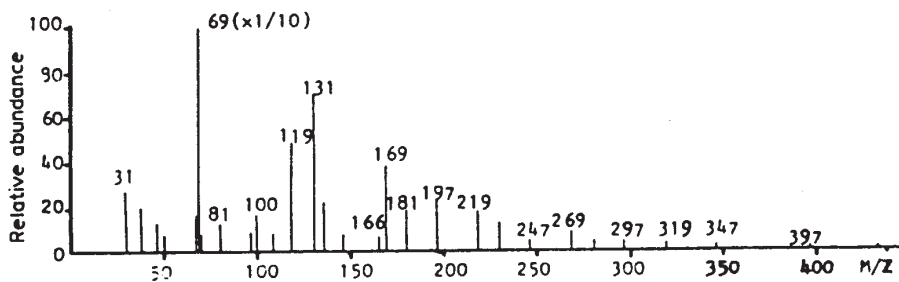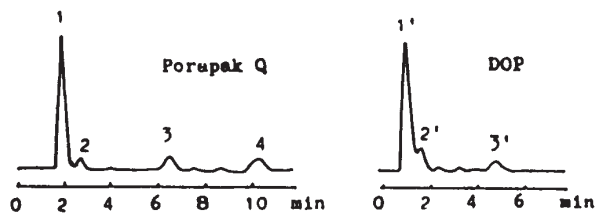

Fig. 4. Pyrolysis–mass spectrum of F40.

Fig. 5. Pyrogram of F2. Peaks: $1 = C_2F_2H_2$; $2 = C_2FH_3$; $3 = CF_2HCH_3$; $4 = C_3F_4H_2$; $1' = C_2$, C_3 compounds; $2' = C_4$ compounds; $3' = 1,3,5$-trifluorobenzene.

TABLE 1

Results of Py–GC–MS and Py–MS analysis of fluoropolymers

Polymer	Abbreviation	Major pyrolysis products identified by Py–GC–MS	Major pyrolysis products and their characteristic ions shown by Py–MS *
Polytetrafluoro-ethylene	F4	$CF_2=CF_2$	$C_2F_4(100, 81, 50, 31)$
Polyvinylidene fluoride	F2	$CF_2=CH_2$, $CF_2=CH-CF=CH_2$, 1,3,5-trifluorobenzene	$HF(20)$, $C_2F_2H_2(64, 45)$, $C_4F_3H_3(108)$, $C_6F_3H_3(132)$, allylic ions(77, 95, 113), alkyl ions(51, 65, 115, 133)
Polychlorotrifluoro-ethylene	F3	$CF_2=CFCl$, C_3F_5Cl	$C_2F_3Cl(118, 116, 99, 97, 87, 85)$, $C_3F_5Cl(149, 147, 131)$
Tetrafluoroethylene–hexafluoropropylene copolymer	F46	$CF_2=CF_2$, $CF_3-CF=CF_2$	$C_2F_4(100, 81, 50, 31)$, $C_3F_6(150, 131)$
Vinylidene fluoride–hexafluoropropylene copolymer	F26	$CF_2=CH_2$, $CF_3-CF=CF_2$, $CF_3-CF=CH_2$, $C_2F_4H_2$	$HF(20)$, $C_2F_2H_2(64,45)$, allylic ions(77, 95, 113, 163), alkyl ions(51, 65, 115, 133)
Vinylidene fluoride–chlorotrifluoro-ethylene copolymer	F23	$CF_2=CH_2$, $CF_2=CFCl$, C_3F_5Cl	$HCl(38, 36)$, $C_2F_3Cl(118, 116, 87, 85)$, $C_3F_5H_2^+(133)$, $C_3F_4H_2Cl^+(151, 149)$, $C_5F_6H^+(175)$, allylic ions(95, 113, 131)

Ethylene–chlorotri-fluoroethylene copolymer	F30	$CH_2=CH_2$, $CF_2=CH_2$, C_2F_3H, C_2FH_3, $CF_2=CFCl$, $CH_2=CFCl$	HF(20), HCl(38, 36), $C_2F_2H_3^+$(65), allylic ions(77, 95)
Vinylidene fluoride–tetrafluoroethylene–hexafluoropropylene copolymer	F246	$CF_2=CF_2$, $CF_2=CH_2$, $CF_3–CF=CF_2$, $CF_3–CF=CH_2$	HF(20), $C_2F_2H_2$(64), C_5F_7H(194), allylic ions(95, 113, 163), alkyl ions(51, 69)
Tetrafluoroethylene–perfluoromethyl vinyl ether copolymer	F40	$CF_2=CF_2$, $CF_3–CF_3$, $CF_3–CF=CF_2$, $CF_3–CF_2–CF_3$, C_4F_8, C_4F_{10}, $CF_3O–C_2F_3$, $CF_3O–C_3F_5$	C_2F_4(100, 81), $CF_3OC_2F_3$(166, 147), $C_nF_{2n+1}^+$(69 + 50p, p = 0–9), $C_nF_{2n-1}^+$(31 + 50p, p = 0–9), $C_nF_{2n-1}O^+$(47 + 50p, p = 0–9)
Vinylidene fluoride–tetrafluoroethylene–perfluoromethyl vinyl ether copolymer	F240	$CF_2=CF_2$, $CF_2=CH_2$, $CF_3–CF=CF_2$, $CF_3OC_2F_3$, $C_2F_4H_2$, $CF_3–CF=CH_2$	HF(20), C_2F_4(100), $C_2F_2H_2$(64, 45), $C_3F_3H(OCF_3)^+$ (179), allylic ions(77, 95, 113), alkyl ions(51, 65, 69, 101, 133), oxygen-containing ions(47, 66, 91, 197, 255, 277, 297)

* Mass/charge ratios (m/z) of the molecular ions and their related fragment ions are given in parentheses.

(see Figs. 3 and 4). Figs. 3 and 4 show the pyrogram and the pyrolysis-mass spectrum of F40, respectively.

For tetrafluoroethylene-perfluoromelhyl vinyl ether copolymer its degradation- mode can be described as follows: (1) depolymerization reaction forming the monomers; (2) random chain cleavage accompanied by F transfer.

(A) For the sequences with $-OCF_3$ as side groups:

$$n = 1, 2, 3 \ldots \ldots$$
$$n = 0, 1, 2 \ldots \ldots$$
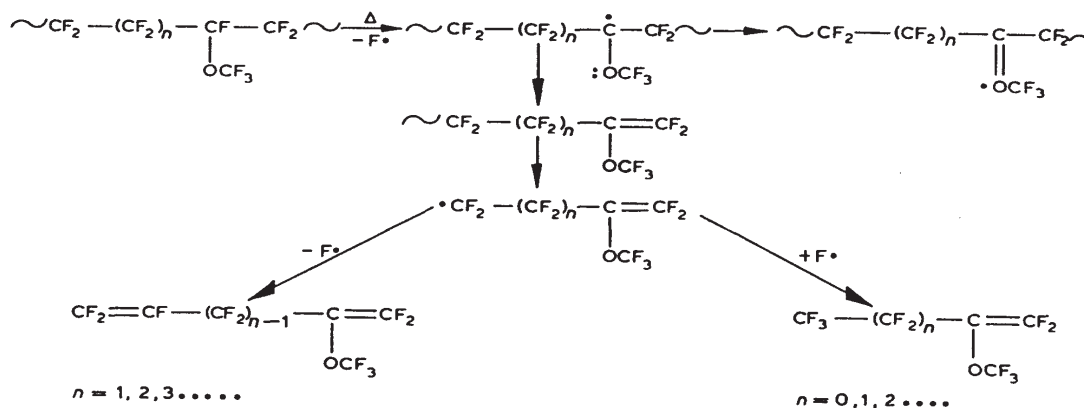
(B) For the sequences without $-OCF_3$ as side groups:
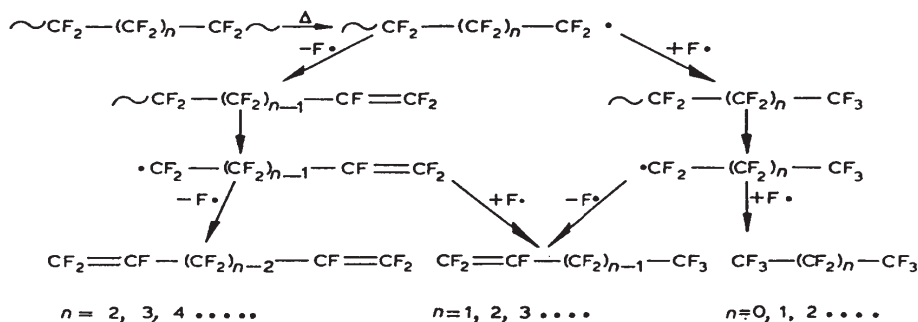
$$n = 2, 3, 4 \ldots \ldots \qquad n = 1, 2, 3 \ldots \ldots \qquad n = 0, 1, 2 \ldots \ldots$$

When the F atoms of perfluoropolymers are partly replaced by H atoms, elimination of hydrogen fluoride and chain cleavage accompanied by H
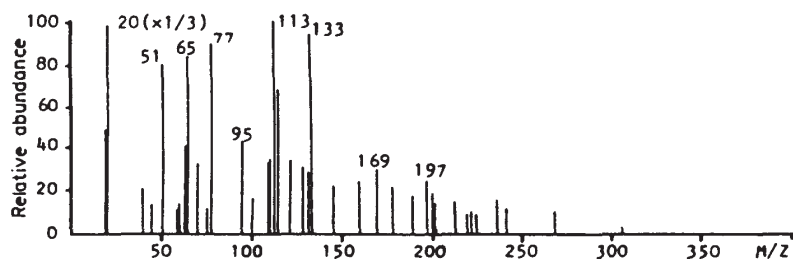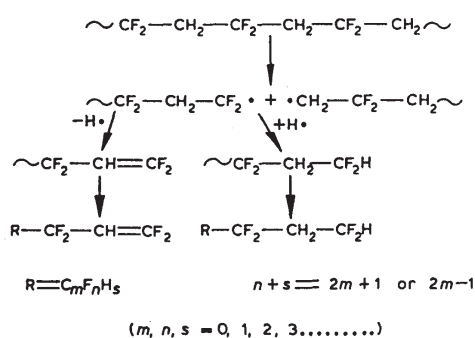

Fig. 6. Pyrolysis–mass spectrum of F2.

transfer will occur with great ease. Polyvinylidene fluoride may be taken as an example to illustrate the pyrolysis behaviour of hydrogenated fluoropolymers.

Figs. 5 and 6 show the pyrogram and the pyrolysis-mass spectrum of F2, respectively. The degradation mode of F2 can be described as follows: (1) depolymerization reaction forming vinylidene fluoride; (2) elimination of hydrogen nu9ride followed by cyclization to form trifluorobenzene; (3) random chain cleavage accompanied by H transfer forming various terminal olefins and alkanes. One of the chain cleavage modes is represented as follows:

$$\sim CF_2-CH_2-CF_2-CH_2-CF_2-CH_2\sim$$

$$\sim CF_2-CH_2-CF_2 \cdot \; + \; \cdot CH_2-CF_2-CH_2\sim$$
$$-H\cdot \qquad\qquad\qquad +H\cdot$$
$$\sim CF_2-CH=CF_2 \qquad \sim CF_2-CH_2-CF_2H$$

$$R-CF_2-CH=CF_2 \qquad R-CF_2-CH_2-CF_2H$$

$$R=C_mF_nH_s \qquad\qquad n+s = 2m+1 \; or \; 2m-1$$

$$(m, n, s = 0, 1, 2, 3\ldots\ldots\ldots)$$

The degradation mode described above for F2 is basically the same for the other hydrogenated nuoropolymers, with the exception of the formation of trifluorobenzene which is characteristic of F2. According to the assumed pyrolysis mechanisms, the sequence $-(CF_2-CH_2)_n-$ (n> 3) is a prerequisite for the formation of trinuorobenzene. However, as the probability of forming the sequence $-(CF_2-CH_2)a$ (n>3) is very small, trinuorobenzene is not observed on the corresponding pyrograms.

As shown in Fig. 6, for F2 various hydrogenated nuoropolymers generally yield characteristic allylic ions in the corresponding mass spectra. Therefore, these characteristic ions shown in Table 2 might be usable for differentiating the various hydrogenated fluoropolymers. For example, much more abundant allylic ions $(CH_2-CH=CF_2)+$ (m/z 77) for F30 than the other hydrogenated fluoropolymers indicate more sequences of $-(CH_2-CH_2-CF_2)-$ along the chain structures. Probably the allylic ions $[CF_2-CH=CF(CF3)]+$ (m/I 163) for F26 indicate the existence of -(CF$_2$-CH$_2$- $\underset{CF_3}{CF}$)- along the chain structures, and the allylic ions $[CF_2-CH=CF(OCF_3)]+$(m/z 179) for F240 indicate the existence of -(CF$_2$-CH2- $\underset{OCF_3}{CF}$)- sequences.

For fluoropolymers containing H, Cl and OCF$_3$ as side groups, such as F23 and F240, the depolymerization, the elimination or HCl and HF and

TABLE 2

Relative abundances of allylic ions shown by Py-MS of hydrogenated fluoropolymers (normalized to a base of m/z 113)

Allylic ion	m/z	F2	F30	F26	F246	F240	F23
$C_3F_2H_3^+$	77	90	500	49	13	6	–
$C_3F_3H_2^+$	95	45	175	37	31	12	57
$C_3F_4H^+$	113	100	100	100	100	100	100
$C_3F_5^+$	131	–	–	–	–	–	109
$C_3F_3H(CF_3)^+$	163	–	–	164	94	–	–
$C_3F_3H(OCF_3)^+$	179	–	–	–	–	24	–

the random chain cleavage accompanied by H and F transfer would occur simultaneously and compete with each other. In the general case, the depolymerization reaction occurs to a lesser extent, whereas the elimination of HCl and HF tends to occur to a major extent and more HCl than HF is eliminated. Random chain cleavage accompanied by H and F transfer often predominates in the competition.

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