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PYROLYSIS GAS CHROMATOGRAPHY OF SOME FLUORINE-CONTAINING POLYMERS

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SUMMARY

Pyrolysis gas chromatography of the polymers of 1,3,3,3-tetrafluoropropene, 3,3,4,4,5,5,5-heptafluoropentene-1 and of the copolymers of tetrafluoroethylene with the above and with 3,3,3-trifluoropropene and with isobutene in all instances gave only 3 to 19% of volatiles below C₁₆, distributed among many peaks. This and the absence of significant char indicate predominantly a random scission mechanism of decomposition.

INTRODUCTION

A number of hydrogen and fluorine bearing polymers have been synthesized in this laboratory [1-4]. These polymers have several reaction pathways open for their pyrolytic decomposition, yielding diverse products [5]: (i) reverse propagation of polymer radicals, yielding monomer molecules; (ii) random scission and/or intermolecular chain transfer, yielding a random assortment of all molecular sizes small enough to evaporate; (iii) intramolecular chain transfer, also called "back-biting," yielding molecules in the dimer and trimer range; and (iv) stripping of HF molecules, yielding conjugated unsaturation and ultimately a charred residue. The composition and amount of the products therefore furnish some clues as to the mechanism.

RESULTS AND DISCUSSION

The polymers in Table 1 were examined by pyrolysis gas chromatography. In addition to those listed, several TFE - 3,3,3-trifluoropropene copoly-

TABLE 1

Volatiles from Pyrolysis Gas Chromatography
of Polymers and TFE Copolymers^a

Monomer or Co-monomer	Mol Fraction TFE in Polymer	% C ₁ -C ₁₆ in Volatiles
TFE	1.00	-
1,3,3,3-Tetrafluoropropene	0	6
3,3,4,4,5,5,5-Heptafluoropentene-1	0	9
3,3,4,4,5,5,5-Heptafluoropentene-1	0.17	6
3,3,4,4,5,5,5-Heptafluoropentene-1	0.48	3
3,3,4,4,5,5,5-Heptafluoropentene-1	0.94	4
1,3,3,3-Tetrafluoropropene	0.25	5
1,3,3,3-Tetrafluoropropene	0.46	4
1,3,3,3-Tetrafluoropropene	0.94	-
Isobutene	0.27	19
Isobutene	0.46	7
Isobutene	0.56	7

a) Pyrolysis at 760°C, 20 seconds.

mers were examined qualitatively. In almost all instances a large number of peaks, 15 or 20, appeared in the range C₁ to C₁₆. Monomer was not a major product, and it is evident from Table 1 that the total amount of all this material was a small weight fraction of the polymer sample. By all indications almost all the sample volatilized. This is confirmed by TGA in the cases of the TFE - 3,3,3-trifluoropropene copolymers [1], the TFE - 1,3,3,3-tetrafluoropropene copolymers [2], and the TFE - heptafluoropentene copolymers [4]. Furthermore, none of the samples listed showed any pyrolysis residue visually on the ribbon filament used, although admittedly this is not a sensitive test for a small sample. Pyrolyses at a temperature 100°C lower than the one used in the experiments comprising Table 1 gave nearly the same amount of volatiles. Most of the material volatilized was therefore evidently above the range of the gas chromatograph column used, that is, in the so-called wax fraction. This indicates that all the polymers listed degraded approximately by a random scission

path. Pyrolysis gas chromatography on poly - 3,3,3-trifluoropropene, done earlier [6], gave similar results. The results are not surprising in the light of the known random decomposition of polyvinyl fluoride [7], polytrifluoroethylene [7], and vinylidene fluoride hexafluoropropene copolymer, [8], despite their structure which is potentially susceptible to hydrogen fluoride stripping. Recent "fingerprint" chromatograms of several well-known commercial fluorine-bearing polymers [9] (ethylene tetrafluoroethylene copolymer, vinylidene fluoride hexafluoropropene copolymer, and ethylene chlorotrifluoroethylene copolymer) can be interpreted likewise as indicating predominantly random scission.

The absence of pure samples of expected pyrolysis products prevented identification of pyrolysis products from the polymers. Pure polyheptafluoropentene gave a moderately strong peak at the retention time characteristic of the monomer, and another moderately strong one in the C_{16} region. Mass spectra were taken on three samples, inconclusively: (A), retention time 3 to 5.5 min., gave peaks to 151 with 51, 69 and 101 prominent; (B), retention time 6 to 7 min., gave mass peaks to 169 with 65, 69 and 77 prominent; and (C), retention time 11 to 13 min., gave peaks to 291. The pure monomer gave 177, $C_5F_6H_3$, as the highest mass peak and 77, $C_3F_2H_3$ as the most prominent.

PTFE under our conditions gave only two important gas chromatogram peaks, monomer and another with the retention time of perfluorocyclobutane, in the ratio 1.9:1, although hexafluoropropene and octafluoroisobutene might also have been anticipated according to the literature [9-12]. Possibly the hexafluoropropene was not resolved from the perfluorocyclobutane. The recently reported occurrence [9] of a tetrafluoromethane peak from PTFE is incidentally difficult to reconcile with the extraordinarily low sensitivity of the flame ionization detector to this compound [13]. None of the tetrafluoroethylene copolymers examined here yielded very much tetrafluoroethylene monomer. Even in a 94 mole percent TFE copolymer with heptafluoropentene, the ratio of TFE to total chromatographically recorded volatiles was only 0.06 compared with 0.34 in PTFE. A species in the C_4 range, of retention time longer than perfluorocyclobutane, was the major volatile component in this copolymer. Likewise, from a copolymer of TFE with 1,3,3,3-tetrafluoropropene containing 94% TFE, the ratio of the TFE peak to total volatiles recorded was only 0.10. The low yields of TFE, even from a polymer rich in it, are consistent with observations on the

pyrolysis of PTFE in hydrogen [14] where mixed hydrogen-bearing compounds such as C_5HF_9 occur. Apparently a radical bearing a $-CF_2CF_2$ end can react with available hydrogen in its surroundings in competition with peeling off a molecule of C_2F_4 . The tetrafluoroethylene isobutene copolymer containing 0.27% TFE has an appreciable proportion of the "fingerprint" pattern of polyisobutene at high retention times. This behavior is consistent with its known composition--a highly alternating copolymer plus additional ionically-polymerized polyisobutene [3].

EXPERIMENTAL

Preparation and characteristics of the polymers have been described [1-4]. Conditions for chromatography were: Column: silica gel [15-16] D-08 chromatograph grade, 60/80 mesh, 6 ft. by 1/8 in. Helium carrier gas velocity 35 ml/min., hydrogen 30 ml/min., air 560 ml/min., interface 260°C, temperature program 50-280°C at 16°C/min. A double flame ionization detector was used. The pyrolysis was done on a platinum ribbon unit. Usual conditions were 760°C, 20 seconds [4], but supplementary studies were made at other times and temperatures. Most polymers and copolymers, except those quite high in TFE, were soluble in hexafluorobenzene. For these polymers an amount of a standard solution chosen to contain 0.3 mg of polymer was measured out on to the ribbon pyrolyzer. With insoluble polymers, either a 1 - mg. weighed portion or an unweighed small portion was placed on the ribbon. Computation of the yield of volatiles was made using the crude assumption that equal numbers of carbon atoms give equal peak areas [17]. The expected area for 100% yield was easily computed from sample weight and composition. Base line drift at higher retention times led to uncertainties in area of the order to 50%, which is not too serious for the small percentages of volatiles encountered. This may have been due to unresolved broad peaks, as there was a tendency to return slowly toward the original base line. The assumption of equal peak areas for equal numbers of carbon atoms is known to be very seriously violated by tetrafluoromethane and hexafluoroethane [13] but was obeyed roughly by all of our calibrating substances capable of measurement. Because of quantitative difficulties with gas injection, gases were calibrated relative to isobutene and liquids relative to 2,4,4-trimethylpentene. The sensitivity values of Table 2, although of no better than 10% precision, are of some interest because of the known very abnormal behavior of the lowest perfluoroparaffins [13]. A few other relative numbers are given in Ref. [18].

TABLE 2

FID Sensitivities and Retention Times
of Fluorine Organic Compounds

Compound	Retention Time Minutes	Sensitivity ^a
[Methane]	0.2	--
Tetrafluoroethylene	1.6	1.0 i
Vinyl fluoride	1.8	--
Vinylidene fluoride	1.8	1.31 i
Octafluorocyclobutane	3.4	0.71 i
[Propene]	4.4	--
1,2-Difluoroethylene	4.7	1.58 i
2-Fluoropropene	5.4	1.57 i
3,3,4,4,4-Penta fluorobutene-1	5.6	0.71 i
2-Trifluoromethylpropene	5.8	0.94 i
Tetradecafluoromethylcyclohexane	7.2	1.22
3,3,4,4,5,5,5-Heptafluoropentene-1	7.5	b
Hexafluorobenzene	8.0	1.17
Pentafluorobenzene	9.3	0.96
[Benzene]	9.4	--
1,2,3,4-Tetrafluorobenzene	10.0	1.00
Octafluorotoluene	10.0	0.81
α -Hydrononafluoroethylbenzene	12.2	0.79
[n-Dodecane]	14.5	--
[n-Hexadecane]	19.0	--

a) Area per carbon atom relative to 2,4,4-trimethylpentene-1 (unmarked) or to i-butene (marked "i").

b) Several-fold variation, perhaps due to condensation during injection.

i) Relative to isobutene.

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