Thermal degradation of PTFE studied by ultraviolet photoelectron spectroscopy (u.p.s.)

D. Betteridge and N. R. Shoko
Chemistry Department, University College of Swansea, Swansea, UK

and M. E. A. Cudby and D. G. M. Wood
ICI, Plastics Division, Welwyn Garden City, UK
(Received 2 November 1979; revised 2 April 1980)

The early stages of the thermal degradation of PTFE were followed by ultraviolet photoelectron spectroscopy in order to evaluate the technique and to establish the effects of changes in molecular weight and sample thickness, also γ-irradiation and copolymerization on the degradation reaction. The rate of decomposition and the concentration–time profile for the evolution of monomer from homopolymers was that predicted for a first order reaction, and depended on sample weight and area. Copolymers and γ-ray irradiated samples showed some differences in products and rates.

INTRODUCTION

The main object of this study was to evaluate ultraviolet photoelectron spectroscopy (u.p.s.) as a tool for investigating the thermal degradation of a polymer to gaseous products. Polytetrafluoroethylene (PTFE) was chosen as the polymer, as much was known already about its thermal degradation, which proceeds by an overall first order process, with a mechanism that involves chain scission followed by rapid unzipping of the monomer unit from the radicals[1–3]. U.p.s. offered the possibility of conveniently examining the early stages of the degradation and so clarifying several points of technical interest, namely, the initial rate and products of the reaction and the effects thereon of changes in molecular weight, sample thickness, x-ray irradiation and copolymerization. Rate constants were also measured.

U.p.s. is a spectroscopic technique based on the ionization of electrons from molecular or atomic orbitals by the impact of monoenergetic photons[4–7]. The spectrum reflects the molecular orbitals energy levels of the sample molecules and consequently provides unique identification of the sample. The technique is also suitable for continuous quantitative determination and identification of microgram amounts of components in a mixture of two or three gases with a lower limit of detection of the order of 0.1–1.0% depending on the degree of overlap of spectral bands. The capability of u.p.s. to detect small molecules like CO_2, H_2O, N_2 and O_2 and molecules which react readily with g.l.c. column packing makes the technique a useful complement to mass spectrometry and g.l.c.

EXPERIMENTAL

PTFE samples

These were provided by the Research Department of ICI Plastics Division, (Mr L. S. J. Shipp) and taken largely from the commercial range of 'Fluon' polymers. They can be divided into three groups; homopolymers, copolymers and γ-ray irradiated polymers, (*Table* 1). The homopolymers can be differentiated from each other by their number average molecular weight ($\bar{M}_n$) as determined by the standard specific gravity method[8]. The copolymers contained a small percentage of either hexafluoro propylene (HFP) or perfluoro propyl perfluoro vinyl ether (PPVE).

The samples were powders with the exception of one homopolymer which was also in the form of skived tapes and sintered mouldings. Sample amounts 20–500 mg were decomposed at temperatures 420–470°C. Below 420°C decomposition is negligible.

Table 1 Samples and the detected products of decomposition

Nature of sample	Sample	Number average molecular weight $\bar{M}_n \times 10^{-6}$	Products of decomposition as detected by PES
Homopolymer	1	73.0790	TFE
	2	48.9390	TFE
	3	19.6383	TFE
	4	9.6108	TFE
	5	6.9237	TFE
	6	0.9237	TFE, H_2O[a]
	7	–	TFE
	8	–	TFE
0.1% HFP–Copolymer	9		TFE
0.11% HFP–Copolymer	10		TFE, Depositions
0.115% HFP–Copolymer	11		TFE
0.24% HFP–Copolymer	12		TFE
0.25% HFP–Copolymer	13		TFE
10% HFP–Copolymer	14		TFE, HFP
1.1% PPVE–Copolymer	15		TFE
3.0% PPVE–Copolymer	16		TFE, Deposition
10 Mrad γ-ray irradiated	17		TFE
5 Mrad γ-ray irradiated	18		TFE, H_2O, CO_2
1 Mrad γ-ray irradiated	19		TFE

[a] The water was recorded in the first few minutes of the run

0032-3861/80/111309-08$02.00

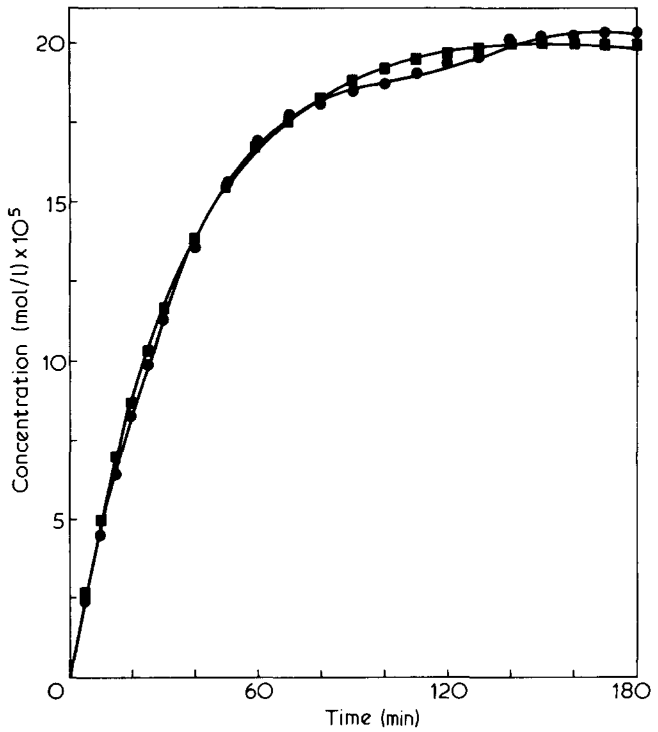

Figure 1 Experimental and theoretical plots of monomer concentration versus time; ●, experimental, ■, theoretical

Instrumentation and experimental procedure

Apparatus: The photoelectron spectrometer constructed was connected to a standard degradation vessel via a stainless steel needle tube and a micrometer valve as described earlier[9–11]. When a new reaction vessel was used, CO_2 and H_2O were detected and shown to originate from the reaction between the polymer and the quartz[9], in accord with the findings of Madorsky and others[12]. After a few runs the reaction vessel becomes seasoned and no longer brings about the generation of those gases. The spectra were recorded in a Data Lab DL450 microcomputer.

Analysis of products: A small amount of the product was allowed to leak continuously into the spectrometer. This served for both qualitative and quantitative analysis. The monomer, tetrafluoroethylene (TFE) was detected as the major product of the decomposition. In some samples HFP, CO_2 or H_2O were detected. Quantitative measurements were made by monitoring the area under a selected spectral band for each product. These measurements were complemented by monitoring the pressure of the reaction products.

Kinetic measurements: For quantitative analysis, the pump-out rate (rate of leakage of monomer into the spectrometer) was determined at various temperatures. It was found to be first order and independent of temperature. The model used to fit the experimental results was two consecutive first order processes.

$$A \xrightarrow{k} B \xrightarrow{k_p} C \qquad (1)$$

in which A is the polymer, B the monomer, k the reaction rate constant for the decomposition of the polymer and k_p the spectrometer's pump-out rate constant. The mathematical model that would give the concentration (C) of the monomer at any time, t, is[13]:

$$C = \frac{C\infty k}{k_p - k}(e^{-kt} - e^{-k_p t}) \qquad (2)$$

in which $C\infty = \dfrac{\text{weight of sample}}{\text{molecular weight of monomer}} \times \dfrac{1}{\text{volume of system}}$ for a decomposition that yields 100% monomers.

The experimental results were fitted to a polynomial by the method of least-squares. Evaluation of the reaction rate constant was carried out by a computer program that minimized the differences between the experimental function and the theoretical function 2 starting with an approximate value of k. The initial rate was determined by measuring the slope of the tangent drawn at $t=0$ on the experimental profile. The pump-out rate constant was used to compute the point at which the rate of generation of monomer equals the rate of pump-out of monomer i.e. $C_{max}\, k_p$[14]. This computation enabled a check of the mass balance to be made.

In the cases in which the experimental profile is complicated by either the evolution of more than one product or the repolymerization of monomer the reaction rate constant was calculated from the relationship[14]:

$$\text{Initial rate} = k_i(C - C_i) \qquad (3)$$

in which k_i is the reaction rate constant, C is the concentration of monomer at $t=\infty$ and C_i is the monomer concentration in the initial stages of the run.

RESULTS AND DISCUSSION

In general for homopolymers the rate of decomposition and the concentration time profile for the evolution of TFE is that predicted for a first order reaction and is consistent with the mechansim proposed by other workers. The actual values for the rate of decomposition however depend upon the sample weight and thickness. Copolymers or samples which have been subjected to γ-ray irradiation do not always conform to this pattern. These copolymers may give off more than one decomposition product and in some cases TFE repolymerizes in the decomposition vessel. Consequently the discussion falls into two parts. The first considers samples in which TFE is the only significant decomposition product and the second considers those in which more than one product is given off.

Rate studies for samples that decompose to give the monomer only

In an attempt to define the kinetics of thermal decomposition of PTFE the reaction rate constant approach has been adopted and as a check, initial rate measurements were carried out. The former requires that the spectrometer's response be calibrated as described earlier[9].

Reaction rate constant: The reaction rate constant was determined as described in the section on 'instrumentation and experimental procedure'. *Figure* 1 shows the

Table 2 Reaction rate constant for homopolymers as calculated from expression 2

Form of sample	Sample	Initial weight (mg)	Temperature (°C)	Reaction rate constant, $k \times 103$
Powder	1	200.4	450	0.1390
Powder	1	492.9	450	0.8525
Powder	1	20.3	470	1.4300
Powder	1	50.1	470	1.1620
Powder	1	200.5	470	0.5140
Powder	1	504.8	470	0.38625
Sintered moulding	1	203.7	470	0.1285
Sintered moulding	1	508.0	470	0.0965
0.127 mm tape	1	33.7	470	1.4960
0.254 mm tape	1	92.7	470	0.6610
0.381 mm tape	1	107.0	470	0.5155
0.127 mm tape	1	126.8	470	0.8025
0.508 mm tape	1	142.6	470	0.4425
0.254 mm tape	1	292.6	470	0.4610
0.381 mm tape	1	368.2	470	0.3655
Powder	2	201.8	450	0.3600
Powder	3	200.9	450	0.4145
Powder	4	201.5	450	0.3610
Powder	5	202.8	450	0.4060
Powder	5	507.0	450	0.0450
Powder	5	504.0	470	0.1395
Powder	6	201.7	450	0.4225
Powder	6	503.4	450	0.1845
Powder	8	511.6	450	0.0480
Powder	8	498.4	470	0.1805

theoretical (given by expression 2) and the experimental profile. The results are summed up in *Tables* 2 and 3. The reaction rate constant decreases exponentially with increasing initial weight of sample as shown in *Figure* 2. The relationship between the rate constant k and initial weight (IW) of sample, for sample weights up to 200 mg was found to be

$$\ln k = -0.01145\, IW - 6.07 \qquad (4)$$

at 470°C when the initial weight is in mg and the units of k are min^{-1}. This is consistent with the rate of evolution of monomer from the thermal decomposition of PTFE being diffusion controlled. An additional logarithmic factor is the effect of temperature gradient which would be more pronounced in a bulky sample, resulting in the sample particles towards the centre of the whole mass decomposing at a progressively lower temperature than the sample particles in contact with the reaction vessel walls.

For a given initial weight of sample, the reaction rate constant increases with increasing temperature as expected.

Initial rate: The initial rate values determined are summed up in *Tables* 4 and 5. The initial rate for homopolymers approximately equal to the pump-out rate ($C_{max}k_p$) at the experimental levelling off concentration C_{max}. In the case of PPVE copolymers a low mass balance is shown by the fact that the initial rate is consistently higher than the pump-out rate at C_{max}. This low mass balance exhibited by PPVE copolymers points to the removal of the monomer by repolymerization or some other process.

Effects of sample thickness on the rate of decomposition of PTFE: Skived tapes, 5–20 thou in thickness, from a sintered block of sample 1, a homopolymer, were used.

The overall rates of weight loss were worked out from the initial and final weights of the samples. Normalized rates of weight loss (NRW) and normalized initial rates (NIR) were obtained by dividing the rates of weight loss and the initial rates respectively by sample weights.

It was observed that the reaction rate constant, NRW, and NIR decrease exponentially with increasing sample thickness as can be seen from *Figure* 3 (*a–c*). The decrease

Table 3 Reaction rate constant for powders of copolymers and γ-ray irradiated samples as calculated from expression 2

Nature of sample	Sample	Initial weight (mg)	Temperature (°C)	Reaction rate constant, $k \times 103$
0.1% HFP—Copolymer	9	506.2	450	0.1308
0.1% HFP—Copolymer	9	50.5	470	0.8945
0.115% HFP–Copolymer	11	504.0	450	0.1595
0.24% HFP–Copolymer	12	502.1	450	0.1740
0.25% HFP–Copolymer	13	480.8	450	0.1630
0.25% HFP–Copolymer	13	499.7	470	0.3095
10 Mrad γ-ray irradiated	17	200.7	450	0.1840
10 Mrad γ-ray irradiated	17	501.2	450	0.0705
10 Mrad γ-ray irradiated	17	494.5	470	0.1970
1 Mrad γ-ray irradiated	19	202.8	450	0.1985
1 Mrad γ-ray irradiated	19	504.1	450	0.0715
1 Mrad γ-ray irradiated	19	506.3	470	0.2235

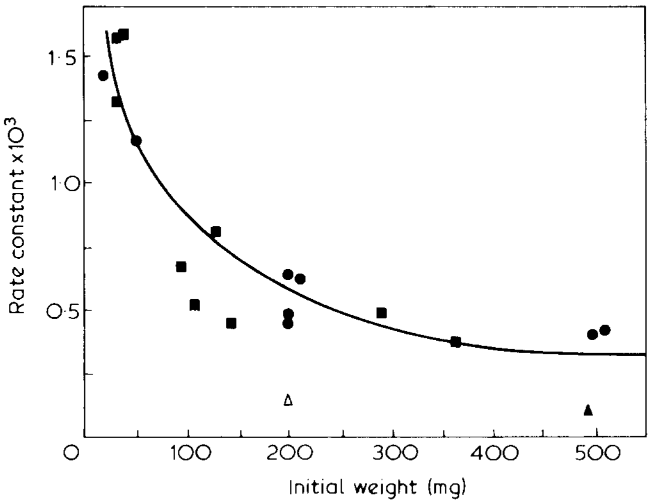

Figure 2 Plot of rate constant versus initial weight for sample 1 at 470°C; ●, powders, ■, tapes, ▲, sintered mouldings

Table 4 Comparison of the initial rate and rate of leakage of monomer into the spectrometer at the experimental levelling off concentration, C_{max} for homopolymers

Form of sample	Sample	Initial weight (mg)	Temperature (°C)	Initial rate (mol/l/min) x 10^5	$C_{max} k_p$	$\frac{C_{max} k_p{}^a}{\text{Initial Rate}}$
Powder	1	201.0	450	0.4949	0.2480	0.5010
Powder	1	500.8	450	0.3650	0.3266	0.8947
Powder	1	21.8	470	0.2209	0.2571	1.1641
Powder	1	50.1	470	0.2143	0.3280	1.5305
Powder	1	202.7	470	0.6430	0.6477	1.0073
Powder	1	504.8	470	1.3100	1.0124	0.7728
						$\bar{x}$ = 1.0406[b] σ = 0.3832
Sintered moulding	1	203.7	470	0.0900	0.18626	2.0695
Sintered moulding	1	508.0	470	0.1532	0.2257	1.4734
0.127 mm Tape	1	33.7	470	0.2317	0.2865	1.2365
0.254 mm Tape	1	92.7	470	0.2750	0.3725	1.3546
0.381 mm Tape	1	107.0	470	0.2525	0.3336	1.3212
0.127 mm Tape	1	126.8	470	0.9200	0.6033	0.6557
0.508 mm Tape	1	142.6	470	0.3040	0.3725	1.2254
0.254 mm Tape	1	292.6	470	1.3440	0.8118	0.6040
0.381 mm Tape	1	368.2	470	1.5875	0.7784	0.4903
						$\bar{x}$ = 1.0716 σ = 0.3837
Powder	2	201.8	450	0.4267	0.4392	1.0294
Powder	3	200.9	450	0.9467	0.4726	0.4992
Powder	4	201.5	450	0.4200	0.4309	1.0259
Powder	5	202.8	450	0.5789	0.5089	0.8788
Powder	5	505.5	450	0.3260	0.2702	0.8288
Powder	6	201.8	450	0.6833	0.4782	0.6998
Powder	6	503.4	450	0.7920	–	–
Powder	8	511.6	450	0.1082	0.1835	1.6942
Powder	8	498.4	470	0.4233	0.5754	1.3596
						$\bar{x}$ = 0.9955 σ = 0.3352

[a] $\frac{C_{max} k_p}{\text{Initial Rate}}$ shows mass balance. It is equal to one for an ideal case

[b] $\bar{x}$ and σ are respectively the mean and the standard deviation of the ratio $\left(\frac{C_{max} k_p}{\text{Initial Rate}}\right)$

in reaction rate constant and NRW can be attributed to the diffusion-controlled evolution of TFE and temperature gradient effects. The 4 cm^2 tapes have a generally higher NIR than the 1 cm^2 tapes. Thus, surface area contributes signifcantly to the initial rate of the decomposition of PTFE.

The low reaction rate constants observed for sintered mouldings may be due to a combination of diffusion-control and temperature gradient effects since the sintered mouldings were very thick compared with the skived tapes.

Molecular weight effects on the rate of decomposition of PTFE: Homopolymers, whose number average molecular weight, as determined by the standard specific gravity (ssg) method[8] ranged from 0.90×10^6 to 73.10×10^6 were used in this experiment. The results are summarized in *Table* 6.

Siegle and coworkers[2] observed no dependance of the reaction rate constant on molecular weight up to 40×10^6. We confirm this up to 49×10^6 but note a fall off at greater molecular weight (*Table* 6).

Rate studies for samples that decompose to give monomer and other products

Figure 4*a* shows representative experimental profiles of the decomposition of PPVE copolymers and the 0.11% HFP copolymer sample.

Figure 4*b* compares the experimental profile with the one expected from expression 2 by assuming a mechanism similar to that of homopolymers.

If the monomer were not being removed from the system the experimental and the expected profiles would be very close to each other. The difference is due to repolymerization of monomer which occurred in these samples as evidenced by a low mass balance, the shape of the experimental profile and fine particles deposited onto the cooler parts of the reaction vessel, which were identified by infra-red spectroscopy as a low molecular weight polymer of high crystallinity.

In the case of sample 15 the evolved monomer apparently repolymerized as evidenced by the low mass balance (*Figure* 4*b*) although no solid was deposited on the wall of the sample vessel. There was no change in the observed PE spectrum.

Table 5 Comparison of the initial rate and rate of leakage of monomer into the spectrometer at the experimental levelling off concentration, C_{max} for powders of copolymers and γ-ray irradiated polymers

Form of sample	Sample	Initial weight (mg)	Temperature (°C)	Initial rate (mol/l/min) x 10^5	$C_{max}\,k_p$ x 10^5	$\frac{C_{max}\,k_p}{\text{Initial Rate}}$ [a]
0.1% HFP–Copolymer	9	503.4	450	0.4528	0.4338	0.9582
0.1% HFP–Copolymer	9	50.5	470	0.3330	0.2571	0.7715
0.1% HFP–Copolymer	9	202.3	470	0.6709	0.5240	0.7810
0.11% HFP–Copolymer	10	501.8	450	0.7217	0.5560	0.7703
0.11% HFP–Copolymer	10	503.3	470	1.9857	1.0904	0.5490
0.115% HFP–Copolymer	11	504.0	450	0.6720	0.4967	0.7391
0.24% HFP–Copolymer	12	502.1	450	0.7520	0.5045	0.6709
0.25% HFP–Copolymer	13	480.8	450	0.6360	0.4781	0.7618
0.25% HFP–Copolymer	13	499.7	470	1.9667	0.9285	0.4721
						$\bar{x}$ = 0.7687[b] σ = 0.1719
1.1% PPVE–Copolymer	15	202.8	420	0.3143	0.1182	0.3759
1.1% PPVE–Copolymer	15	509.6	420	1.0095	0.2335	0.2313
1.1% PPVE–Copolymer	15	514.8	450	1.1320	0.4851	0.4285
1.1% PPVE–Copolymer	15	49.9	470	0.5467	0.2655	0.4856
1.1% PPVE–Copolymer	15	508.8	470	1.9600	0.9118	0.4652
3.0% PPVE–Copolymer	16	201.0	420	0.4250	0.1390	0.3270
3.0% PPVE–Copolymer	16	501.8	420	1.000	0.2224	0.2224
3.0% PPVE–Copolymer	16	506.4	450	1.750	0.1932	0.1104
						$\bar{x}$ = 0.3445 σ = 0.1246
10 Mrad γ-ray irradiated	17	501.2	450	0.3137	0.2126	0.6779
10 Mrad γ-ray irradiated	17	200.7	450	0.4100	0.2224	0.5424
10 Mrad γ-ray irradiated	17	494.5	470	1.0720	0.5838	0.5446
1 Mrad γ-ray irradiated	19	202.8	450	0.3120	0.2460	0.7885
1 Mrad γ-ray irradiated	19	511.7	470	0.8286	0.6449	0.7783
						$\bar{x}$ = 0.6663 σ = 0.1075

[a] $\frac{C_{max}\,k_p}{\text{Initial Rate}}$ shows mass balance. It is equal to one for an ideal case

[b] $\bar{x}$ and σ are respectively the mean and the standard deviation of the ratio $\frac{C_{max}\,k_p}{\text{Initial Rate}}$

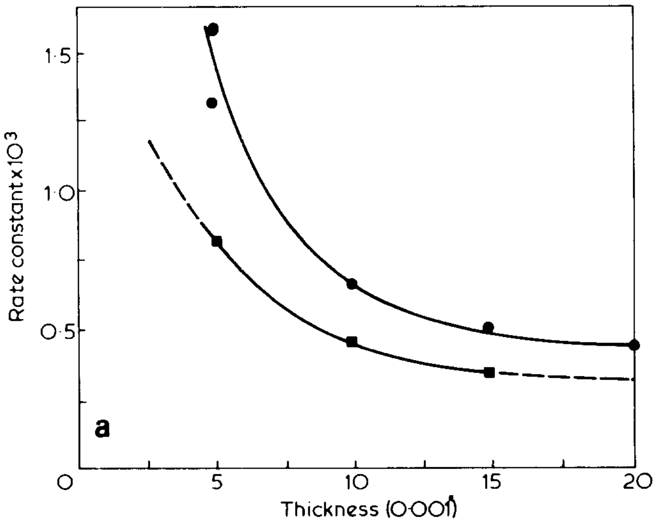

Figure 3a Plot of reaction rate constant versus sample thickness; ●, 1 cm^2 sample, ■, 4 cm^2 sample

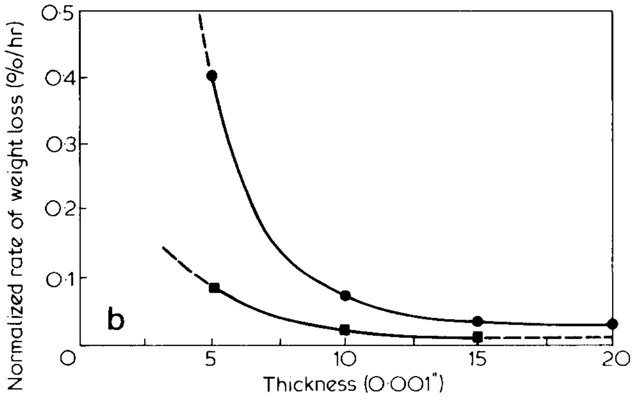

Figure 3b Plot of normalized rate of weight loss versus sample thickness; ●, 1 cm^2 sample, ■, 4 cm^2 sample

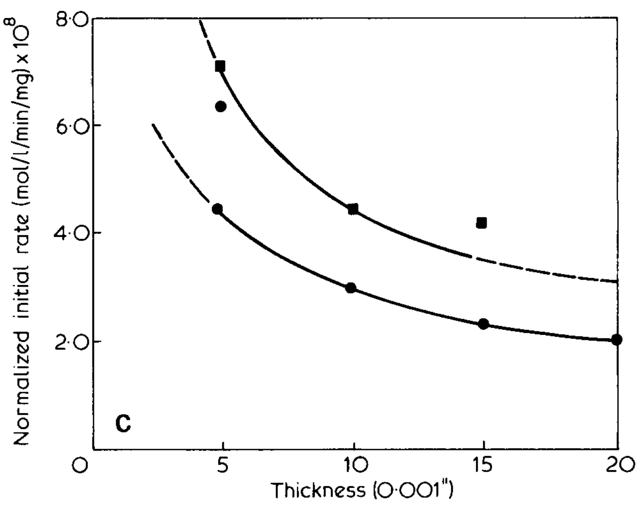

Figure 3c Plot of normalized initial rate versus sample thickness; ●, 1 cm^2 sample, ■, 4 cm^2 sample

Table 6 Molecular weight effects on the rate of decomposition of PTFE homopolymers, T = 450°C, initial weight = 200 mg

Sample	Number average molecular weight $\bar{M}_n \times 10^{-6}$	Initial rate $\times 10^5$	Reaction rate constant $k \times 10^3$
1	73.0790	0.4253	0.1550
1	73.0790	0.3875	0.1230
2	48.9390	0.4267	0.3600
3	19.6383	0.9467	0.4145
4	9.6108	0.4200	0.3615
5	6.9956	0.5789	0.4060
6	0.9237	0.6833	0.4225

Table 7 shows the reaction rate constants calculated from expression 3 for one HFP copolymer and the PPVE copolymers. *Table* 8 presents approximate data on rate constants and normalized initial rates (NIR) for homopolymer, copolymers and irradiated homopolymers, all as powders, so that comparisons under comparable conditions of temperature and sample weight can be made.

Generally, rate constants and NIR's of copolymers are higher than those of homopolymers, probably as a consequence of weak links introduced into the main chain and reduction of the shielding effects of the highly electronegative fluorine atoms.

Surprisingly, γ-irradiation proved to have little effect on rate constant and NIR.

The experimental profile of the 5Mrad γ-ray irradiated polymer that decomposed to give TFE, H_2O and CO_2 was presented earlier[9]. The photoelectron spectrum of the products is shown in *Figure* 5.

Figures 6*a* and 6*b* show the spectra recorded at 2 and 110 min of the run respectively for the 10% HFP copolymer that decomposed to give HFP and TFE. HFP is the major reaction product at the beginning of the run and TFE at the end.

CONCLUSIONS

The value of u.p.s. for the identification of major decomposition products and its ability to monitor these quantitatively was confirmed. The principal limitation of the

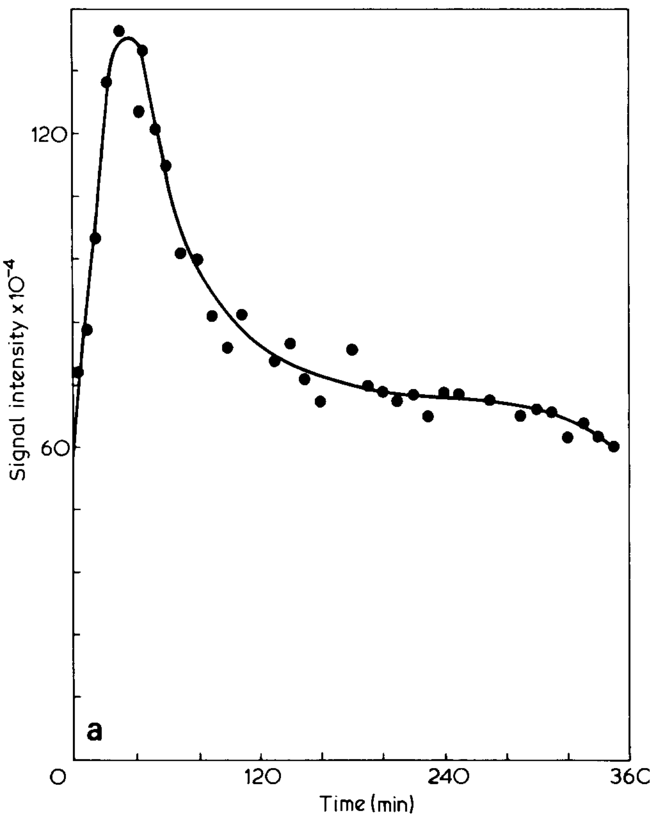

Figure 4a Experimental profile characteristic of PPVE copolymers

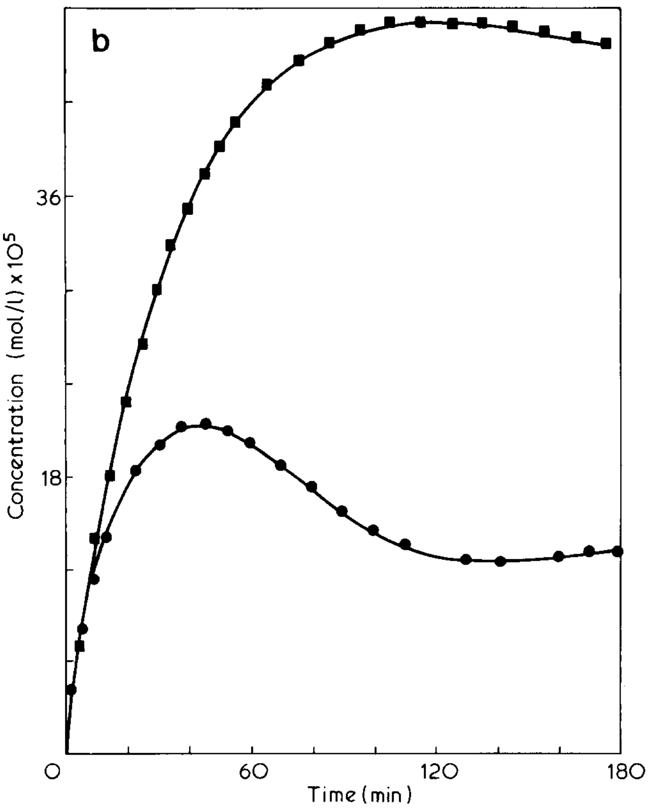

Figure 4b Experimental and theoretical (expected) profile for sample 15: ●, experimental, ■, expected

Table 7 Reaction rate constant calculated from expression III

Sample	Temperature (°C)	Initial weight (mg)	Reaction rate constant $k_i \times 10^3$
10	450	508.1	0.2161
10	470	503.8	0.4698
15	420	202.8	0.2327
15	420	509.6	0.2974
15	450	514.8	0.3330
15	470	49.9	1.6571
15	470	201.2	1.0018
15	470	508.8	0.5804
16	420	201.0	0.3173
16	420	501.8	0.299
16	450	502.6	0.5538

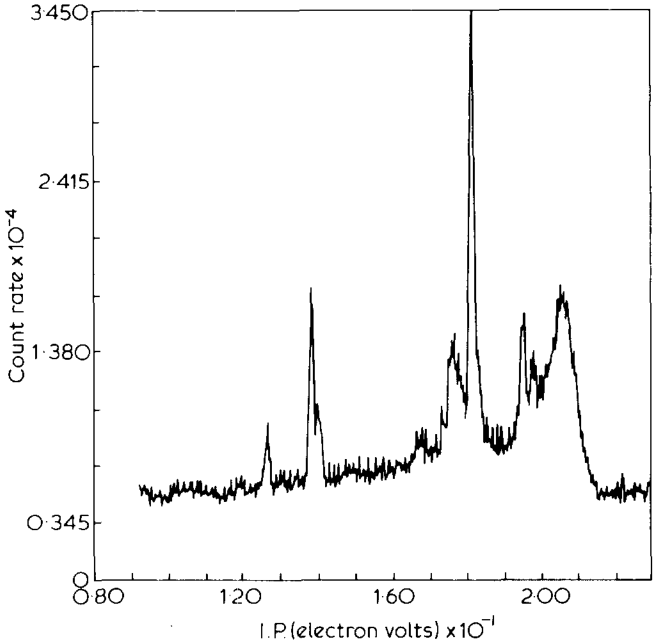

Figure 5 Photoelectron spectrum of TFE, H_2O and CO_2 recorded from the 5 Mrad γ-ray irradiated polymer

technique is its inability to detect minor products, and in this connection we note the failure to detect gaseous dimer or trimer in systems where their presence was indicated by a low mass balance and lack of deposition (sample 15). However water and carbon dioxide were easily monitored.

The decomposition of homopolymers generally follows a first order reaction from the earliest stages of decomposition. Apparently initial rates and/or rate constants are affected by surface area and sample thickness and to some extent, by molecular weight.

When the samples have been γ-ray irradiated or copolymerized, a more complex mechanism of decomposition is observed. Generally, the initial rate is greater than for homopolymers. Water and carbon dioxide may be additional decomposition products. With PPVE copolymers there is evidence of repolymerization of monomer.

ACKNOWLEDGEMENTS

We are grateful to the International University Exchange Fund for a studentship (NRS), to the ARC and SRC for

Table 8 Mean rate constants and normalized initial rates for the various types of powder sample

		Rate constants x 10^3							Normalized initial rates mol/l/min/mg x 10^8						
			Co–HFP		Co–PPVE		γ-Irrad			Co–HFP		Co–PPVE		γ-Irrad	
Temp. (°C)	Approx. weight (mg)	Homo–TFE	ca 0.1%	ca 0.25%	1.1%	3.0%	1 Mrad	10 Mrad	Homo–TFE	ca 0.1%	0.25%	1.1%	3.0%	Mrad	Mrad
420	200				0.23	0.32						1.5	2.1		
	500				0.30	0.30						2.0	2.0		
450	200	(0.35)	(0.21)				0.20	0.18	2.9					1.5	2.0
	500	0.09	0.15	0.17	0.33	0.55	0.07	0.07	0.79	1.2	2.2	2.2	3.5		0.6
470	50	1.33	0.89		1.7				4.3	6.6		11.0			
	200	0.51			1.0				3.2	3.3					
	500	0.24	(0.47)	0.31	0.58		0.22	0.20	1.7	3.9	3.9	3.9		1.6	2.2

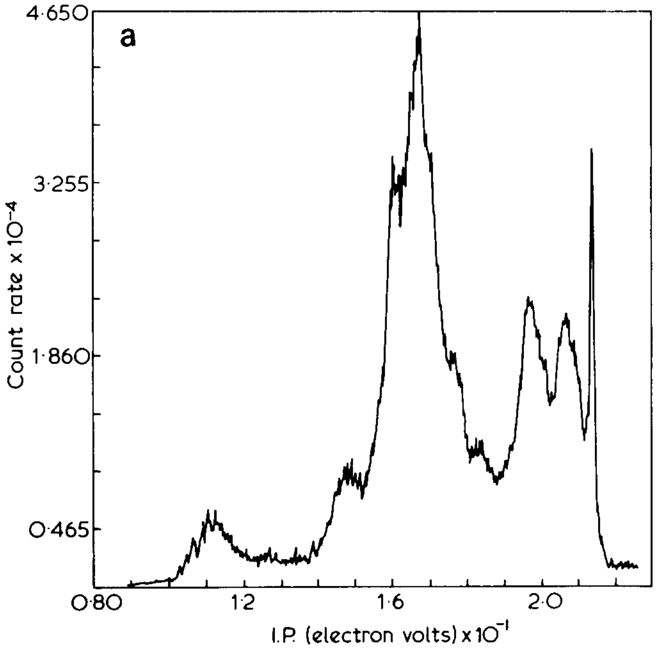

Figure 6a Photoelectron spectrum of HFP recorded after 2 min of the run from the 10% HFP copolymer

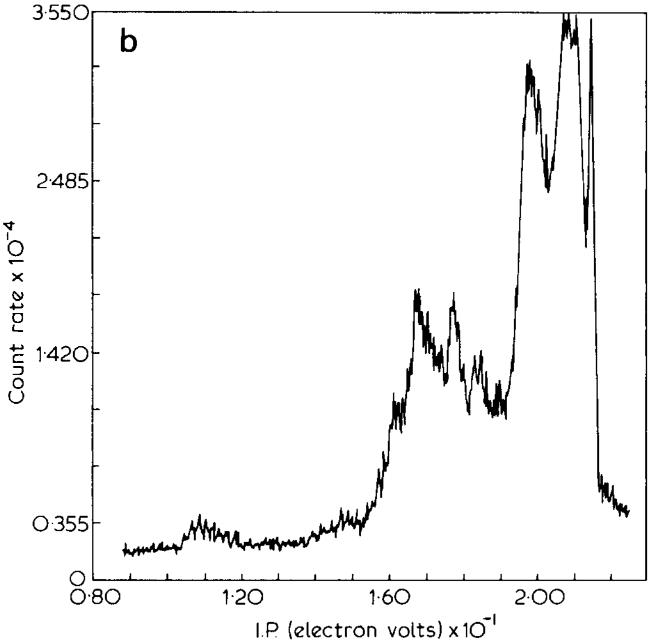

Figure 6b Photoelectron spectrum of HFP and TFE recorded after 110 min of the run from the 10% HFP copolymer

instrumental support, to Dr G Stedman of the Department of Chemistry, University College of Swansea for most helpful discussions of the kinetic data, and to Mr L. S. J. Shipp for the supply of samples.

REFERENCES

1 Reich, L. *J. Appl. Poly. Sci.* 1967, **11**, 699

2 Siegle, J. C., Muus, L. T., Lin, T. P. and Larsen, H. A. *J. Poly. Sci.* 1964, **A-2**, 391

3 Madowsky, S. L. and Straus, S. *J. Nat. Bur. Stand.* 1954, **53**, 361

4 Turner, D. W., Baker, C., Baker, A. D. and Brundle, C. R. 'Molecular Photoelectron Spectroscopy', Wiley, 1970

5 Baker, A. D. and Betteridge, D. 'Photoelectron Spectroscopy, Chemical and Analytical Aspects', Pergamon, 1972

6 Eland, J. H. D. 'Photoelectron Spectroscopy, and Introduction to Photoelectron Spectroscopy in the Gas Phase', Butterworths, 1974

7 Rabalais, J. W. 'Principles of Photoelectron Spectoscopy', Wiley, 1977

8 Sherratt, S. in 'Encyclopaedia of Technology', (Eds. R. E. Kirk and D. F. Othmer) 1966, **9**, 2nd ed., 805

9 Betteridge, D., Joyner, D. J., Greening, F., Shoko, N. R., Cudby, M. E. A., Willis, H. A., Attwood, T. E. and Henriksen, L. *Physica Scripta*, 1977, **16**, 339

10 Betteridge, D., Baker, A. D., Bye, P., Hasanuddin, S. K., Kemp, N. R. and Thomson, M. *J. Electron Spectroscopy Related Phenomena*, 1974, **4**, 163

11 Bye, P. and Betteridge, D. *ibid*, 1975, **7**, 355

12 Madowsky, S. L. 'Thermal Degradation of Organic Polymers', Wiley, 1964, p. 135

13 Eggers, D. E. 'Physical Chemistry' Wiley, 1964, p. 465

14 Stedman, G. Private communications