

Thermal Degradation of Fluorine-Containing Polymers. Part I. Degradation in Vacuum

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Synopsis

The thermal degradation in vacuum of a number of fluorine-containing polymers has been studied by using a weight loss technique. The relative thermal stabilities of the different polymers have been determined and where possible the overall activation energy and frequency factors for their breakdown. The methods of assessment of the weight loss results are discussed. The most stable of the polymers are those which are fully fluorinated.

INTRODUCTION

The exceptionally high thermal stability of polytetrafluoroethylene has been known for some twenty-five years and has prompted a search for other useful thermally stable materials among the fluorine containing polymers. That this search, at least in respect of useful materials, has been successful is evidenced by the fact that about a dozen such polymers and copolymers have been produced commercially. The thermal stabilities in vacuum of many of these, and also of a number of experimental polymers, have been assessed using a weight loss technique. Preliminary results on some of these polymers have previously been reported.¹

EXPERIMENTAL

Materials

All polymer samples were heated to constant weight at 100°C. in vacuum (10^{-4} to 10^{-5} mm. Hg) before use in thermal stability determinations.

Polytetrafluoroethylene was Fluon, supplied by Imperial Chemical Industries Ltd. Polyvinylidene fluoride was prepared by the Imperial Smelting Corporation under the conditions cited by Hamilton.²

Polychlorotrifluoroethylene was available in three forms: (a) prepared as for polyvinylidene fluoride, (b) prepared by the method of Elliott et al.,³ and (c) prepared by γ -irradiation of the monomer. Poly-1-chloro-1,2-difluoroethylene was obtained by photopolymerization with azobisisobutyronitrile as initiator. Tetrafluoroethylene/hexafluoropropylene copolymer was Teflon 100X (supplied by du Pont).

Vinylidene fluoride/hexafluoropropylene copolymers were Viton A and A-HV (70% CF_2CH_2 , 30% C_3F_6) and LD-234 (60% CF_2CH_2 , 40% C_3F_6) supplied by du Pont. Chlorotrifluoroethylene/vinylidene fluoride copolymers used were Kel-F 800 (81% $\text{CF}_2\text{CF Cl}$, 19% CF_2CH_2), Kel-F 5500 (47% $\text{CF}_2\text{CF Cl}$, 53% CF_2CH_2), and Kel-F3700 (33% $\text{CF}_2\text{CF Cl}$, 67% CF_2CH_2) supplied by M. W. Kellogg Co.

Tetrafluoroethylene/trifluoronitrosomethane (1:1) copolymer and trifluoroethylene/trifluoronitrosomethane (1:1) copolymer were prepared by Prof. Haszeldine⁴ of the Manchester College of Science and Technology. Copolymers of octafluorocyclohexa-1,3-diene with butadiene, 1,1,2-trifluorobutadiene, chloroprene, ethylene, methyl methacrylate and vinyl-*n*-butyl ether were prepared by the Imperial Smelting Corp.⁵ (Some samples were also supplied by Prof. Musgrave of Durham University; these were prepared by γ -irradiation.)

Polyhexafluoropentylene adipate and polyhexafluoropentylene adipate/isophthalate (which contains 25 mole-% isophthalate) were supplied by the Hooker Electrochemical Co. Polyoctafluorohexylene fumarate and polyoctafluorohexylene terephthalate were prepared by condensation of the acid chloride and octafluorohexane-1,6-diol by Dr. J. Burden of Birmingham University.

Fluorinated silicone polymer was supplied by Dow Corning Corporation (two samples A and B; both containing 30.7% C, 4.5% H, 36.1% F, 18.4% Si).

Apparatus and Experimental Procedure

These have been fully described previously.¹

RESULTS AND DISCUSSION

Form of Weight Loss Curves

Except for the condensation polymers obtained with octafluorohexane-1,6-diol and terephthalyl or fumaryl chloride, and the copolymer of octafluorocyclohexa-1,3-diene with butadiene, all the samples examined decomposed completely to volatiles at the highest temperatures used. The exceptions yielded residues which were stable at the temperature of pyrolysis, the effect being more marked in the polymers containing the butadiene and vinylene groupings, i.e., those already containing unsaturation in the chain.

The course of the breakdown to volatiles varied considerably. Wall et al. have pointed out in several papers⁶⁻⁸ that a plot of the rate of breakdown against conversion yields information on certain aspects of the degradation mechanism. If transfer is ignored then, regardless of the method of initiation (end or random), a large "zip" length yields a rate which decreases linearly with per cent conversion. With a small "zip" length end initiation gives a rate which remains constant with conversion, whereas with random initiation there is a maximum in the rate curve. The effect of

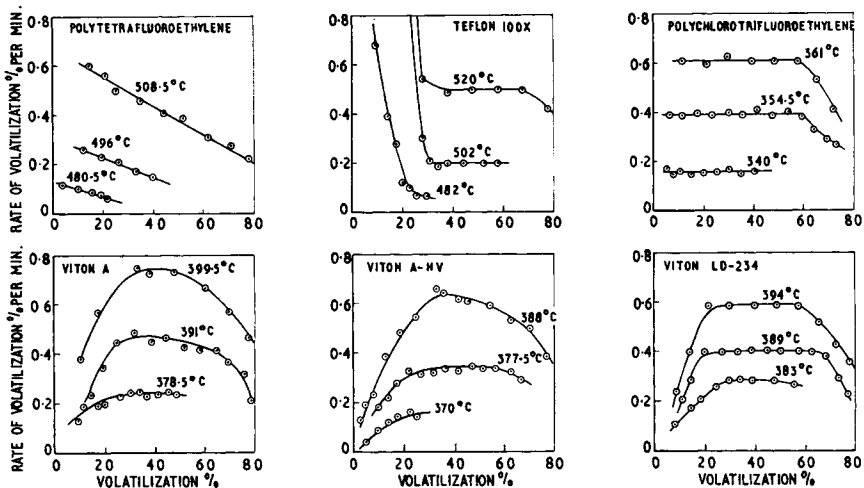


Fig. 1. Rate of volatilization versus per cent volatilized for fluorine-containing polymers.

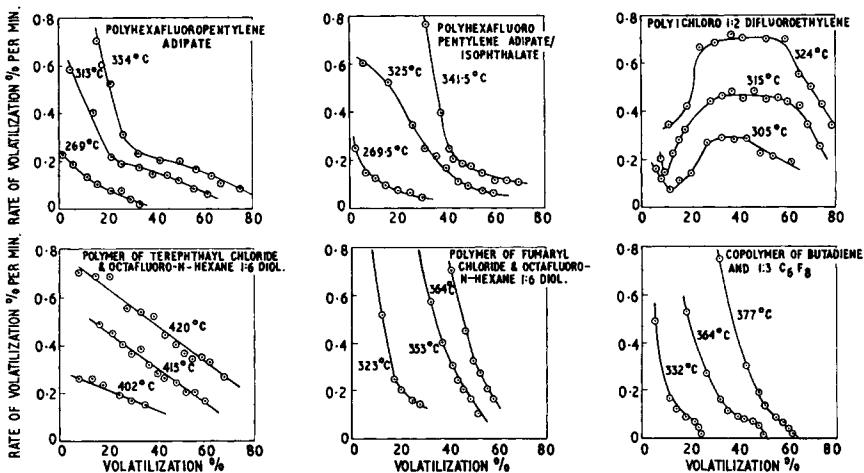


Fig. 2. Rate of volatilization vs. per cent volatilized for fluorine-containing polymers.

transfer is towards maximum type curves. Wall has also shown⁹ that the effect of branching in paraffinic hydrocarbons is to eliminate the maxima obtained with linear polymers provided the branches contain two or more carbon atoms.

Plots of rate of volatilization against conversion are given in Figures 1-4 for all the polymers reported on here. For the sake of clarity the results for three temperatures only are included on the graphs, though normally experiments were done at a minimum of five different temperatures. As predicted by Wall, two main types of curve were obtained, those in which the rate decreased throughout with per cent conversion (linearity was the exception rather than the rule) and those for which a maximum rate was observed. Division of the polymers examined into the two types was as shown in Table I.

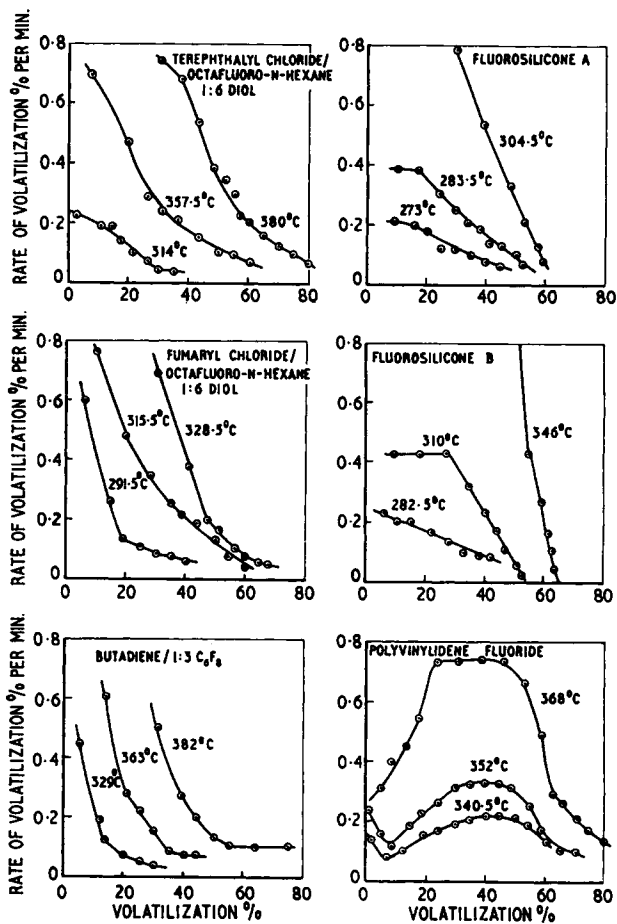


Fig. 3. Rate of volatilization vs. per cent volatilized for fluorine-containing polymers.

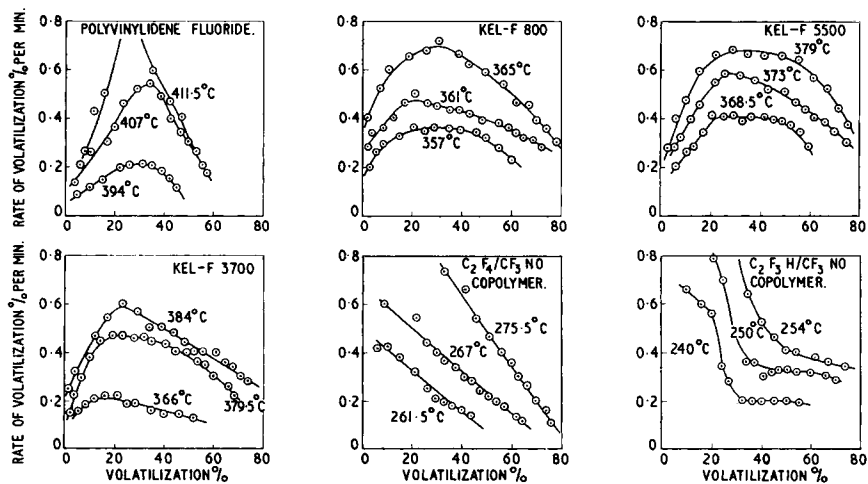


Fig. 4. Rate of volatilization vs. per cent volatilized for fluorine-containing polymers.

TABLE I
Type of Volatilization Rate Curves

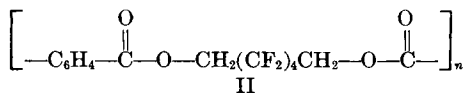
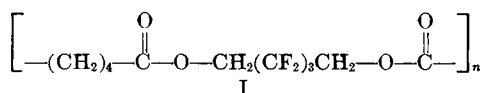
Rate falling with conversion	Maximum type curve
Polytetrafluoroethylene	Copolymers of vinylidene fluoride and hexafluoropropylene
Copolymer of tetrafluoroethylene and hexafluoropropylene	Poly-1-chloro-1,2-difluoroethylene
Polyhexafluoropentylene adipate	Polyvinylidene fluoride
Polyhexafluoropentylene adipate/ isophthalate	Copolymers of vinylidene fluoride and chlorotrifluoroethylene
Copolymers of octafluoro- <i>n</i> -hexane-1,6-diol with terephthalyl or fumaryl chloride	
Copolymers of perfluorocyclohexa-1,3-diene with butadiene, styrene, methyl methacrylate	
Fluorosilicone A	
Copolymers of trifluoronitrosomethane with tetrafluoroethylene or trifluoroethylene	

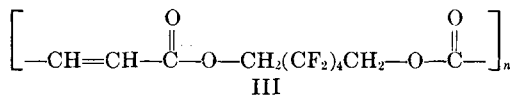
Polychlorotrifluoroethylene (all three samples examined) and fluorosilicone B were exceptions, giving a constant rate of volatilization, i.e., an apparent zero-order reaction, up to conversions of the order of sixty %.

Of those polymers with a falling rate, a linear relationship with per cent volatilization (i.e., an apparent first-order reaction) was observed for polytetrafluoroethylene, the copolymer of octafluoro-*n*-hexane-1,6-diol and terephthalyl chloride, fluorosilicone A, and the copolymer of trifluoronitrosomethane and tetrafluoroethylene. The shape of the other falling rate-volatilization curves indicated a rather more complex breakdown mechanism.

As mentioned earlier this type of curve indicates that regardless of the point of initiation there should be a subsequent large "zip" length. That this is so with polytetrafluoroethylene and the copolymer of tetrafluoroethylene and hexafluoropropylene is evidenced by the monomeric character of the breakdown products.^{10,11} The initial rapid rate of volatilization of the copolymer suggests a lower stability of the chain due to the introduction of the hexafluoropropylene units. The copolymer of tetrafluoroethylene and trifluoronitrosomethane could also "unzip" to give its breakdown products perfluoromethylenemethylamine and carbonyl fluoride.⁴

Polyhexafluoropentylene adipate (I) and the copolymers of terephthalyl chloride (II) and fumaryl chloride (III) with octafluoro-*n*-hexane-1,6-diol are structurally analogous, and hence their behavior would be expected to be similar:





Polyhexafluoropentylene adipate on pyrolysis yielded only a small fraction of material volatile at room temperature¹¹ and of complex composition. One would intuitively expect that these polymers would only have a small "zip" length and hence should show a maximum in the rate curve. Wall and Straus¹¹ suggest that in the case of hexafluoropentylene adipate a hydrolytic decomposition may also come into play, which could be catalyzed by hydrogen fluoride eliminated from the chain. No hydrogen fluoride or silicon tetrafluoride (formed by the attack of the former on glass) were detected in the reaction products however.

The homopolymers of butadiene, methyl methacrylate, and styrene (the monomers copolymerized with perfluorocyclohexa-1,3-diene) on pyrolysis gave falling rate,¹² falling rate,¹³ and maximum rate¹⁴ curves, respectively. Since the 1,3-diene is the minor component in all the copolymers, the over-all behavior might be expected to be governed by that of the comonomer. A further complicating factor is that from all these copolymers elimination of hydrogen fluoride is feasible. In the case of the copolymer with

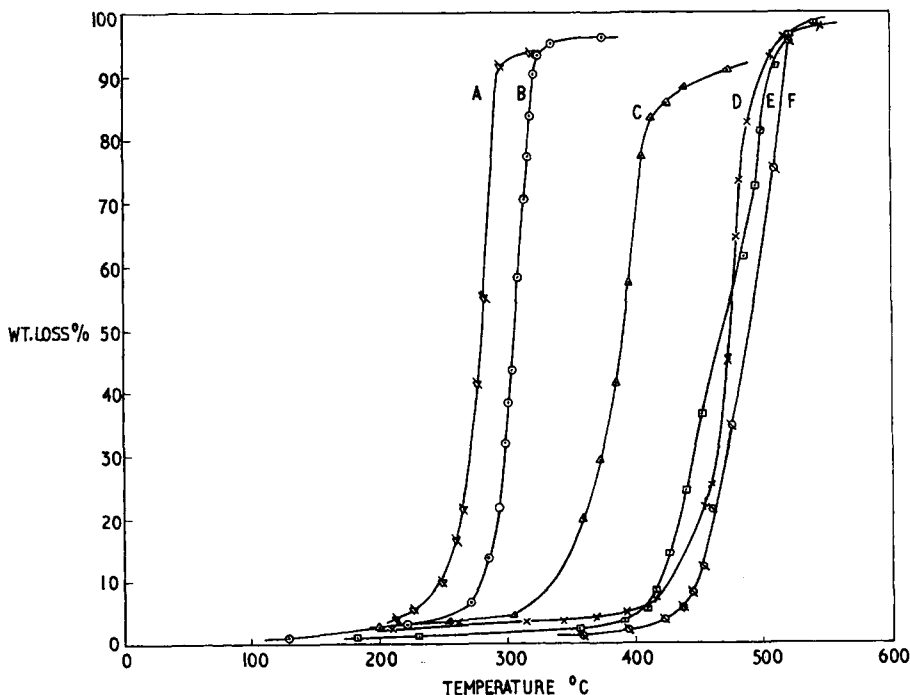


Fig. 5. Effect of presence of base on the stability of a fluorosilicone: (A) fluorosilicone B + 0.75% KOH; (B) fluorosilicone A; (C) fluorosilicone A + 5% Al_2O_3 ; (D) fluorosilicone A neutralized with dilute HCl and then washed and dried; (E) fluorosilicone A washed and dried; (F) fluorosilicone B.

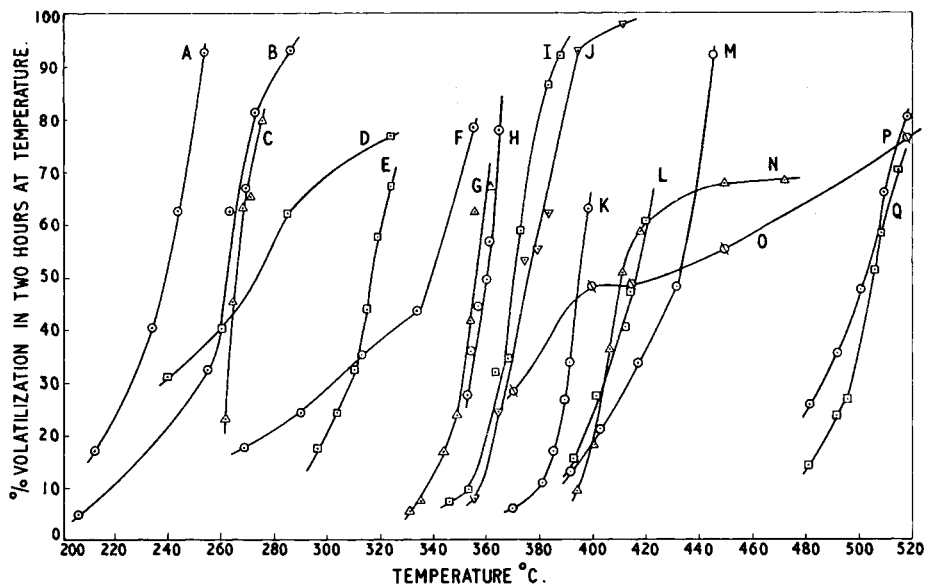


Fig. 6. Comparison of thermal stabilities of fluorine-containing polymers: (A) $\text{CF}_3\text{NO}/\text{CF}_2\text{CFH}$ copolymer; (B) $\text{CF}_3\text{NO}/\text{CF}_2\text{CF}_2$ copolymer; (C) fluorosilicone A; (D) methyl methacrylate/ C_6F_8 copolymer, γ -irradiated; (E) $[\text{CHF}(\text{CFCl})_n]$; (F) polyhexafluoropentylene adipate; (G) $[\text{CF}_2\text{CFCl}]_n$; (H) Kel-F 800; (I) Kel-F 5500; (J) Kel-F 3700; (K) Viton A; (L) terephthalyl chloride/octafluorohexane-1,6-diol polymer; (M) fluorosilicone B; (N) $[\text{CF}_2\text{CH}_2]_n$; (O) butadiene/ C_6F_8 copolymer, γ -irradiated; (P) Teflon 100X; (Q) $[\text{CF}_2\text{CF}_2]_n$.

butadiene this would lead to a fairly highly conjugated chain and accounts for the stabilization effect observed.

With the fluorosilicone an effect akin to depolymerization is possible, and this would explain the falling rate curve for sample A. The great difference in the thermal stability of two nominally identical samples, however, and the change from apparent zero to first order reaction points to trace impurities having considerable influence on this type of compound. This has been observed for dimethylpolysiloxane oils,^{15,16} though in that case maxima in the rate curves were obtained. A recent paper¹⁷ suggests that residual basic catalyst in polydimethylsiloxane causes degradation to occur by an ionic mechanism, this taking place at a temperature at least 100°C . below that for free radical breakdown. Neutralization of the residual catalyst led to a considerable increase in stability. Accordingly, samples of fluorosilicone A were dissolved in isobutyl methyl ketone and washed with either water or 0.01N hydrochloric acid solution followed by water, and the polymer precipitated with methanol and dried. Another sample was milled with 5 wt.-% of alumina and the relative thermal stabilities determined by thermogravimetric analysis with a heating rate of $3^\circ\text{C}/\text{min}$. The results are shown in Figure 5. The samples which had been washed with hydrochloric acid solution and water, or water alone, had comparable stabilities, which were very close to that of fluorosilicone B. The incorporation of

alumina also resulted in an increase in stability, but it was by no means as marked. Addition of 0.75% of potassium hydroxide to fluorosilicone B reduced its stability to below that of sample A, indicating that the poor stability of the latter was due to residual basic catalyst.

All those polymers giving maximum type curves contained vinylidene fluoride or were structurally similar, permitting the elimination of hydrogen fluoride from the polymer followed by breakage of the chain adjacent to the double bond so formed. Wall and Straus have reported¹¹ similar rate-volatilization curves for a number of these polymers.

Relative Thermal Stabilities

The relative thermal stabilities of the different polymers have been compared by plotting the loss in weight after an arbitrary time (2 hr.) at temperature against temperature. The loss in weight (except where stabilization occurred within 2 hr. from the start of the experiment) has been expressed as a percentage of the polymer present when constant temperature was attained. This choice of zero time allows for any variation in the time taken to attain constant temperature and for the fact that more material is lost during this heating-up period the higher the temperature used. Results are shown in Figure 6. Easily the most stable polymers were the fully fluorinated polytetrafluoroethylene and the copolymer of tetrafluoroethylene and hexafluoropropylene. Substitution of one of the fluorine atoms in polytetrafluoroethylene by chlorine dropped the stability by about 150°C., while substitution with a chlorine and a hydrogen atom caused a drop of a further 40°C. Some features of the results, which would not

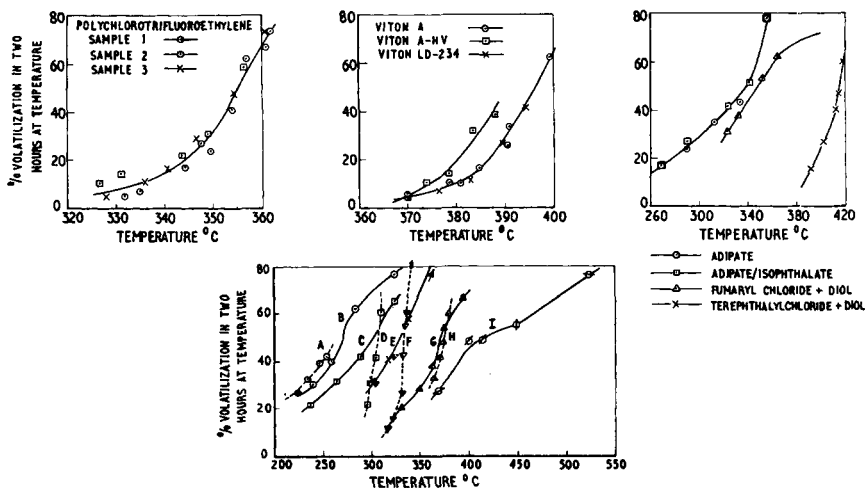


Fig. 7. Comparison of sets of polymers of related structure: (A) polymethyl methacrylate, M.W. 150,000; (B) methyl methacrylate/ C_6F_8 copolymer, γ -irradiated; (C) methyl methacrylate/ C_6F_8 copolymer; (D) polymethyl methacrylate, M.W. 5×10^6 ; (E) styrene/ C_6F_8 copolymer, γ -irradiated; (F) polystyrene, M.W. 230,000; (G) polybutadiene/ C_6F_8 copolymer; (H) polybutadiene; (I) butadiene/ C_6F_8 copolymer, γ -irradiated.

have been apparent by inclusion in Figure 6, are given in Figure 7. From this it is evident that there was little difference in the stability of three samples of polychlorotrifluoroethylene prepared by different methods, except perhaps at the lowest temperatures used.

Variation of the composition of the vinylidene fluoride-hexafluoropropylene (VF/HFP) copolymers within narrow limits did not appear to alter the stability. This is in contrast with the vinylidene fluoride-chlorotrifluoroethylene copolymers examined, which covered a much wider range of composition. The higher molecular weight VF/HFP copolymer appeared to be slightly less stable at the higher temperatures used, than the lower molecular weight material.

Incorporation of 25 mole-% of isophthalate in the hexafluoro-adipate polymer (i.e., replacement of approximately 50% of the tetramethylene grouping by the phenylene group) did not affect the thermal stability. Substitution of the vinylene grouping for the tetramethylene also had relatively little effect, except at the highest temperatures used, where stabilization was occurring. Complete substitution of phenylene groups for the tetramethylene resulted in an increase of stability of approximately 110°C.

A number of points of interest arise from the results for the perfluorocyclohexa-1,3-diene (C_6F_8) copolymers. The stability varied over a wide range and appeared to be largely dependent on the stability of the comonomer. Curves for polymethyl methacrylate, polystyrene, and polybutadiene derived from Madorsky's results¹²⁻¹⁴ are included in Figure 7. The points for polystyrene and polybutadiene were taken from curves of weight loss versus time at constant temperature. Those for polymethyl methacrylate were derived from plots of rate of volatilization against per cent volatilization (the actual weight loss curves are not published) but are unlikely to be much in error. As can be seen the stability of the C_6F_8 /methyl methacrylate copolymers lay between those of two polymethyl methacrylates of molecular weight 150,000 and 5,000,000. The C_6F_8 /styrene and C_6F_8 /butadiene copolymers degraded in the same temperature range as polystyrene and polybutadiene respectively, though there was a tendency for the copolymers to start degrading at a lower temperature than the homopolymers and to lose less weight at the highest temperatures used. The C_6F_8 /methyl methacrylate copolymer prepared by γ -irradiation was less stable, and the C_6F_8 /butadiene copolymer prepared by γ -irradiation more stable than their conventional analogs. This may be associated with the fact that polymethyl methacrylate itself degrades and polybutadiene cross links upon irradiation. Increase in the amount of C_6F_8 in the methacrylate copolymer from 17 to 31 mole-% did not alter the thermal stability. This is in contrast to the butadiene copolymers, where the stability decreased as the C_6F_8 content increased from 22 to 49 mole-%.

Results for single experiments at constant temperature ($388 \pm 1^\circ C$.) for various other copolymers are given in Figure 8. Curves for poly-1,1,2-trifluorobutadiene and a copolymer of vinyl *n*-butyl ether and perfluorocyclohexa-1,4-diene are also included as being of general interest.

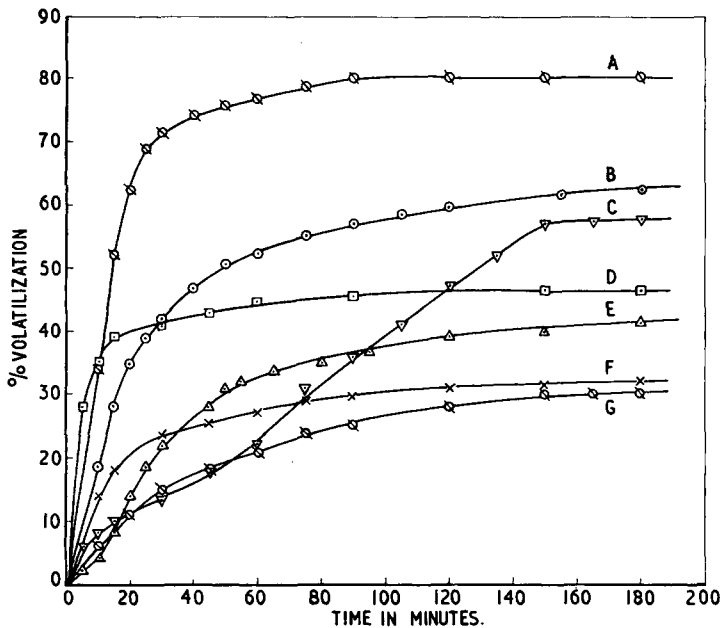


Fig. 8. Comparison of thermal stabilities of octafluorocyclohexadiene copolymers at $388 \pm 1^\circ\text{C}$.; (A) vinyl *n*-butyl ether/1,4- C_6F_8 copolymer; (B) vinyl *n*-butyl ether/1,3- C_6F_8 copolymer; (C) ethylene/1,3- C_6F_8 copolymer; (D) chloroprene/1,3- C_6F_8 copolymer; (E) 1,1,2-trifluorobutadiene/1,3- C_6F_8 copolymer; (F) butadiene/1,3- C_6F_8 copolymer; (G) poly-1,1,2-trifluorobutadiene. Copolymers of styrene and methyl methacrylate with 1,3- C_6F_8 volatilize to greater than 90% in less than 1 hr. at temperature lower than 388°C .

Stabilization was evident in all cases and the order of stability based on the final weight loss figures is poly-1,1,2-trifluorobutadiene, C_6F_8 /butadiene > C_6F_8 /1,1,2-trifluorobutadiene > C_6F_8 /chloroprene > C_6F_8 /ethylene > C_6F_8 /vinyl *n*-butyl ether > 1,4- C_6F_8 /vinyl *n*-butyl ether > C_6F_8 /styrene > C_6F_8 /methyl methacrylate.

Overall Activation Energies for the Degradation Processes

The overall activation energy determined from weight loss studies is complex, depending on initiation, depropagation, termination, and transfer reactions. It does, however, give some indication as to whether the bond strength of the backbone chain is being approached and hence whether initiation is a random breaking of this chain. It also gives a means of estimating approximately the weight loss of a polymer during long-term use at comparatively low temperatures. This involves the assumption that the same reaction mechanisms are in operation over the whole of the temperature range involved.

Methods of interpreting weight loss data have varied considerably. Some investigators have considered that their results have been straight lines within experimental error and hence have used average rates for their

calculations. Madorsky has plotted rates of volatilization, expressed either as a function of the original weight of polymer or of the weight of residues, against the per cent volatilized. These plots were extrapolated to zero weight loss to give apparent initial rates of volatilization which were used for calculation of the activation energy. Wall and Florin⁸ have constructed theoretical curves of this type (assuming overall random decomposition) and have shown continuous curvature in both types of plot, that based on initial weight of sample giving a maximum. They have wherever possible used this maximum rate for calculation of the activation energy, reverting to Madorsky's method if a maximum in the rate curve was not obtained.

The results given here have normally been treated on the basis of apparent zero-order or first-order reactions. It was considered questionable whether the more refined techniques would lead to a more accurate value of the activation energy, as the mode of breakdown of many of the polymers is complex and the reaction mechanism unknown. For an apparent zero-order reaction the plot of weight loss against time should be a straight line, i.e., the rate should be independent of the percentage weight loss. For an apparent first-order reaction the plot of log residue against time should be a straight line, i.e., the rate should decrease proportionately to the percentage volatilized. To check the validity of the use of apparent zero-order or first-order reactions for calculating activation energies, the weight loss results have been treated as appropriate by the methods of Madorsky and Wall. A comparison of the values obtained is given in Table II. With the exception of the tetrafluoroethylene/trifluoronitrosomethane copolymer, the values of the activation energy calculated either in some cases from zero-order plots and from maximum rates or, in other cases from first-order plots and from initial rates based on original weight of sample, do not differ by more than 2 kcal./mole. The tendency is for the apparent zero-order plot to give a slightly lower value than that obtained from the maximum rate plot. Attempts to obtain results by using rates based on the residue were unsuccessful except for two of the polychlorotrifluoroethylene samples and fluorosilicone B. In all other cases, either the actual plot curved, making extrapolation to the initial rate difficult, or the initial rates obtained gave a curved Arrhenius plot. The discrepancy in the values obtained for the tetrafluoroethylene/trifluoronitrosomethane copolymer is possibly due to the first-order plot taking more account of the early stages of the reaction, whereas the extrapolation to apparent initial rate is from points from 20% volatilization onwards. A later paper¹⁸ confirms the first-order reaction and quotes an activation energy of 58 kcal./mole.

None of the methods of plotting the results gave satisfactory estimates of the overall activation energy for the fumaryl chloride/octafluorohexane-1,6-diol polymer, the copolymers containing octafluorocyclohexa-1,3-diene, and the fluorosilicone A.

The result for polyvinylidene fluoride is of questionable value as it is based on maximum rates in a system where stabilization occurs.

TABLE II
 Comparison of Methods of Assessing Weight Loss Data for the Calculation of Overall Activation Energies

Polymer	Overall activation energy, kcal./mole				
	Apparent zero order	Apparent first order	Maximum in rate plot	Apparent initial rate	
				From rate as function of original weight of polymer	From rate as function of residue
Polytetrafluoroethylene	—	76	—	75	—
Teflon, 100X	—	73	—	71	—
Polychlorotrifluoroethylene ^a					
Sample 1	50	—	49	—	50
Sample 2	49	—	50	—	45
Sample 3	61	—	62	—	(68) Plot curves
Viton A	46	—	45	—	Arrhenius plot curves
Viton A-HV	48	—	50	—	Arrhenius plot curves
Viton LD-234	45	—	46	—	Arrhenius plot curves
Hexafluoropentylene adipate	—	Arrhenius plot curves ($E = 12-40$)	—	Two initial rates possible ($E = 6$ or 12)	—
Hexafluoropentylene adipate/ isophthalate	—	Arrhenius plot curves ($E = 12-40$)	—	Two initial rates possible ($E = 6$ or 34)	—
Polychlorodifluoroethylene	38	—	40	—	Plot curves
Terephthalyl chloride/octafluoro- hexanediol	—	58	—	Arrhenius plot curves	—

Polyvinylidene fluoride	—	71	—	—	—
Kel-F 800	68	69	—	—	Arrhenius plot curves
Kel-F 5500	50	51	—	—	Arrhenius plot curves
Kel-F 3700	54	52	—	—	Plot curves
C ₂ F ₄ /CF ₃ NO copolymer	—	—	56	38	—
C ₂ F ₃ H/CF ₃ NO copolymer	—	—	47	—	Arrhenius plot curves
Fluorosilicone B	—	—	—	—	—
Fluorosilicone	44	44	—	—	40
Fumaryl chloride/octafluorohexane diol					
Butadiene/C ₄ F ₈ copolymer					
Styrene/C ₆ F ₈ copolymer					
Methyl methacrylate/C ₆ F ₈ copolymer					
Fluorosilicone A					

No satisfactory results obtained by any method of calculation with these polymers

^a Sample 1 prepared with ferrous sulfate/citric acid recipe; sample 2 prepared by γ -irradiation; sample 3 prepared with a silver nitrate recipe.

TABLE III
Comparison of Results on Fluoropolymers

Polymer	This work			N.B.S. results ^a			
	Activation energy kcal./mole	A factor, sec. ⁻¹	Rate at 350°C., %/min.	Activation energy, kcal./mole	A factor, sec. ⁻¹	Rate at 350°C., %/min.	Ref.
Polytetrafluoroethylene	76	10 ¹⁹	2.6 × 10 ⁻⁶	81	10 ¹⁹	2 × 10 ⁻⁶	10
Teflon 100X	73	10 ¹⁸	1.8 × 10 ⁻⁶	55	10 ¹²	2 × 10 ⁻⁴	11
Fluorosilicone B	44	10 ¹³	0.01	—	—	—	—
Polyvinylidene fluoride	71	10 ²⁰	0.005	48	10 ^{16*}	0.02	10
Terephthalyl chloride/octafluorohexanediol	58	10 ¹⁶	0.008	—	—	—	—
Viton A	46	10 ¹³	0.04	57	10 ^{13*}	0.04	11
Viton A-HV	48	10 ¹⁴	0.05	—	—	—	—
Viton LD-234	45	10 ¹³	0.05	—	—	—	—
Kel-F 3700	54	10 ¹⁶	0.06	61	10 ^{15*}	0.06	11
Kel-F 5500	50	10 ¹⁵	0.12	61	10 ^{15*}	0.06	11
Kel-F 800	68	10 ²¹	0.18	—	—	—	—
Polychlorotrifluoroethylene	50	10 ¹⁵	0.30	50	10 ^{12*}	0.2	20
Sample 1	49	10 ¹⁵	0.29	—	—	—	—
Sample 2	61	10 ¹⁹	0.26	—	—	—	—
Sample 3	—	—	~1.7	32	10 ⁸	2.0	11
Hexafluoropentylene adipate	—	—	~2.3	—	—	—	—
Hexafluoropentylene adipate/isophthalate	38	10 ¹²	2.6	—	—	—	—
Polychlorodifluorodethylene	56	10 ²¹	1200	—	—	—	—
CF ₂ NO/C ₂ F ₄ copolymer	47	10 ¹⁷	1000	—	—	—	—
CF ₂ NO/C ₂ F ₄ H copolymer	—	—	—	—	—	—	—

^a N.B.S. results starred are based on maximum rates and include a factor $L/2.7$, where L is the critical size for decomposition and is assumed to be 2,000. The application of this factor to the present results would lower them by 10³.

The higher activation energy for one of the chlorotrifluoroethylene polymers would not have been expected and is not obvious from the relative thermal stability curves (Fig. 7). An Arrhenius plot¹ showed that at the higher temperatures used there was very little difference in the rates of breakdown of the three polymer samples. At the lower temperatures the rates, and hence the calculated values of the activation energies, differed. A further difference is shown in the plot of the rate of weight loss calculated as a percentage of the residue versus the per cent volatilized. Two of the samples gave straight lines over the major part of the range, whereas the plot for the third sample was curved throughout. This difference must be related to the methods of preparation and a detailed characterization of the three polymer samples is necessary.

A comparison of the values obtained in this work with those published by the National Bureau of Standards is given in Table III. Estimates of the Arrhenius factor and the rate of weight loss at 350°C. are also included. The polymers are listed in decreasing order of the stability based on Figure 6. (Another study of the pyrolysis of polytetrafluoroethylene¹⁹ quotes an activation energy of 83 kcal./mole and an Arrhenius factor of 3×10^{19} .) There are quite considerable differences in the values for the activation energies and Arrhenius factors. Considering these the 350°C. rates are rather surprisingly in quite good agreement. It should be noted in respect of the Arrhenius factors that the National Bureau of Standards results based on maximum rates include a factor equal to $L/2.7$, where L is the critical size for decomposition and is assumed to be 2000. This if applied to the present results would lower them by 10^3 . Discrepancies in values of overall activation energies may be attributed to differences in experimental techniques, differences in the polymer samples (i.e., method of preparation and hence molecular weight, molecular weight distribution, and purity), and method of interpretation of the results. Assessing the same weight loss results Madorsky and Wall quote values of 57 and 50 kcal./mole, respectively, for the activation energy for degradation of polychlorotrifluoroethylene. The experimental techniques used in determining both sets of results were very similar and assessment of the results of this work by a number of different methods gave virtually the same activation energy in all but one case. It therefore seems that the observed differences must be attributed to differences in the polymer samples used. Support for this is given by the results observed on the three chlorotrifluoroethylene polymers.

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Résumé

On a étudié la dégradation thermique sous vide d'une série de polymères contenant du fluor en utilisant une technique par perte de poids. On a déterminé les stabilités thermiques relatives, et lorsque cela fut possible, on a déterminé l'énergie d'activation totale et les facteurs de fréquence de leur décomposition. On a discuté les méthodes d'évaluation des résultats obtenus par la technique de perte de poids. Les polymères les plus stables sont ceux qui sont complètement fluorés.

Zusammenfassung

Der thermische Abbau einer Reihe fluorhaltiger Polymerer wurde im Vakuum unter Verwendung einer Gewichtsverlustmethode untersucht. Die relative thermische Stabilität der verschiedenen Polymeren und, wenn möglich, die Bruttoaktivierungsenergie und der Frequenzfaktor für die Abbaureaktion wurden bestimmt. Die Auswertungsmethoden für die Ergebnisse des Gewichtsverlustes werden diskutiert. Die gänzlich fluorierten Polymeren sind die stabilsten.

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