Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Thermal Decomposition of Polytetrafluoroethylene Oxide

A. Donato[a]; M. Lenzi[a]; A. Mele[a]
[a] LABORATORIO DI CHIMICA DELLE RADIAZIONI E CHIMICA NUCLEARE DEL C.N.E.N., ISTITUTO DI CHIMICA GENERALE ED INORGANICA, UNIVERSITÀ DI ROMA, ROME, ITALY

To cite this Article Donato, A. , Lenzi, M. and Mele, A.(1967) 'Thermal Decomposition of Polytetrafluoroethylene Oxide', Journal of Macromolecular Science, Part A, 1: 3, 429 — 438

To link to this Article: DOI: 10.1080/10601326708053981

URL: http://dx.doi.org/10.1080/10601326708053981

J. MACROMOL. SCI. (CHEM.), A1(3), 429–438 (1967)

Thermal Decomposition of Polytetrafluoroethylene Oxide

A. DONATO, M. LENZI, and A. MELE
LABORATORIO DI CHIMICA DELLE
RADIAZIONI E CHIMICA NUCLEARE DEL C.N.E.N.,
ISTITUTO DI CHIMICA GENERALE ED INORGANICA,
UNIVERSITÀ DI ROMA,
ROME, ITALY

Summary

The thermal degradation of polytetrafluoroethylene oxide has been examined by the isothermal and thermogravimetric methods in the temperature range 450 to 650°C. The main components of the volatile gas are trifluoroacetyl fluoride, carbonyl fluoride, and tetrafluoroethylene. The thermogravimetric decompositions of polytetrafluoroethylene oxide and of polytetrafluoroethylene have been compared.

The available results on the thermal stability of fluorinated polymers concern mainly polytetrafluoroethylene, which has been studied by several authors (*1*,*2*).

Recently polytetrafluoroethylene oxide has been prepared by solid-state γ-irradiation of the monomer (*3*). This polymer with oxygen atoms in the main chain is the first example of heterochain fluorocarbon. In this work an investigation of the thermal decomposition of this polymer was made. The nature of the products given off and the rate of the reaction were also examined.

EXPERIMENTAL

Material

Polytetrafluoroethylene oxide (PTFEO) was prepared by γ-irradiation of tetrafluoroethylene oxide in the solid state (*3*). Samples of various molecular weights were obtained from different preparation and used without fractionation. Polytetrafluoroethylene (PTFE) was a commerical sample.

Apparatus and Procedure

Thermal decomposition was measured by the isothermal method and by thermogravimetry. The apparatus used for the isothermal decomposition consisted of a fused quartz spring balance and a platinum crucible.

The heating furnace was a nichrome wire-wound quartz tube connected to a vacuum line. The quartz spring balance was cooled by a condenser through which water was circulated. The temperature was controlled with two chromel-alumel thermocouples placed near the platinum crucible suspended in the center of the furnace. The temperature could be kept within ±3°C.

The experiments were carried out with samples of 50 mg or more in vacuum (10^{-4} torr) and the gas evolved was trapped in a liquid nitrogen condenser. The time to warm-up to the temperature required was about 3 min. Thermogravimetric experiments were carried out with an A.D.A.M.E.L. thermobalance system P. Chevenard No. 243, at a heating rate of 0.5°C/min under an argon flow.

Analyses and Viscosity Measurements

The pressure of condensed gas obtained from pyrolysis in vacuum was measured in a known volume. The gas was analyzed by IR spectrophotometry with a Perkin-Elmer Infracord apparatus. The absorption bands used for the quantitative determinations of the products were 1960 cm^{-1} for carbonyl fluoride, 1900 cm^{-1} for trifluoroacetyl fluoride, and 1030 cm^{-1} for SiF_4. Viscosity determinations were carried out at 25°C in $C_8F_{16}O$ (FC75-3M mixture of isomers).

RESULTS

Isothermal Method

The decomposition of polytetrafluoroethylene oxide has been examined in the temperature range 450 to 585°C. The results of these experiments are shown in Fig. 1, where the conversion rate

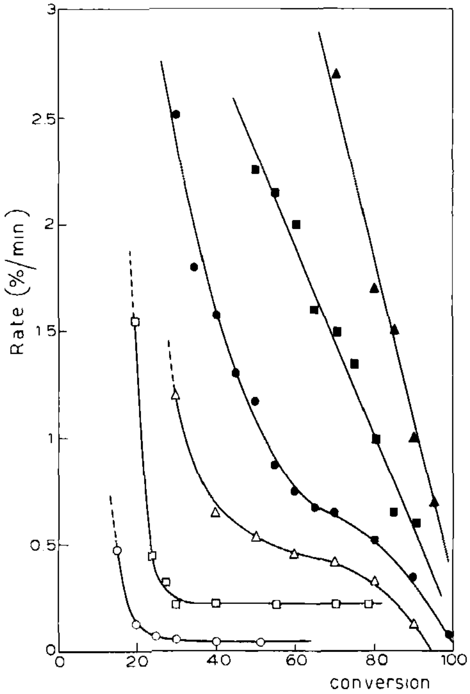


FIG. 1. Rates of thermal degradation as function of conversion for PTFEO at: ○, 500°C; □, 515°C; △, 545°C; ●, 560°C; ■, 565°C; ▲, 575°C.

is plotted versus the per cent of conversion. The decomposition curves differ markedly from one another, depending on the temperature. At temperatures below 515°C, an initial rapid weight loss is followed by a slow reaction with an invariance of the conversion rate. Assuming for this decomposition a zero-order reaction, the Arrhenius plot gives a fairly straight line with an activation energy of 50 kcal/mole.

It should be noted that in the initial rapid stage, the final weight loss increases with decomposition temperature. The curves of Fig. 1 refer to experiments made on the same sample with $[\eta] = 0.365$. The viscosity during decomposition at 515°C does not seem to change significantly. As shown in Fig. 1, a first-order decomposition takes place at higher temperature. This trend is shown also in Fig. 2 at three temperatures. A value of 83 kcal/mole for the activation energy is obtained in this temperature range. As shown in Table 1,

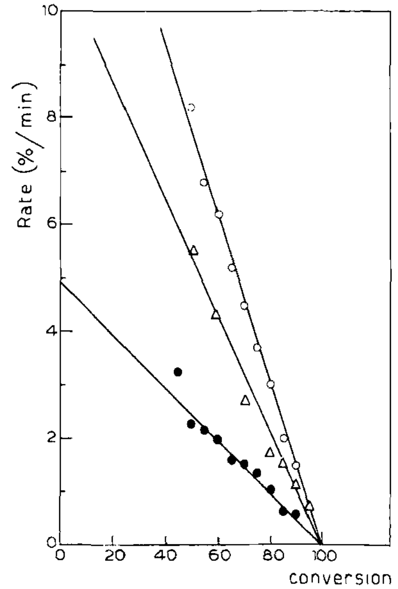


FIG. 2. Rates of thermal degradation as function of conversion for PTFEO at: ●, 565°C, △, 575°C; ○, 585°C.

the first-order decomposition rate does not depend on the molecular weight of the polymer.

The pyrolysis in vacuum leads to a volatile fraction collected in the liquid nitrogen condenser and a nonvolatile product that remained in the cool part of the furnace. The volatile fraction increased with decomposition temperature and in the experiments at high temperature accounted for about 100% of the polymer decom-

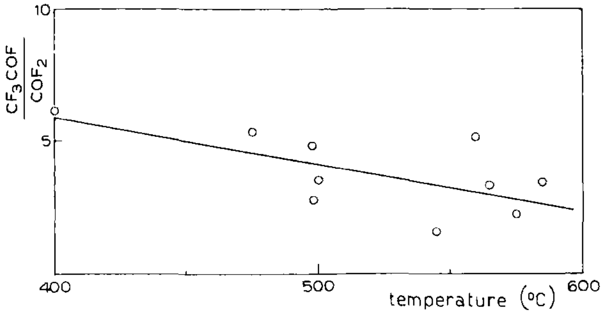


FIG. 3. Ratio between CF_3COF and COF_2 obtained in thermal degradation of PTFEO as a function of temperature.

posed. In the low-temperature range, most of the volatile gas is formed during the slow reaction. The condensed gas in the first rapid stage accounts for only about 20% of the weight loss. This volatile fraction was analyzed by IR spectrophotometry at various stages of the reaction, and trifluoroacethyl fluoride, carbonyl fluoride, SiF_4, and small amounts of C_2F_4 were the main components.

The ratio between CF_3COF and COF_2 formed at the end of the pyrolysis is plotted in Fig. 3 against decomposition temperature. A decrease of this ratio with temperature may be observed. Decomposition of CF_3COF to form COF_2 at higher temperature cannot justify this result, as direct experiments have shown.

Thermogravimetric Method

The thermal stabilities of PTFEO and PTFE have been compared by carrying out thermogravimetric decompositions under the same conditions.

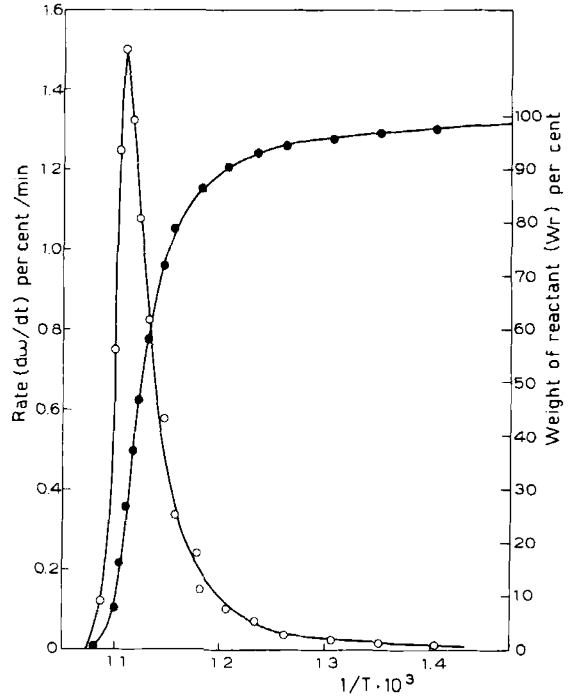


FIG. 4. Thermogravimetric (●) and differential thermogravimetric (O) curves for thermal decomposition of PTFEO.

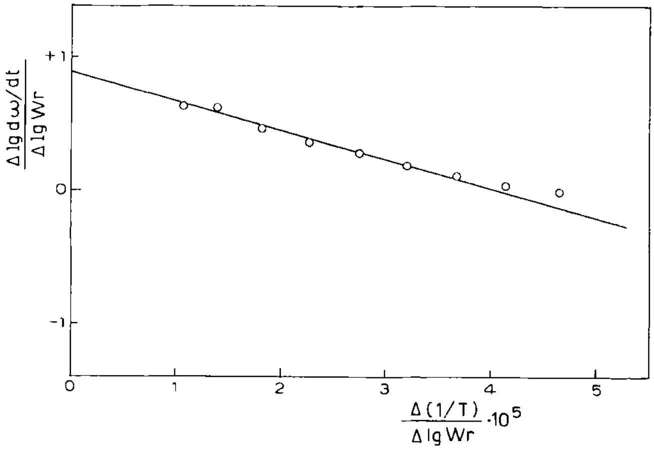


FIG. 5. Kinetics of the thermal decomposition of PTFEO by thermogravimetry.

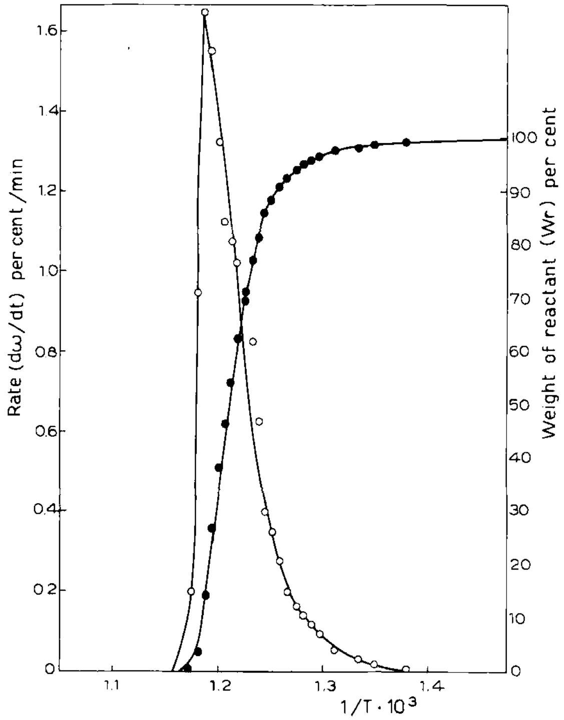


FIG. 6. Thermogravimetric (●) and differential thermogravimetric (○) curves for thermal decomposition of PTFE.

The curves of thermogravimetric analysis have been treated according to the modified method of Freeman and Carroll (*4,5*) based on the following equation:

$$\log (dw/dt) = x \, \Delta \log Wr - (\Delta E/2.3R) \, \Delta \, (1/T) \qquad (1)$$

where dw/dt and x are the rate and the order of reaction, respectively. ΔE is the activation energy, $Wr = \Delta Wc - \Delta W$ is proportional to the amount of reactant present, ΔW is the weight loss when the rate is measured, and ΔWc is the total weight loss.

Polytetrafluororoethylene Oxide. In Fig. 4 a typical thermogravimetric curve with the first derivative for the pyrolysis of the polymer is shown. The decomposition rate has a maximum at 628°C. The plot of Fig. 5 is obtained from the graph of Fig. 4 using Eq. (1). Accordingly, between 595 and 625°C, a first-order reaction takes place from 8.5% up to 85% of weight loss. The activation energy is 98 kcal/mole.

Polytetrafluoroethylene. The thermogravimetric curves for the decomposition of this polymer are shown in Fig. 6. The maximum rate is observed at 568°C. A first-order reaction (0.88) between 523 and 571°C is confirmed and the activation energy is 85 kcal/mole.

DISCUSSION

The rate curves of Fig. 1 for the isothermal degradation of PTFEO show a different trend at low and at high temperature, respectively. At temperatures below 515°C, the kinetic curves show first a reaction with a rapid weight loss followed by a zero-order decomposition. A detailed study of the rapid reaction in this range of temperature could not be made under the experimental conditions adopted in the present work. The reaction was almost completed during the time of heating to the temperature of the experiment. This rapid weight loss is due to volatilization of low-molecular-weight polymeric material, as indicated by the fact that in this stage only a small amount of volatile gas is formed. Further, the infrared spectra of the viscous oil formed on the wall of the furnace is similar to that of the initial product. This volatilization however, does not seem to change significantly the average molecular weight as determined by viscosity measurements.

The slow reaction that follows, with a zero-order kinetics, would indicate a thermal degradation end-initiated, with small zip length.

According to this mechanism, the degree of polymerization should decrease with conversion and coincide with the diagonal of the plot (*6–9*). This is not the behavior found. The viscosity measurements of the polymer at various stages of the thermal treatment at 515°C do not show an appreciable change from the initial product.

A definitive conclusion on the mechanism of degradation in this range of temperature cannot be drawn. The rate curves would suggest that the materials is most heterogenous and that at low temperature the depropagation process has a short zip length, so that much material may volatilize.

Above 565°C, up to 585°C, a linearly decreasing rate of decomposition as a function of conversion is observed. This trend is predicted by the theory either for end or random initiation with large zip (*6–9*). A distinction between the two mechanisms may be obtained by examining the decomposition rate of samples of different molecular weight. Random initiation would produce a higher rate with samples of a higher molecular weight. With end initiation and large zip the rate of decomposition should not depend on the molecular weight of the initial polymer, as actually found for the samples of PTFEO examined (Table 1).

TABLE 1

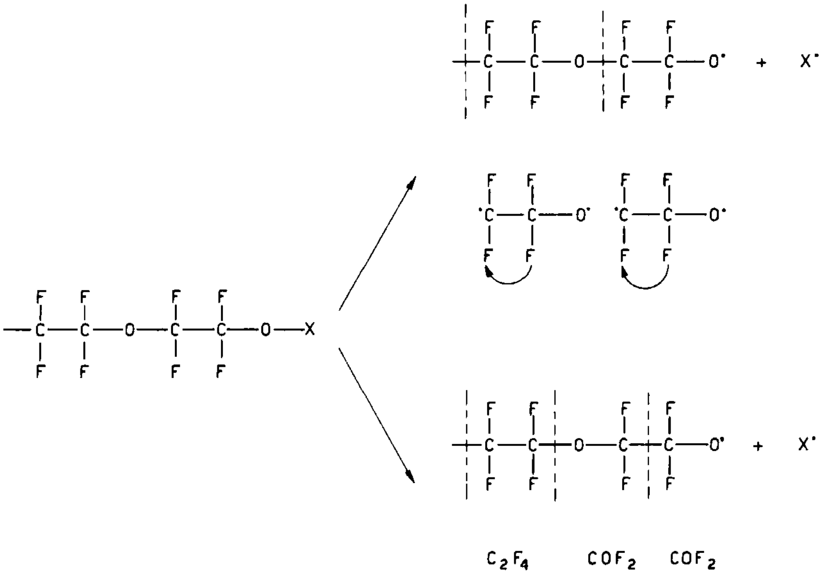
First-Order Rate Constants for Decomposition of Samples of PTFEO of Different Intrinsic Viscosity at 585°C

$[\eta]$, dl/g	k, min^{-1}
0.585	0.095
0.475	0.133
0.365	0.098
0.195	0.099

The experimental results obtained from the isothermal and from the thermogravimetric methods, respectively, seem to be in fairly good agreement. The two methods have both shown the first-order process in the high-temperature range (565°C) and provide reasonable values of the activation energy (83 and 98 kcal/mole). A comparison of the results of the low-temperature processes would be meaningless. At low temperature the weight loss determined thermogravimetrically corresponds to the rapid reaction observed by the isothermal method.

The activation energy for the first-order decomposition is 98 kcal/mole for PTFEO and 85 kcal/mole for PTFE (previously found, 80 kcal/mole) (*10*). A comparison between these values that were obtained from thermogravimetric measurements under the same experimental conditions would indicate that PTFEO is a more stable polymer. It should be pointed out that the activation energy obtained by thermogravimetry may correspond to the theoretical value only in the low conversion range (*11*). At high conversion, $E_{calc} > E_{theory}$. A higher thermal stability is also shown from the maximum of the decomposition rate that was found at 628°C for PTFEO and at 568°C for PTFE. Transfer reactions in the depolymerization reaction probably may be neglected for both polymers, since fluorine-atom abstraction is a highly energetic process.

It could be suggested that radicals formed in PTFEO degradation may be more stable than in PTFE. The end-initiated pyrolysis of PTFEO may be represented as follows:



The exact nature of the terminal groups cannot be defined. At some early stage of the degradation process unzipping may lead to monomeric units that by fluorine-atom transfer ultimately give trifluoroacetyl fluoride. Unzipping may alternatively produce carbonyl fluoride and tetrafluoroethylene. This latter process is favored at high temperature.

Acknowledgments

The authors wish to thank Dr. L. A. Wall for reading the manuscript and for helpful suggestions. The TGA were made by Dr. G. Rigato, and he is gratefully aknowledged. One of us (A.D.) is thankful to the Consiglio Nazionale delle Ricerche for a fellowship.

REFERENCES

1. J. M. Cox, B. A. Wright, and W. W. Wright, *J. Appl. Polymer Sci.*, **8**, 2935 (1964).
2. A. R. Schultz, N. Knoll, and G. A. Morneau, *J. Polymer Sci.*, **62**, 211 (1962).
3. P. Barnaba, D. Cordischi, M. Lenzi, and A. Mele, *Chim. Ind.* (*Milan*), **47**, 1060 (1965).
4. D. A. Anderson and E. S. Freeman, *J. Polymer Sci.*, **54**, 253 (1961).
5. E. S. Freeman and B. Carrol, *J. Phys. Chem.*, **62**, 394 (1958).
6. D. W. Brown and L. A. Wall, *J. Phys. Chem.*, **62**, 848 (1958).
7. R. Simha, L. A. Wall, and P. J. Blatz, *J. Polymer Sci.*, **5**, 615 (1950).
8. R. Simha and L. A. Wall, *J. Polymer Sci.*, **6**, 39 (1951).
9. R. Simha, L. A. Wall, and J. Bram, *J. Chem. Phys.*, **29**, 894 (1958).
10. S. L. Madorsky, V. E. Hart, E. Strauss, and V. A. Sedlack, *J. Res. Natl. Bur. Std.*, **51**, 327 (1953).
11. J. H. Flynn and L. A. Wall, *Polymer Preprints*, **6**, 945 (1965).

Zusammenfassung

Der thermische Abbau von Polytetrafluoroäthylen durch isotherme und thermogravimetrische Methoden wurde im Temperaturbereich von 450 bis 650° untersucht. Die Hauptbestandteile des flüchtigen Gases sind Trifluoroacetylfluorid, Carbonylfluorid und Tetrafluoroäthylen. Die thermogravimetrische Zersetzung von Polytetrafluoroäthylenoxid und Polytetrafluoroäthylen werden miteinander verglichen.

Résumé

L'étude de la dégradation thermale de l'oxyde de polytetrafluoroethylène par des méthodes isothermales et thermogravimétriques dans l'intervalle de températures de 450 à 650°C. Les composants principaux des gaz bolatiles sont le fluorure de trifluoroacethy, le fluorure de carbonyle et le tetrafluoroethylène. La décomposition thermogravimetrique de l'oxyde de polytétrafluoroethylène et du polytétrafluoroethylène est comparée.

Received by editor August 25, 1966
Submitted for publication November 14, 1966