PER-38

RADIATION POLYMERIZATION OF TETRAFLUOROETHYLENE IN FREON-22

by

NORMAN G. SCHNAUTZ
JASPER C. THOMPSON

PER-38

ATOMIC ENERG: BOARD

RADIATION POLYMERIZATION OF TETRAFLUOROETHYLENE IN FREON-22

by

NORMAN G. SCHNAUTZ*
JASPER C. THOMPSON

*Chemistry Division
Postal Address:
Private Bag X256
Pretoria
0001

CONTENTS

SAMEVATTING

Die stralingsgeïnduseerde oplossingspolimerisering van tetrafluoroetileen in Freon-22 is oor die temperatuurstrek −62 °C tot 0 °C ondersoek. Daar is gevind dat die polimeriseringstempo vir die proses in die bron regstreeks eweredig aan monomeerkonsentrasie was en 'n aktiveringsenergie van slegs 7,66 kJ/mol is bepaal. Die getalgemiddelde molekuulmassa van die produk-PTFE het van 2×10^4 tot 6×10^4 gewissel en was betreklik onafhanklik van die gewone reaksieparameters. Daar is ook gevind dat die napolimeriseringstempo regstreeks eweredig aan die monomeerkonsentrasie was. Die napolimeriseringsproses het geen verbetering van die aanvanklike PTFE-molekuulmassa tot gevolg gehad nie.

ABSTRACT

The radiation-induced solution-polymerization of tetrafluoroethylene in Freon-22 has been investigated over a temperature range of −62 °C to 0 °C The rate of polymerization for the in-source process was found to be directly proportional to monomer concentration and an activation energy of only 7,66 kJ/mole was calculated The number-average molecular mass of the product PTFE ranged from 2×10^4 to 6×10^4 and was relatively independent of the usual reaction parameters. The rate of postpolymerization was also found to be directly proportional to monomer concentration. The postpolymerization process did not result in any enhancement of the initial PTFE molecular mass.

1. INTRODUCTION

... tetrafluoroethylene) (PTFE) is a relatively ... polymer, and yet from the standpoint of chemical, mechanical and physical properties extremely important, PTFE is used widely in both commercial and military applications. Some of the more favourable properties of PTFE are its outstanding chemical inertness, thermal stability, and low coefficient of friction.

At present PTFE is not produced in South Africa, but is imported from European sources, namely Hoechst and ICI. An estimated 30 000 kg of extrusion-grade PTFE is imported annually at a before-shipment price of R10-50 per kg.

Because PTFE is an import item, its cost is beyond the control of the South African consumer market. Furthermore the supply of PTFE may at some future date be subject to the influence of international politics. Thus, because of the strong South African position in fluorspar (CaF$_2$), the present commercial source of fluorine, and the ready availability of local radiation-polymerization technology, it would seem advisable to investigate the radiation polymerization of PTFE.

2. REVIEW

Naturally the preparation of PTFE must proceed through its monomeric form, viz. tetrafluoroethylene (TFE). Virtually all commercial preparations of TFE proceed by means of the following scheme: fluorination of chloroform by hydrogen fluoride, yielding chlorodifluoromethane (Freon-22) followed by pyrolysis of Freon-22, affording TFE.

$$CHCl_3 \xrightarrow{HF} CHClF_2 \xrightarrow{\Delta} CF_2=CF_2$$

The first literature report of the preparation of Freon-22 was in 1932 by Booth and Bixby [1]. They found that the fluorination of chloroform by antimony trifluoride in the presence of antimony pentachloride afforded Freon-22 in high yield. In 1948 Benning reported a method for converting chloroform to Freon-22 by treatment with hydrogen fluoride and a catalyst consisting of a mixture of antimony tri- and pentachlorides [2]. Baldwin has reported the conversion of chloroform to Freon-22 using the hydrogen fluoride/antimony trichloride system [3], and Posta and Hudlicky a hydrogen fluoride/antimony pentachloride catalyst system [4]. A more recent industrial process utilized hydrogen fluoride and a mixture of tri- and pentavalent antimony sulfides [5]. This process yields a fluorination product consisting of 99 % Freon-22, 0,9 % dichloromethane, and 0,1 % trifluoromethane. The high-temperature vapour-phase fluorination of chloroform has been investigated by Balf who reported that when a stream of chloroform and hydrogen fluoride was passed over activated charcoal at 350 °C a fluorination product was obtained consisting of 6,1 % trifluoromethane, 44,9 % Freon-22, 34,8 % dichlorofluoromethane, 3 % dichlorodifluoromethane, and 0,6 % methylene chloride [6].

A number of novel Freon-22 syntheses have been reported, but they are characterized by low yields and many side products, making separation difficult. For example, Freon-22 has been isolated after treatment of chloroform with potassium fluoride in the presence of ultraviolet light [7]. Also by electrolysis of methylene chloride in the presence of hydrogen fluoride and lithium fluoride [8], and by γ-irradiation of a mixture of chlorine and difluoromethane [9].

Clearly the method of choice for the preparation of Freon-22 is the reaction between chloroform and hydrogen fluoride, using a pentavalent antimony catalyst system. This method should lend itself to either batch or continuous processes. Unfortunately the literature is devoid of any kinetic data concerning this process. However, several of the above-cited references list detailed experimental procedures for both batch [7] and continuous processes [2,3,5,6].

The pyrolysis of Freon-22 to afford TFE in high yield was first reported by Downing, Benning and McHarness in 1945 [10]. They found that when Freon-22 was passed through a silver- or platinum-lined tube at 700 °C, conversions of Freon-22 ranging from 15 to 100 % could be obtained with yields of TFE ranging from 60 to 99 %. They reported that high temperature, pressures and contact times favoured Freon-22 conversion but lowered TFE yields, whereas low conversions and pressures (<1 atm) favoured high yields of TFE. This process was reported on in some detail in 1947 [11]. Numerous modifications of this procedure have been reported and are listed in Table I.

A major experimental problem encountered in the pyrolysis of Freon-22 is the corrosive effects of hydrogen chloride at temperatures exceeding 700 °C. Also there is some hydrogen fluoride generated. This is the reason for the initial use of platinum, silver, and carbon as tube-lining materials. Although the use of sodium chloride/sodium carbonate melt with carbon dioxide as diluent in the gas stream would appear to produce both conversions and yields in excess of 90 %, the use of and replenishing of such a melt system must produce serious problems in equipment design and maintenance. The use of ammonia has been shown to alleviate the corrosion problem to a great extent. At present the use of superheated steam appears a popular commercial procedure. Usual inlet conditions are Freon-22 at 400 °C and superheated steam at 1 000 °C, resulting in a reaction temperature of approximately 800 °C.

Numerous other reaction systems have been reported by which TFE may be prepared in low yield, for example passing fluorine [18], carbonyl difluoride [19], and bromine trifluoride [18] through a carbon arc. However, yields of TFE are less than 10 %. The pyrolysis of PTFE at 600 °C produces TFE in very high yield at low pressures [20], but this method is obviously self-defeating.

One other preparative technique has been used which will produce TFE in high yield. The reaction between 1,2-dichlorotetrafluoroethane (Freon ...) ... in methanol [21].

$$CClF_2-CClF_2 \xrightarrow{Zn} CF_2=CF_2$$
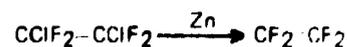
However, this procedure has not found commercial ...

Table I
Pyrolysis of Freon-22

Pyrolysis Tube Material	Additive	Temp. °C	Conv. %	Yield %	Ref
Pt, Ag, C	–	600–800	15–100	60–99	10,11,12
Quartz+Pt/Rh guaze	H_2	700	66	55	13
Cu+CuCl/Cu guaze	–	800	43	98	14
Ni+NaCl/Na_2CO_3 melt	CO_2	760	92	90	15
Ni	NH_3	700	39	94	16
unlisted metal	H_2O	800	75	95	17

application for several reasons: A) Experimentally, the reaction conditions are more complex than in the pyrolysis of Freon-22, B) the reaction does not lend itself to a continuous process, and C), the use of large quantities of zinc dust which is very expensive. Freon-114 can be prepared by the action of chlorine and hydrogen fluoride on tetrachloroethylene in the presence of antimony pentachloride, as shown below [22].

$$CCl_2{=}CCl_2 + Cl_2 + 4HF \longrightarrow CCIF_2{-}CCIF_2 + 4HCl$$

Commercially, Freon-114 is used widely as a refrigerant and is available at lower unit cost than Freon-22. Thus, for the laboratory-scale preparation of research quantities of pure TFE, the dechlorination of Freon-114 would represent a relatively convenient method. However, for the preparation of quantities of TFE exceeding several kilograms, the pyrolysis of Freon-22 is the preferred process.

Although the pyrolysis of Freon-22 has for years been the preferred choice for the commercial preparation of TFE, only one literature report is available concerning the kinetics of this reaction. In 1966 Gozzo and Patrick published their work on the kinetics of Freon-22 pyrolysis [23]. They suggested that the pyrolysis proceeds by way of a two-step mechanism, as shown below.

$$CHCIF_2 \xrightleftharpoons[k_2]{k_1} CF_2 + HCl$$

$$2CF_2 \xrightarrow{k_3} CF_2{=}CF_2$$
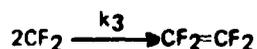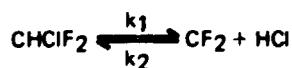
In the first step Freon-22 decomposes reversibly to form the difluorocarbene CF_2 which subsequently dimerizes to TFE. The authors also report that CF_2 formation is the rate-controlling step, with an activation energy of 205, 1±10,5 kJ/mole and $k_1 = 10^{12,36±0,56}Exp(-205100/RT)$. The activation energy for the reaction between CF_2 and HCl was reported to be 62,8±20,9 kJ/mole, and for CF_2 dimerization nearly zero. For low conversions of Freon-22 they also present the following kinetic expression for the disappearance of Freon-22:

$$\frac{-d(CHCIF_2)}{dt} = k_1(CHCIF_2)\left[1 - \frac{k_2(HCl)}{(k_1k_3(CHCIF_2))^{1/2}}\right]$$

Unfortunately the authors do not report a value for the ratio $k_2/k_3^{1/2}$. This ratio and its temperature dependence are necessary if computer simulation techniques are to be employed.

Some of the methods reported for the chemically -initiated polymerization of TFE are shown in Table II below.

Table II
Polymerization of TFE

Temp. °C	Pressure kPa	Catalyst System	Ref
50–250	20 000–30 000	Amine Oxide	24
60	45 (initial)	H_2O_2	25
0–150	20 000	CoF_3/AsF_5	26
55–240	7 000	aqueous H_2O_2	27
70	2 000	aqueous $(NH_4)_2S_2O_8$	28

Present commercial procedures favour polymerization in aqueous medium at 40–80 °C and at pressures of 300 to 3 000 kPa using ammor   persulfate catalyst and an emulsifying agent, if desired [29]. In the presence of an emulsifying agent an aqueous dispersion of PTFE is formed, and in the absence of an emulsifying agent a granular polymer is obtained. Under the above-described conditions the polymerization of TFE is a hazardous procedure requiring high-pressure equipment. Clearly there is a requirement for a more controlled polymerization process.

In 1960 Tabata first demonstrated the radiation-induced polymerization of TFE in both liquid and solid states [30]. And in 1967 Tabata reported the liquid state γ-radiation-induced polymerization activation energy to be 9,6 kJ/mole and only ca 1,3 kJ/mole for the solid-state polymerization process [31]. Later the solution activation energy for the bulk mutual irradiation process was updated to 11,3 kJ/mole and 43,1 kJ/mole for the bulk postpolymerization process [32].

The γ-radiation-induced polymerization of TFE proceeds very rapidly, with doses as low as 1,5 kGy producing over 95 % conversion in the mutual process at −40 °C. Tabata has also reported the γ-radiation-induced polymerization of TFE in Freon-22 solution [33]. The activation energy for the mutual irradiation polymerization in Freon-22 is 18,0 kJ/mole, compared to 11,3 kJ mole for

... ...nal bulk process. Also the conversion rates for a given dose rate exceed even those rates exhibited by the bulk process. Furthermore, the solution process eliminates temperature and pressure transients that occur in the bulk process. The solution postpolymerization process was also investigated [33]. Although reaction times of 6 to 8 h at −30 ºC were required to reach 50 to 80 % conversion, depending upon the initial radiation dose, this method does produce a very high molecular mass PTFE. With an initiating dose of 0,20 kGy, number-average molecular masses as high as 1×10^6 were reported [33].

Although the lower reaction rates of the postpolymerization process dictate time requirements much in excess of that required for mutual irradiation, the postpolymerization process possesses the advantage that the irradiation part of the process occurs at low conversions, below 20 %. Thus the bulk of the polymerization process is carried out in a radiation-free environment. This is important because of the high suseptibility of PTFE to radiation-induced degradation.

3. EXPERIMENTAL
3.1 Materials

Freon-22 was DuPont refrigeration grade of 99,9 % purity (GC). Tetrafluoroethylene was prepared by the pyrolysis of Freon-22. To this end a 50 % molar mixture of Freon-22 and helium was passed through an 8 mm OD quartz pyrolysis tube at 750 ºC and at a total gas flow rate of 2,5 ml/s. The effluent gas was passed counter current through a water washing tower, then through a calcium chloride drying tower, and collected at −196 ºC. Purification was by double rectification through a 2 m long Podbielniak-type low-temperature distillation column. The purity of the product tetrafluoroethylene exceeded 99,9 % (GC).

3.2 Irradiation Source

Irradiations were carried out in an AECL Gammabeam 650 (50 kCi) irradiation source. Dose rates were determined by Fricke dosimetry. Irradiations at different temperatures were carried out using appropriate slush baths. Temperature control over the range of −65 ºC to −10 ºC was maintained to an accuracy of ±0,2 ºC.

3.3 Sample Preparation

Tetrafluoroethylene-Freon-22 mixtures were prepared by vacuum transfer of air-free known quantities of the respective gasses into glass ampoules and sealing under vacuum.

3.4 Analyses

The poly(tetrafluoroethylene) which was formed was transfered to preweighed vials and dried in vacuo at 90 ºC to a constant mass.

Gas-chromatographic analyses were carried out on a Perkin-Elmer 900 gas chromatograph. Gas-sample purities were determined using a 3 mm diameter stainless steel column 2 m long packed with Porapak Q/S active solid support.
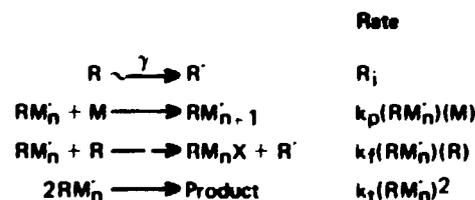
Mass spectra were determined using a GC-MS system consisting of a Varian Aerograph Series 1200 gas chromatograph coupled to a Varian Mat (Gmbh) CH7 mass spectrometer.

Number-average molecular masses were calculated from the mathematical relationship between number-average molecular mass and heat of crystallization of poly(tetrafluoroethylene), as established by Suwa, Takehisa and Machi [34]. Required thermal analyses were carried out on a Perkin-Elmer DSC 18 differential scanning calorimeter.

4. RESULTS AND DISCUSSION

4.1 In-Source Polymerization

The solution-phase polymerization of TFE in Freon-22 was carried out at −42 ºC, a dose rate of 0,50 kGy/h and at a monomer concentration of 40 mole per cent. A plot of the conversion as a function of reaction time is shown in Fig. 1. The following reaction sequence describing the polymerization of TFE may be written as

Rate

$$R \xrightarrow{\gamma} R^{\cdot} \qquad R_i$$

$$RM_n^{\cdot} + M \longrightarrow RM_{n+1}^{\cdot} \qquad k_p(RM_n^{\cdot})(M)$$

$$RM_n^{\cdot} + R \longrightarrow RM_nX + R^{\cdot} \qquad k_f(RM_n^{\cdot})(R)$$

$$2RM_n^{\cdot} \longrightarrow Product \qquad k_t(RM_n^{\cdot})^2$$

From the above reaction sequence the classical polymerization equation may be derived, as shown by eqn. (1), where $R_p = -d(M)/dt$.

$$R_p = k_p k_t^{-\frac{1}{2}} R_i^{\frac{1}{2}}(M) \qquad \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

When the generation of initiating free radicals $R^{\cdot}$ originates primarily from the solvent, Freon-22 in this case, the rate of polymerization R_p will be first-order with respect to monomer concentration. Antidifferentiation of both sides of eqn. (1) followed by substitution of the relationship $(M) = (M)_0(1-Z)$, where Z is the degree of conversion, leads to the expression of eqn. (2)

$$-\ln(1-Z) = k_p k_t^{-\frac{1}{2}} R_i^{\frac{1}{2}} t \qquad \ldots \ldots \ldots \ldots (2)$$

In order to test the predicted first-order relationship between R_p and monomer concentration, $-\ln(1-Z)$ is plotted as a function of reaction time [35]. As is shown by Fig. 2, there exists a reasonable linear relationship between $-\ln(1-Z)$ and reaction time t.

The effect of temperature on the polymerization process was determined at a dose rate of 0,50 kGy/h and a monomer concentration of 40 mole per cent over the

temperature range of −63 °C to 0 °C. The resulting Arrhenius plot is shown in Fig. 3, from which an activation energy of 7,66 kJ/mole was calculated. This value is considerably lower than the value of 18,0 kJ/mole reported by Tabata [3?]. The value of 18,0 kJ/mole reported by Tabata must be viewed with suspicion, as an examination of Tabata's data appears to show that they are incomplete.

The number-average molecular mass M_n of the product PTFE obtained from the in-source polymerization of TFE in Freon-22 ranged from 2×10^4 to 6×10^4 and was relatively independent of conversion and reaction temperature. The above values are lower than expected and may result from the presence of chain transfer processes.
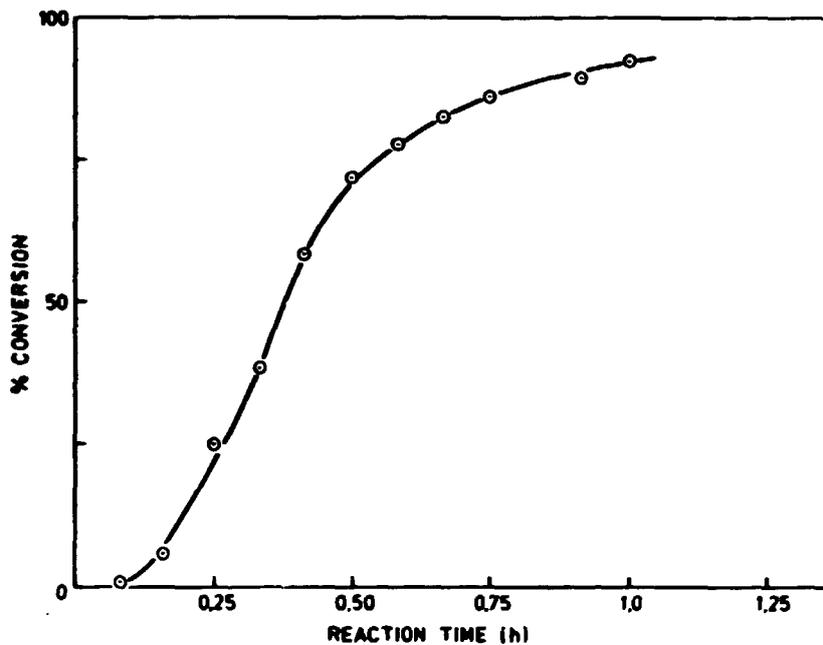

Fig. 1

Solution-phase polymerization of tetrafluoroethylene in Freon-22 at −42 °C, a dose rate of 0,50 kGy/h and a monomer concentration of 40 mole per cent.
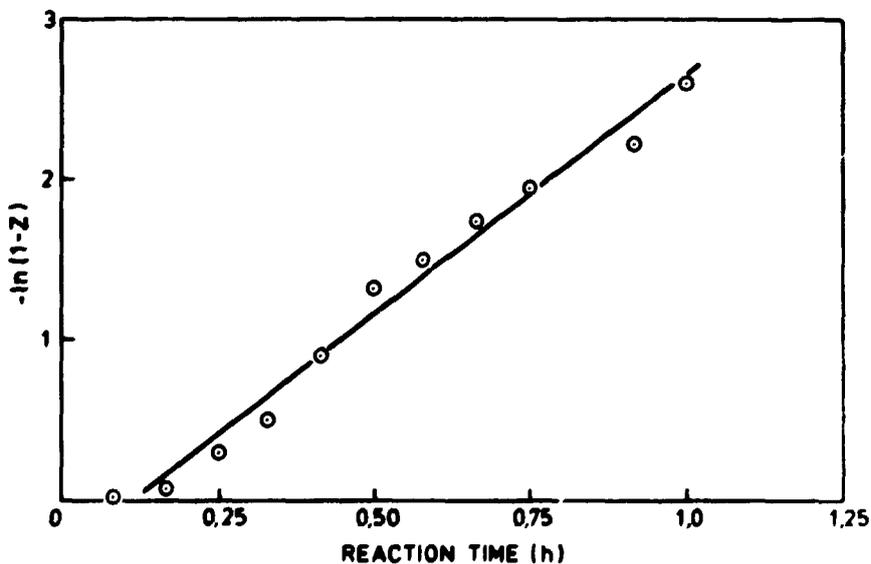

Fig. 2

Test of first-order reaction kinetics of the solution-phase polymerization of tetrafluoroethylene in Freon-22 at −42 °C, a dose rate of 0,50 kGy/h and a monomer concentration of 40 mole per cent.
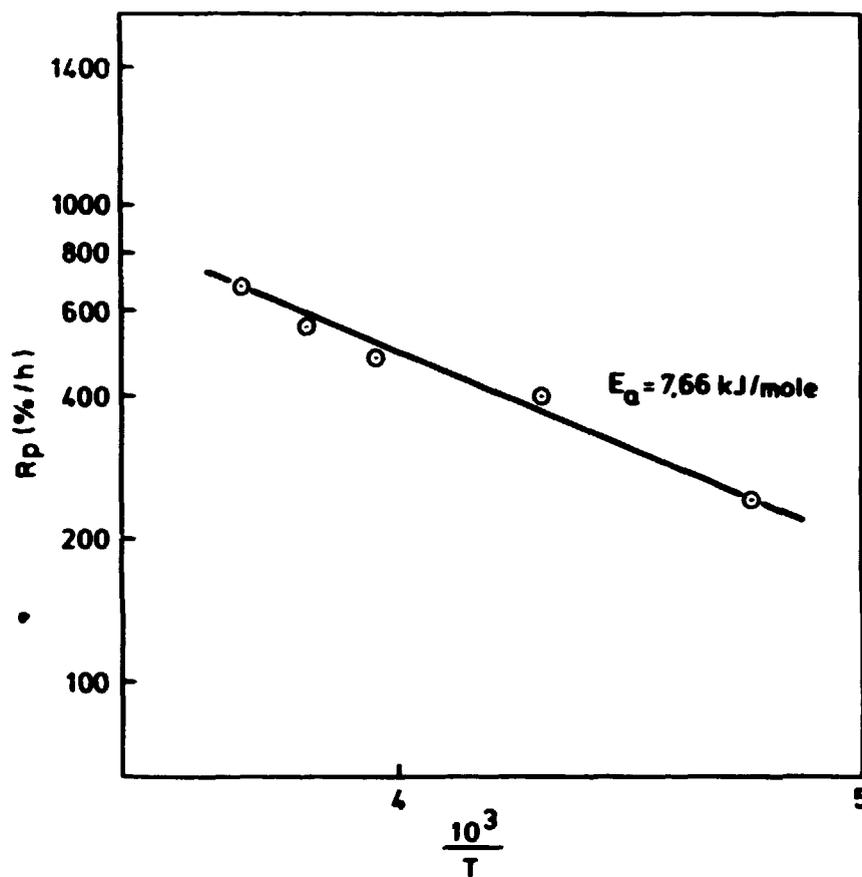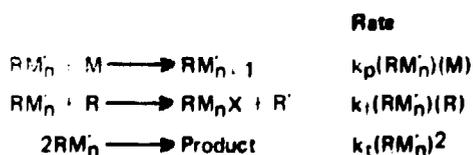
Fig. 3

Rate of polymerization of tetrafluoroethylene in Freon-22
as a function of the irradiation temperature at a dose rate
of 0,50 kGy/h and a monomer concentration of 40 mole
per cent.

4.2 Postpolymerization

Post-irradiation polymerization of TFE in Freon-22 was
carried out at $-20\,^{\circ}C$ and at an initial monomer
concentration of 40 mole per cent. The initial radiation
polymerization was at $-42\,^{\circ}C$ and at a dose rate of
0,50 kGy/h for a period of 15 min. The monomer solution
was radiation-polymerized to a conversion of 16 %, and
after removal from the radiation field the polymerization
process was allowed to proceed unaided to a conversion of
86 %. In Fig. 4 is seen a plot of conversion as a function of
reaction time.

The following reaction sequence may be written for the
postpolymerization process

	Rate
$RM_n + M \longrightarrow RM_{n+1}$	$k_p(RM_n)(M)$
$RM_n + R \longrightarrow RM_nX + R'$	$k_t(RM_n)(R)$
$2RM_n \longrightarrow$ Product	$k_t(RM_n)^2$

From the above reaction sequence the rate of
polymerization may be written as

$$R_p = k_p(RM_n)(M) \qquad \qquad (3)$$

Equation (3) does indicate a first-order dependence of the
rate of polymerization R_p on the monomer concentration.
Indeed, Fig. 5 shows the first-order dependence of R_p on
monomer concentration. Based on the above reaction
scheme it has been shown that the conversion to polymer
may be represented by eqn. (4) where conversion Z is a
function of $\ln(t)$ [33,36]. A plot of Z as a function of $\ln(t)$
shown in Fig. 6 indicates a linear relation. This is further
confirmation that the postpolymerization of TFE in
Freon-22 proceeds by means of the usual polymerization
reaction sequence.

$$Z = k_p k_t^{-1/2} \ln(1 - k_t(RM_n)_0 t) \qquad \qquad (4)$$

It was hoped that the postpolymerization process would
permit a significant increase in the rather low molecular
masses obtained for product PTFE produced by the
in-source process. However, this was not the case. The
results from a typical polymerization experiment are shown
in Table III. For all practical purposes no significant
increase in molecular mass occurs during the

post-irradiation polymerization of TFE in Freon-22, and the value of 1×10^6 reported by Tabata [33] could not be duplicated. The fact that the rate of polymerization was high and the molecular mass relatively constant can best be explained by assuming that chain transfer occurs to a significant extent. This should not be unexpected for Freon-22. For example, the specific rates of chlorine and fluorine abstraction by the $-CF_2$ end-group free radical from Freon-22 are $1,4 \times 10^4$ and $9,0 \times 10^4$ 1/mole.s respectively. By way of comparison the same abstraction rates for Freon-12 are only 1,0 and 2,5 1/mole.s respectively [37]. Clearly a fully halogenated solvent such as Freon-12 would appear to be a superior solvent to Freon-22 for the production of high-molecular-mass PTFE. Certainly the production of high-molecular-mass PTFE does

not seem convenient using the Freon-22 solvent system.

Table III
Post-irradiation polymerization of Freon-22 at −20 °C and an initial monomer concentration of 40 mole per cent

Reaction Time(h)	% Conversion	$\bar{M}_n$
0	16	$2,7 \times 10^4$
0,5	40	$6,7 \times 10^4$
1	62	$3,9 \times 10^4$
2	70	$6,4 \times 10^4$
3	80	$2,1 \times 10^4$

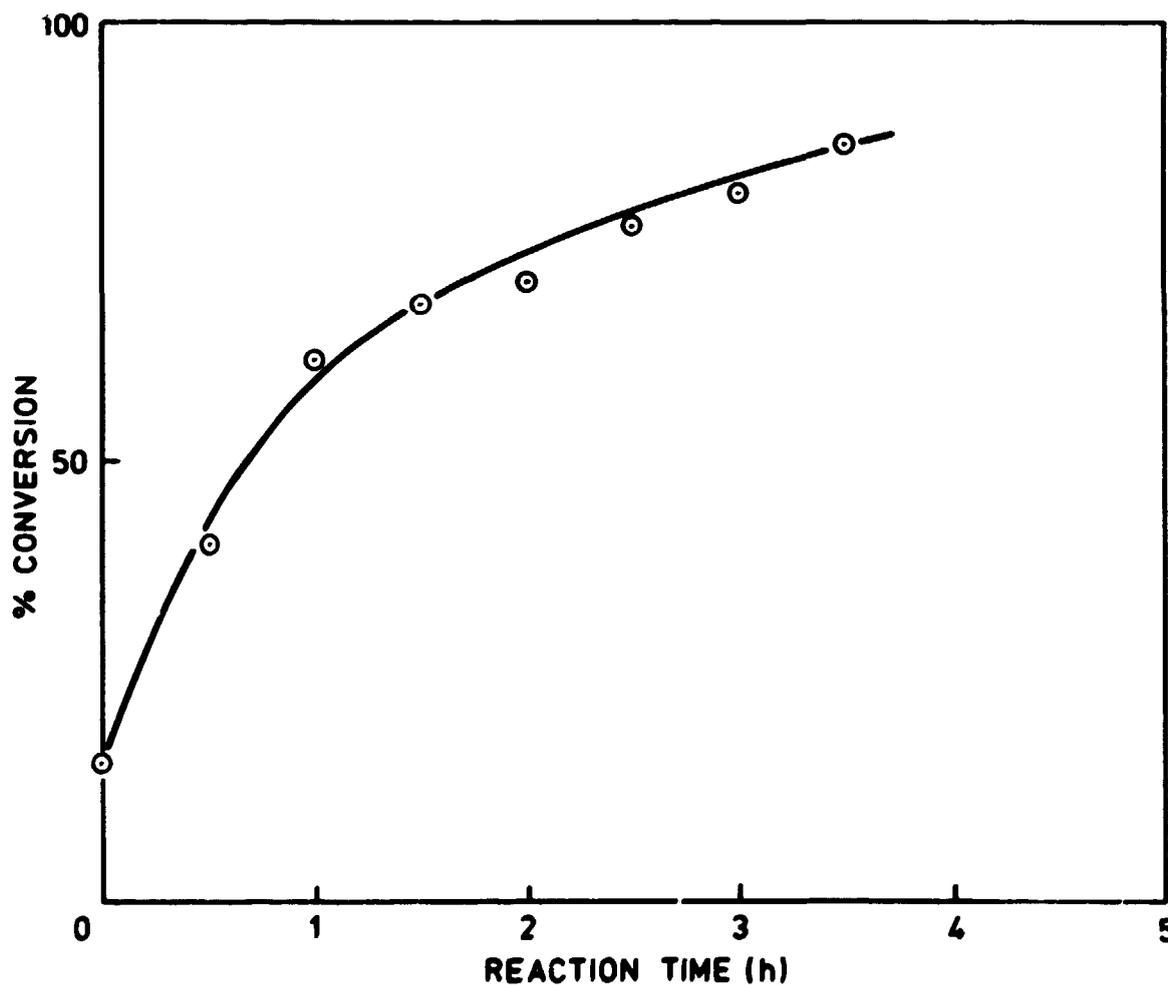*Fig. 4*
Post-irradiation polymerization of tetrafluoroethylene in Freon-22 at −20 °C and a monomer concentration of 40 mole per cent. Irradiation polymerization was at −42 °C and at a dose rate of 0,50 kGy/h for a period of 15 min.
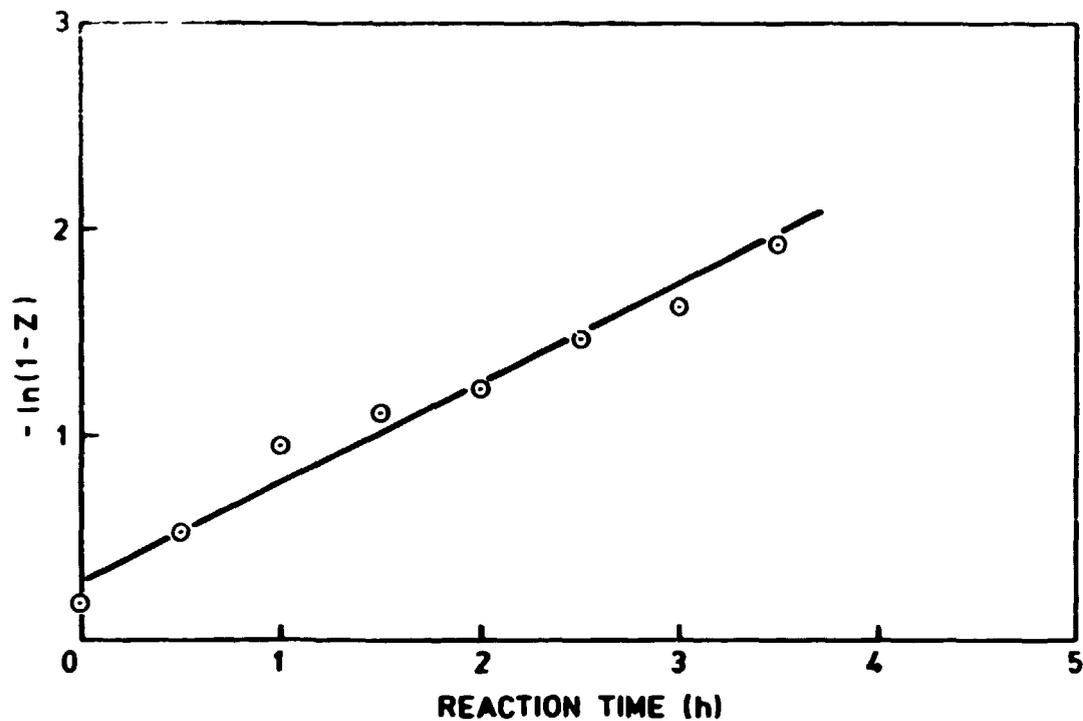
Fig. 5.

Test of first-order reaction kinetics with respect to monomer concentration for the post-irradiation polymerization of tetrafluoroethylene in Freon-22 at −20 °C and a monomer concentration of 40 mole per cent.
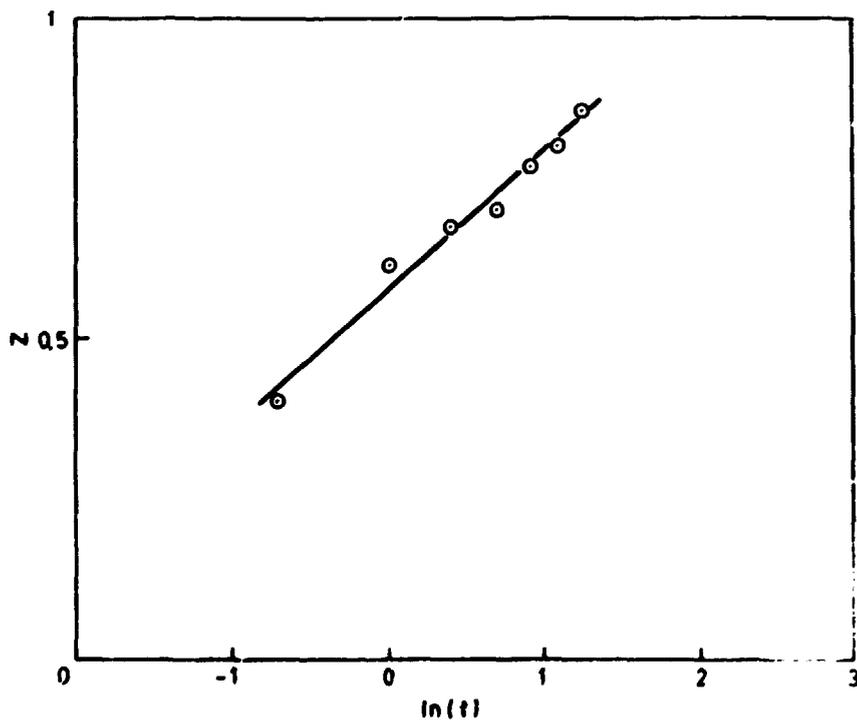

Fig. 6

Plot of conversion as a function of the logarithm of reaction time for the post-irradiation polymerization of tetrafluoroethylene in Freon-22 at −20 °C and a monomer concentration of 40 mole per cent.

5. ACKNOWLEDGEMENTS

6. REFERENCES

1. Booth, H.S.; Bixby, E.M. *Ind. Eng. Chem.* (1932) v. 24 p. 637.

2. Benning, A.F. *US Patent* 2 450 414 (1948).

3. Baldwin, R.H. *US Patent* 2 640 086 (1953).

4. Posta, A.; Hudlicky, M. *Chem. Listy* (1957) v. 51 p. 976.

5. Takizaki, K.; Matsushima, H.; Hirose, K.; Ito, G. *Jap Patent* 7366 (1958).

6. Belf, L.J. *Brit Patent* 816 622 (1959).

7. Olah, G.; Paulath, A. *Acta Chim. Acad. Sci. Hung.* (1954) v. 4 p. 89.

8. Brit Patent 668 609 (1952).

9. Snavely, Jr., W.H.; Mann, P.J. *Belg Patent* 631 356 (1963).

10. Downing, F.B.; Benning, A.F.; McHarness, R.C. *US Patent* 2 384 821 (1945).

11. Park, J.D.; Benning, A.F.; J.F. Laucius; McHarness, R.C. *Ind. Eng. Chem.* (1947) v. 39 p. 354.

12. Downing, F.B.; Benning, A.F.; McHarness, R.C. *US Patent* 2 551 573 (1951).

13. Brit Patent 732 269 (1955).

14. Wada, H. *Ger Patent* 1 228 601 (1966).

15. Revel, K.S. *Brit Patent* 983 222 (1965).

16. Gozza, F.; Ragazzini, M. *Fr Patent* 1 369 777 (1964).

17. Fr Patent 1 354 341 (1964).

18. Farlow, M.W.; Muetterties, E.T. *US Patent* 2 732 410 (1956).

19. Muetterties, E.L. *US Patent* 2 709 189 (1955).

20. Lewis, E.E.; Naylor, M.A. *J. Am. Chem. Soc.* (1947) v. 69, p. 1968.

21. Benning, A.F.; Downing, F.B; Plunkett, R. *US Patent* 2 401 897 (1946).

22. Wiseman, P. *An Introduction to Industrial Organic Chemistry.* Applied Science, London (1972) p. 144.

23. Gozzo, F.; Patrick, C.R. *Tetrahedron* (1966) v. 22 p. 3329.

24. Dorough, G.L. *US Patent* 2 398 976 (1946).

25. Hanford, W.E.; Joyce, R.M. *J. Am. Chem. Soc.* (1947) v. 68 p. 2082.

26. Krespan, C.G. *US Patent* 2 938 889 (1960).

27. Joyce, Jr., R.M. *US Patent* 2 394 243 (1946).

28. Smith, R.P. *Brit Patent* 836 741 (1960).

29. Ref. 22, *Loc. cit.*, p. 252.

30. Tabata, Y.; Sobue, H.; Shibano, H. *Annual Report of Jap. Assoc. for Radiation Research on Polymers* (1960) v. 2 p. 334.

31. Tabata, Y.; Shibano, H.; Oshima, K.; Sobue, H. *J. Polym. Sci.* (1967) Part C p. 2403.

32. Tabata, Y.; Ito, W.; Oshima, K. *J. Macromol. Sci.-Chem.* (1970) v. A4 p. 789.

33. Tabata, Y.; Ito, W.; Oshima, K.; Takagi, J. *J. Macromol. Sci.-Chem.* (1970) v. A4 p. 815.

34. Suwa, T.; Takehisa, M.; Machi, S. *J. Applied Polym. Sci.* (1973) v. 17 p. 3253.

35. Levenspiel, O. *Chemical Reaction Engineering* John Wiley and Sons, New York (1967) p. 48.

36. Chapiro, A. *Radiation Chemistry of Polymeric Systems, High Polymers Volume XV* Interscience, London (1962) p. 211.

37. Hisasue, M.; Ukihashi, H.; Tabata, Y. *J. Macromol. Sci.-Chem.* (1973) v. A7 p. 795.