Polytetrafluoroethylene: Synthesis and Characterization of the Original Extreme Polymer

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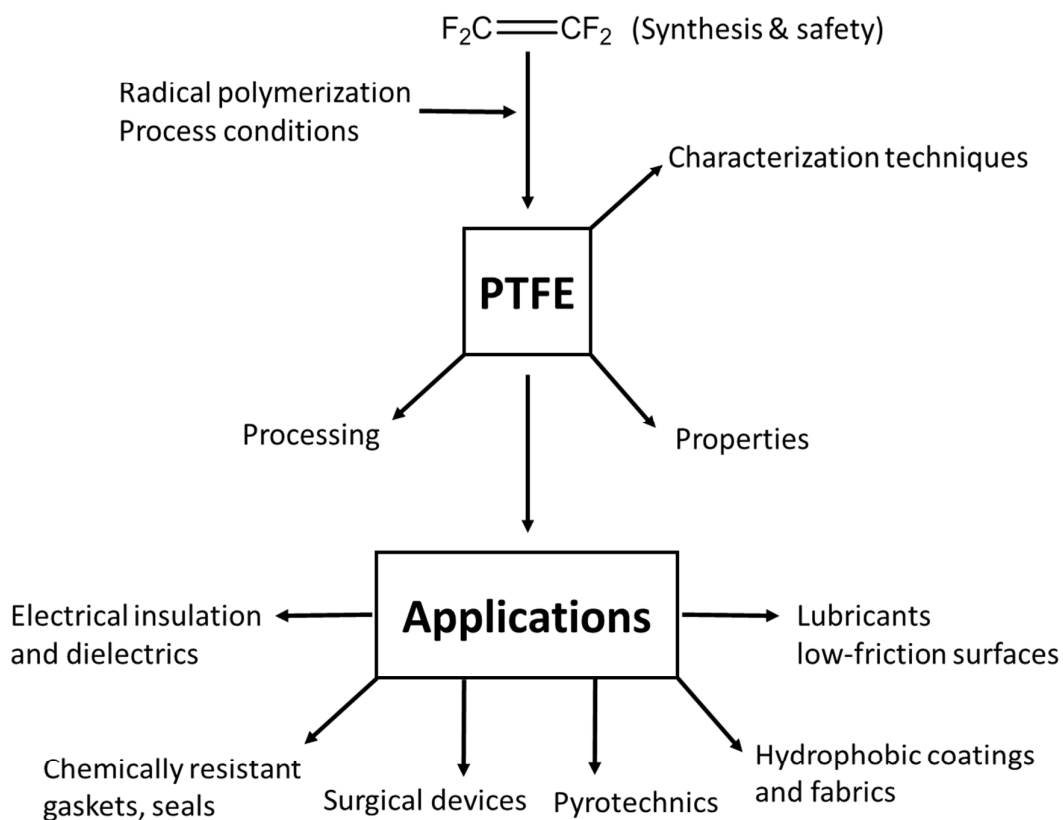
ABSTRACT

This review aims to be a comprehensive, authoritative, and critical review of general interest to the chemistry community (both academia and industry) as it contains an extensive overview of all published data on the homopolymerization of tetrafluoroethylene (TFE), detailing the TFE homopolymerization process and the resulting chemical and physical properties. Several reviews and encyclopedia chapters on the properties and applications of fluoropolymers in general have been published, including various reviews that extensively report copolymers of TFE (listed below). Despite this, a thorough review of the specific methods of synthesis of the homopolymer, and the relationships between synthesis conditions and the physico-chemical properties of the material prepared, has not been available. This review intends to fill that gap.

As known, PTFE and its marginally modified derivatives comprise some 60-65 % of the total international fluoropolymer market with a global increase of ca. 7 % per annum of its production. Numerous companies, such as Asahi Glass, Solvay Specialty Polymers, Daikin, DuPont/Chemours, Juhua, 3F and 3M/Dyneon, etc., produce TFE homopolymers. Such polymers, both high molecular-mass materials and waxes, are chemically inert, hydrophobic, and exhibit an excellent thermal stability as well as an exceptionally low co-efficient of friction. These polymers find use in applications ranging from coatings and lubrication to pyrotechnics, and an extensive industry (electronic, aerospace, wires and cables, as well as textiles) has been built around them. South Africa, being the third largest producer of fluorspar (CaF_2), the precursor to hydrogen fluoride and fluorine, has embarked on an industrial initiative to locally beneficiate its fluorspar reserves, with the local production of fluoropolymers being one projected outcome. As our manuscript focuses specifically on the homopolymerization of TFE (the starting point for all fluoropolymer industries), it will be of considerable use to start-up companies and other commercial entities looking to enter the fluoropolymer market, as well as end-user companies.

After a short discussion on the synthesis and production of TFE (both at industrial and laboratory scales), including the safety aspects surrounding handling (since that monomer is regarded as explosive if brought into contact with oxygen due to the formation of peroxides), transport and storage, and then expands into detailed discussions dealing with aspects such as the various additives used (buffers, chain transfer agents, surfactants etc.), the solvent environment, and the reaction conditions. A further section reports the properties of PTFE with respect to the polymerization conditions as well as an overview on the specialized techniques used to characterize PTFE. Finally, the applications of PTFE into various topics, ranging from electrical insulation, tribological to medical applications, as well as chemically resistant coatings and pyrotechnics are discussed.

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1   INTRODUCTION

Fluorinated polymers are niche macromolecules that play an integral role in modern life [1-10]. Largely due to the properties of fluorine (including, among others, large electronegativity, low polarizability, and small van der Waals radius (1.32 Å)) and to the strong C−F bonds (485 kJ·mol^{-1}), they exhibit unique and remarkable attributes. Their applications span engineering thermoplastics and high performance elastomers for the chemical-process, automotive, and aeronautics industries, weather-proof coatings, biomedical materials, membranes for use in Li-ion batteries, fuel cells and water purification, and many more [2-6,11-15].

Among the fluoropolymers, PTFE (the homopolymer of tetrafluoroethylene) and its marginally modified derivatives rank first, comprising some 60 % of the total international fluoropolymer market in 2015 [16,17], with a global production increase of *ca.* 7 % per annum. These polymers, both high-molecular-mass materials and waxes, are chemically inert, hydrophobic, and exhibit superb thermal stability as well as an exceptionally low coefficient of friction. Numerous companies, such as 3M/Dyneon, 3F, Asahi Glass Corp. (now AGC), Chemours (formerly part of E.I. du Pont de Nemours and Company, hereafter collectively referred to as DuPont/Chemours), Daikin, Gore, Juhua, Solvay Specialty Polymers, Zeus, *etc.*, produce TFE homopolymers. These polymers find use in applications ranging from coatings and lubrication to pyrotechnics, and extensive industries (electronic, aerospace, wires and cables, as well as textiles) have been built around them.

In 1938, Plunkett [18] pioneered the polymerization of tetrafluoroethylene (TFE) under autogenous pressure at 25 °C. The gas was found to autopolymerize at 25 °C, and produced white, dusty powders. The gas was also found to polymerize to foam-like, low-molecular-weight waxes in the presence of $AgNO_3$ and $AgNO_3$ / MeOH mixtures. Plunkett's patent also contained the first known report of PTFE depolymerization, stating that the substance formed in the presence of $AgNO_3$ decomposed to TFE, leaving behind only a small amount of proper polymer.

Brubaker [19] subsequently published, comprehensively, the method for free radical suspension polymerization of TFE in an aqueous medium, using alkali or ammonium persulfate (at 0.1 % mass basis or 0.3 % mol basis) as well as an alkaline buffer (0.5 to 1 % by mass of TFE).

A large number of publications on the homo- and copolymerization of TFE followed (*cf.* [13,20-36]), spanning processes such as free-radical-, coordination- [37], and electrochemical polymerization [38,39], with even plasma-type polymerization being reported [40-43]. So far, a little over 3000 publications have been logged in the publically accessible databases. Figure 1 summarizes the

number of patent- and academic publications each year related to the homo- and copolymerization of TFE. The number of academic publications has been steadily decreasing in the last two decades, reflecting the shrinking academic interest in TFE polymerization. In contrast, number of patent grants has been steadily increasing, reflecting that research into TFE polymerization is still of commercial importance.

It must be noted here that the publications originating from universities and other academic institutions are achieved mostly in collaboration with industry. As far as is known, only Clemson University in the USA, the University of Ottawa in Canada, and the University of Pretoria in South Africa have direct access to multi-gram quantities of TFE and operate independently from commercial entities (Clemson University boasts a multi-kilogram scale TFE generation facility).
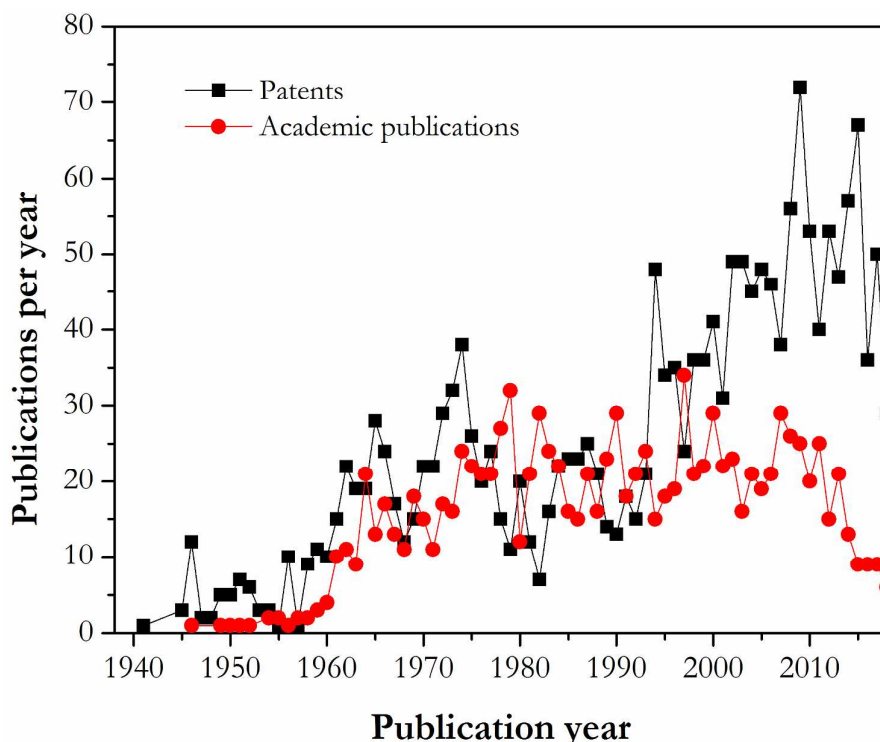
Figure 1:   *Number of publications per year relating to TFE homo- and copolymerization (compiled via the Sci-Finder database).*

Free-radical polymerization remains the most commonly employed method for synthesizing TFE high polymers. Suspension polymerization retains the lion's share of the market, but emulsion polymerization using fluorinated surfactants is also widely employed.

Every commercial producer of PTFE has its own synthesis strategies, and there have been many contradictions in the literature regarding the most effective initiators, optimal reaction

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conditions, and polymer properties as a function of reaction conditions. These contradictions are seemingly due to the fact that only a hand full of commercial entities are capable of managing TFE and they have a financial interest in keeping the technical details of their operations secret.

The objective of this review is to summarize the literature regarding the homopolymerization of TFE. For the sake of convenience to the experimentalist, the literature is discussed in sections organized around the important features of the polymerization procedure, starting with an overview of the various routes to synthesize TFE, before discussing the engineering aspects, including safety, of the polymerization process, followed by an overview of the initiators employed with TFE. The next section discusses the reaction conditions, with special emphasis on monomer purity, solvent environment, temperature and pressure as well as the various polymer additives, including chain transfer agents. Thereafter, the properties of PTFE, as a function of the polymerization conditions are highlighted, followed by a summary of the analytical techniques particular to the analysis of PTFE. The last section provides an overview of the applications of PTFE.

2 SYNTHESIS OF TFE AND CONCOMITANT SAFETY ASPECTS

TFE (CAS No: 116-14-3) is an odorless, colorless, and flammable gas with a density greater than air. TFE is highly unstable under certain conditions, and if heated to above 380 °C the monomer may undergo autodecomposition to carbon and CF_4 [44] and may self-polymerize under pressure or under adiabatic compression [18]. The salient physical and chemical properties of TFE are presented in Table 1.

Table 1: *The physical and chemical properties of TFE (CAS No: 116-14-3).*

Property	Unit and value			Reference
Molecular weight	$(g \cdot mol^{-1})$		100.016	
Heat of formation	$(MJ \cdot mol^{-1})$		-63.31	[45]
Heat of combustion	$(kJ \cdot mol^{-1})$		-674	[45]
Heat of polymerization	$(kJ \cdot mol^{-1})$		-196	[46]
Melting point	(°C)		-142.5	[47]
Boiling point	(°C)	[101.325 kPa]	-76.3	[47]
Triple point	(°C)		-131.2	[48]
Solid density	$(g \cdot cm^{-3})$	[-173.15 °C]	2.1	[49]
Liquid density	$(g \cdot cm^{-3})$	[-76.3 °C]	1.519	[50]
		[-142.5 °C]	1793	[50]
Critical temperature	(°C)		33.3	[51]
Critical pressure	(bar)		39.44	[51]
Critical density	$(g \cdot cm^{-3})$		0.5815	[51]
Acentric factor			0.226	[51]
Solubility		Water at 25 °C	153 $mg \cdot L^{-1}$	[52,53]

TFE cannot be obtained easily from commercial sources, although small quantities can be purchased from specialty chemical suppliers. Transport legislation varies by country and, in the continental USA, bulk transport of the stabilized liquid is permitted. However, most commercially-produced TFE is generated at the usage site, mainly due to safety and regulatory considerations, but also due to the cost of transport. Stabilized TFE has the UN number 1081 and falls in transport class 2 with a classification of 2F. TFE is typically stabilized with monoterpenes (see Section 2.5.2).

Numerous methods to produce TFE have been reported with the most salient examples being ultra-fast pyrolysis of chlorodifluoromethane (R-22 or F-22), ultra-fast plasma pyrolysis of tetrafluoromethane [54,55], dechlorination of CF_2Cl-CF_2Cl, or the debromination of CF_2Br-CF_2Br, pyrolysis of trifluoroacetic acid [56] or the alkali salts of perfluoropropanoic acid [57], and the

pyrolysis of PTFE under vacuum [1]. These methods have been extensively reviewed elsewhere [58] and are summarized in Scheme 1. The following discussion is a brief overview of the synthetic routes for TFE production.
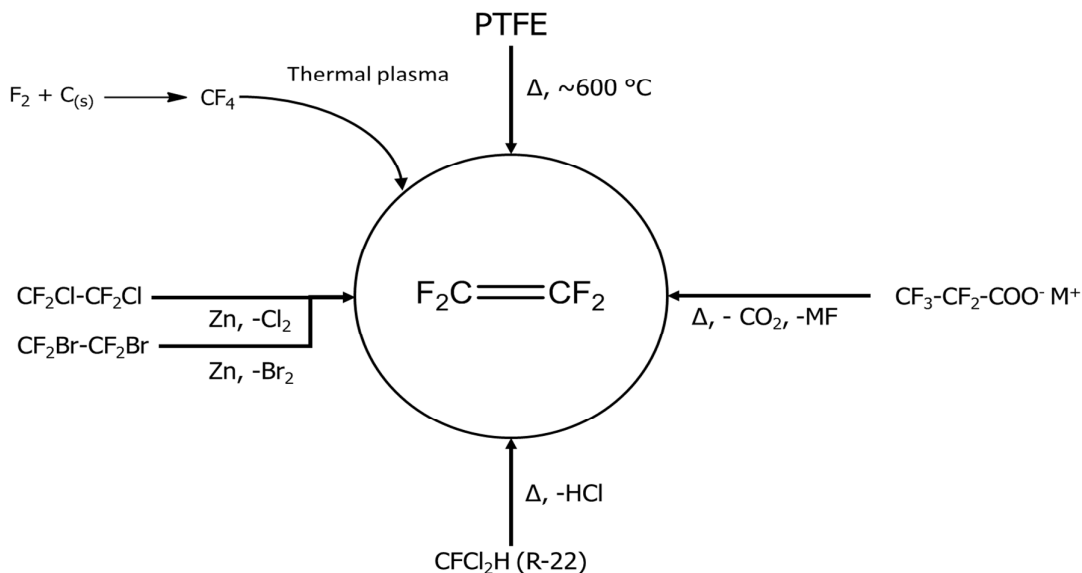
Scheme 1: *Common synthetic routes for the production of TFE.*

2.1 Ultra-fast pyrolysis of CF_2ClH

The industrial synthesis of TFE follows the chlorodifluoromethane route, as depicted in Scheme 2[59,60]. Variations of this method substitute the CF_2ClH for trifluoromethane.

$$CHCl_3 \quad + \quad HF \quad \xrightarrow[SbF_3]{80\ °C} \quad CHClF_2 \quad + \quad Byproducts$$

$$CHClF_2 \quad \xrightarrow[1\ atm.]{750\ °C\ -\ 950\ °C} \quad F_2C{=}CF_2 \quad + \quad Byproducts$$
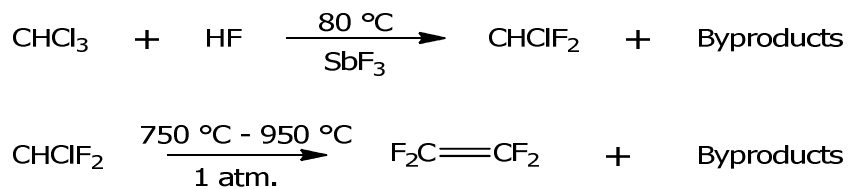
Scheme 2: *The route for the industrial synthesis of TFE via the ultra-fast pyrolysis of chlorodifluoromethane (R-22).*

The major drawback of this, and most other routes is the production of byproducts such as HF, HCl, perfluorocarbon- (such as hexafluoropropylene (HFP), perfluoroisobutene (PFIB), *etc*.), and chlorofluorocarbon side products that must be scrubbed or cryogenically distilled from the TFE. Besides being dirty, such processes require costly equipment and are difficult to operate in batch. Therefore, the ultra-fast methods are not readily usable on a laboratory scale. In contrast, pyrolysis of R-22 is the preferred industrial method. A continuous process can be optimized to

be relatively clean due to HF and HCl recycling, and economy-of-scale makes the process financially attractive.

2.2   Dehalogenation of halofluorocarbons

The first reasonable option for laboratory scale synthesis of TFE is the dechlorination of CF_2Cl-CF_2Cl with zinc [61,62]. The method is facile and safe, calling for the batch reaction of the symmetric chlorofluorocarbon with high surface area zinc dust using methanol as solvent. The reaction takes place from 70 °C and good yields are obtained in reasonable time scales (~5 hours), with non-condensable product consisting of ~ 95 % to 98 % TFE. Availability of the starting material is the only major technical drawback to employing this method as most of the starting materials are banned under the Montreal Protocol [63] due to their ozone depleting potential. An alternative method includes the debromination of CF_2Br-CF_2Br [64].

2.3   Pyrolysis of perfluoropropanoic acid salts

A second option for TFE production is the alkali salt pyrolysis route, which produces CO_2 and TFE in a 1:1 ratio as well as a metal fluoride [57]. This method is facile and safe, but generation of completely pure TFE requires the removal of CO_2 from the gas mixture. This method is not exceptionally expensive, provided one has ready access to commercial entities that can supply the acids. This is the only method of synthesis employed by the Thrasher's Group at Clemson University [57].

2.4   Pyrolysis of PTFE under vacuum

The remaining option for TFE generation on a laboratory scale is the vacuum pyrolysis of PTFE. This option has already been pursued to a great extent in the Fluoro-Materials Group at the University of Pretoria and in the research group at the University of Ottawa. The literature on the pyrolysis of PTFE has already been reviewed[6,65-67]. PTFE may be pyrolyzed under vacuum of around 1 Pa and at 600 °C to yield nearly pure (99.5 %) TFE, with minor amounts of HFP, octafluorocyclobutane (OFCB), and the perfluorobutene isomers. The pyrolysis reactions are summarized in Scheme 3 and Scheme 4. This method is facile and does not require any expensive reagents or costly and complex process equipment. The kilogram-scale PTFE pyrolysis reactor built at the University of Pretoria is shown in Figure 2.
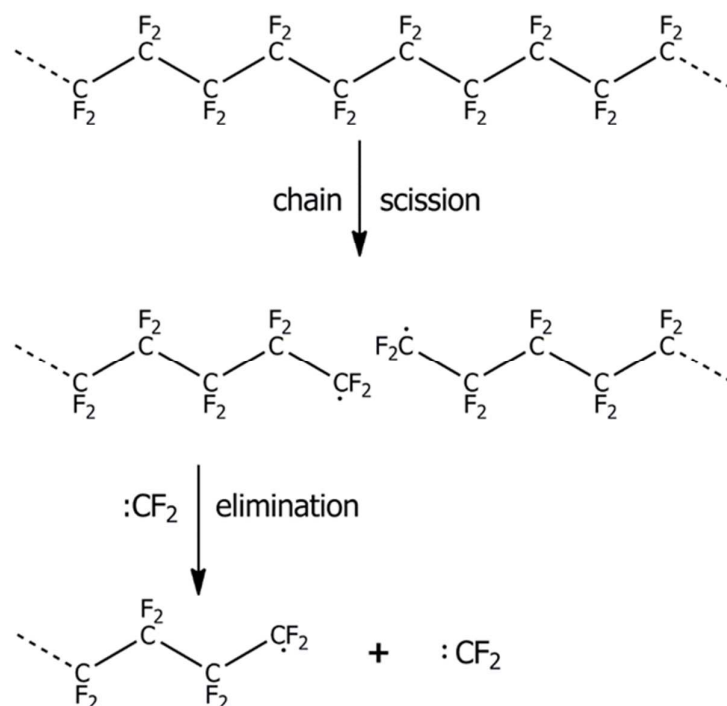
Scheme 3:   *Mechanism of PTFE breakdown by thermal chain scission to release difluorocarbene.*

Extreme care must be taken with the pyrolysis of PTFE as improper pyrolysis conditions will lead to the production of large quantities of perfluorobutene compounds [67]. The effects of temperature and pressure on the composition of the pyrolysis stream has been documented in detail by Bezuidenhoudt *et al.* [67].

Among these by-products, perfluoroisobutene is the most dangerous. This species, existing as a gas at ambient conditions, is classed as a schedule 2 chemical weapon, and its production is banned by treaty [68]. Upper limits on the lethal concentrations for rats of 0.5 ppm in air [69] have been reported and lower limits for the toxicity have been reported in the 150 ppb range [70,71]. The compound primarily attacks the lungs, causing pulmonary oedema [72,73].

Proper containment and analysis of the pyrolysis gas before use in polymerization is critically important, as is the destruction of the leftover gas or any pyrolysis gas that contains too high a level of these toxic perfluorobutenes.
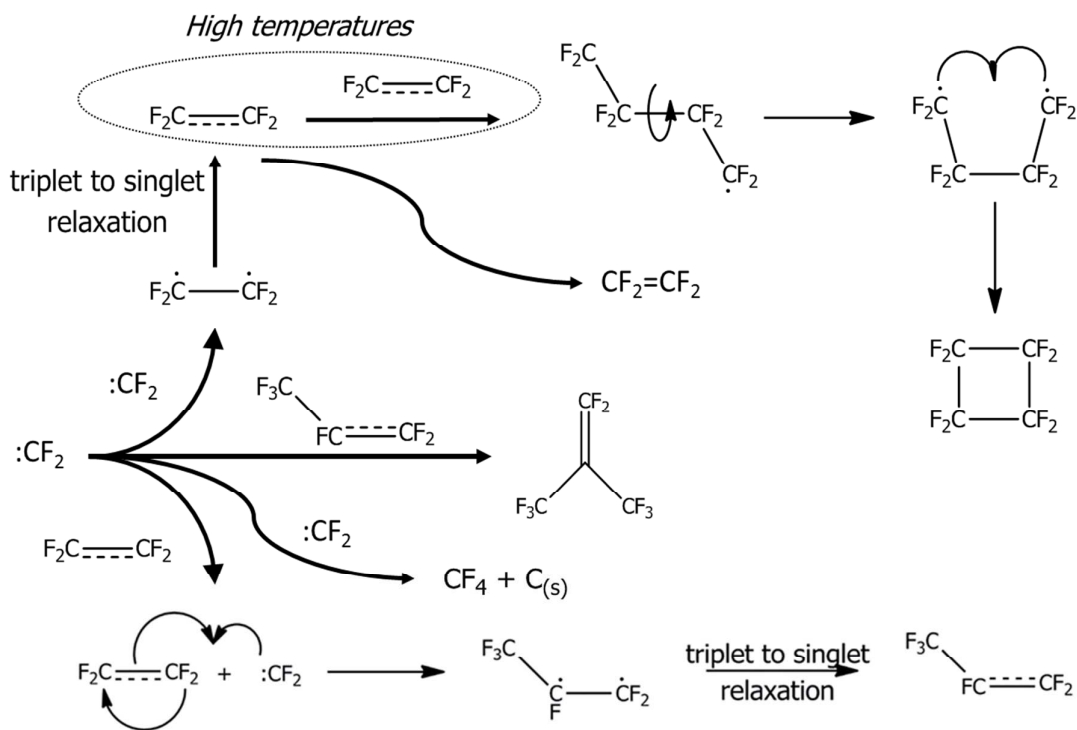
Scheme 4: *Gaseous radical reactions occurring during PTFE pyrolysis that leads to the formation of TFE and fluorocarbon by-products [74].*

2.5   TFE process safety

Safety is paramount when considering working with TFE and it can- and, due to lack of caution on the part of research or production staff, often does deflagrate. While 1- or 2-g quantities may burst a tube or a cylinder, larger amounts tend to do significant damage to infrastructure. At the 10 or 20 g scale, the detonating power of enclosed TFE is something to that even the most cautious and talented experimenters have respect for.

The companies and public entities that engage in working with TFE have developed facilities and expertise through long years of trial and error, many times at the cost of human life. Thrasher's group at Clemson University has spent years developing academic barricades to permit the safe use of large quantities of TFE in their facilities, and their recent book chapter on the topic is comprehensive[75].

The safety aspects detailed here are meant to guide and inform, but are no substitutes for experience. All work undertaken with TFE should first be carried out in sub-gram quantities before being scaled up to any size.

2.5.1   Autogenic decomposition of TFE

TFE is dangerous to work with and care must be taken to avoid subjecting TFE to conditions where it may autopolymerize or decompose. The mechanism of decomposition has been reported in detail [6,44,76-80]. In summary, TFE does not exist in ethylenic form *per se*; that is, electronic and steric factors perturb the electron distribution in the π-orbital to such an extent that the molecule exists as a biradicalloid and not as a canonical ethylenic species [81]. This in turn translates to a molecule that can very easily undergo addition reactions, and TFE may easily undergo self-addition to form cyclo-octafluorobutane (ΔH_R = -103 kJ/mol) [82]. From the heat provided by this reaction, other addition and rearrangement reactions (see Scheme 4 and Scheme 5), and ultimately, rearrangement to form CF_4 and carbon (ΔH_R = -257 kJ·mol^{-1}) may occur.
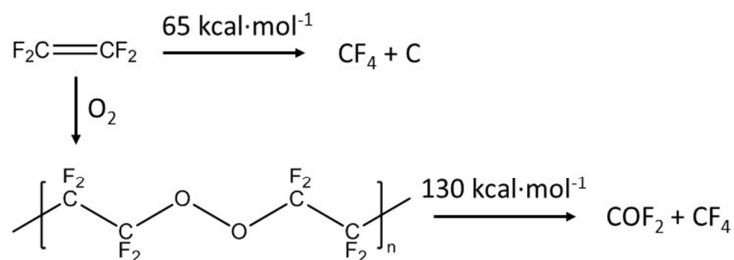
Scheme 5: Possible reaction pathways of TFE that lead to the formation of CF_4

The kinetics of these reactions are strong functions of pressure and temperature, and they occur very slowly, if at all, at room temperature. But, if the pressure and temperature at any point in the gas are such that sufficient internal energy is available for the TFE to undergo cyclization, local "hotspots" may occur that precipitate runaway decomposition reactions. This leads to tremendous pressure spikes and the concomitant explosion of the containing vessel. Studies on the thermal decomposition of TFE in both small (1-L) and large volume (100-L) vessels indicate that the autodecomposition temperature decreases with pressure and decreases with reactor volume [44,76].
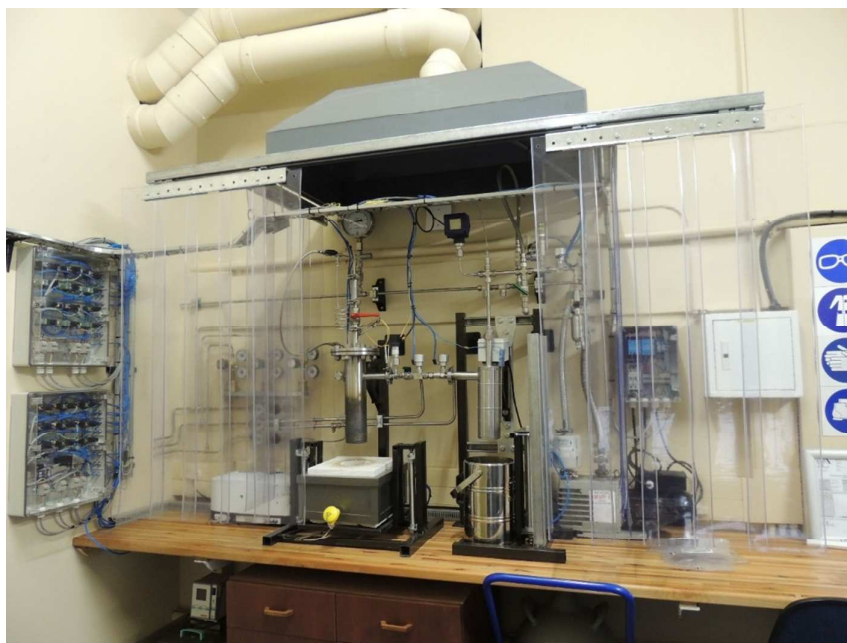
Figure 2:   *The kilogram-scale PTFE pyrolysis reactor built at the University of Pretoria.*

The effect of volume is inferred to be related to an increase in internal vessel surface area. The rearrangement reaction to form CF_4 and carbon may occur in the gas phase, but requires high temperatures (which may also be induced by rapid changes in pressure). Provision of a metal surface on which the gas may rearrange greatly increases the reaction rate and contributes to a lower decomposition temperature. This also implies that the inner diameter of the pipes through which TFE is fed should be as small as possible. There is some evidence that the nickel and chromium in stainless steels and other alloys used in the fluorochemical industry act as catalysts for this rearrangement [65,66,83].

Institutions working with TFE have all developed their own rules for handling TFE. Three rules of thumb can be extracted from the literature:

1) Do not heat TFE above 100 °C when the gas is under a pressure greater than 15 bar.

2) Furthermore, as seen in the case studies [79,84] of the explosions of TFE-polymerization plants, pressure shockwaves and other large fluctuations in pressure within the gas also have the potential to cause decomposition *via* adiabatic heating of the compressed gas to deflagration temperatures. Therefore, do not subject TFE to large pressure changes at any temperature. A technical implication of this rule is that TFE should not be subjected to sudden, drastic changes in flow path diameter. That is, tubing should be of a consistent size throughout and any valves employed should have internal diameters of size similar to the tubing. In a similar vein, the flow

of TFE through a valve should be sufficiently slow to ensure that there is little frictional heating of the gas. This also implies that one should avoid sharp bends in pipes and fittings to eliminate high-shear flow of the gas.

3) Finally, oxygen may act as both inhibitor and initiator to radical polymerization [85]. In the case of TFE, the presence of oxygen will not only inhibit polymerization, but will also worsen any decomposition reaction [80]. Indeed, if sufficient oxygen is present alongside TFE, it may initiate a spontaneous decomposition under pressure. Molecular oxygen also caps the PTFE macroradical, forming unstable peroxides (see Figure 3) [86]. Therefore, it is required to rigorously scrub free oxygen from any closed system containing TFE.
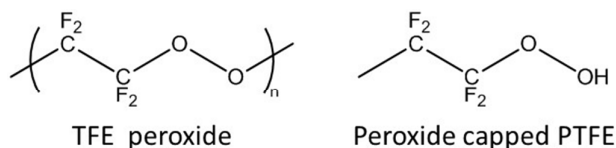
Figure 3: Structures of TFE and PTFE peroxides [86,87].

2.5.2 Storage of TFE

Prolonged storage at pressures greater than about 2.2 bar is not recommended without addition of a radical scavenger. Various amine-based stabilizers [88] are employed in industry and small amounts of limonene, or other monoterpenes may also be used to stabilize TFE for indefinite storage [89]. The patent literature indicates that the monoterpenes form gum-like deposits on prolonged storage due to their reaction with the minute amounts of oxygen, as well as with any other radical forming species, present in the TFE gas. Therefore, the monoterpenes have been superseded by alpha-methyl-vinyl-toluene [90], which permits high pressure transport of the gas without gumming up pipes and valves, *etc.* Typically 0.5 mol % (TFE basis) of the vinyl toluene should be used, but this value may increase depending on the amount of oxygen introduced into the TFE by back diffusion through system leaks during transfer operations. Usually, such contamination falls in the low-single-digit ppm range.

Another strategy employed in the stabilization of TFE involves the use of CO_2 [91]. When contacted with CO_2, TFE shows an apparent increase in stability, and may be stored at very high pressures (up to 11 MPa) and moderately high temperatures for prolonged periods without decomposition. Ideally, a 1:1 molar ratio of TFE and CO_2 should be used, but, even 30 mol % of CO_2 will still stabilize TFE [91].

2.5.3 Heat removal during polymerization

The polymerization reaction itself is also highly exothermic (ΔH_R = -196 kJ/mol TFE) [46], and care must be taken to ensure that the heat generated be quickly removed. Therefore, jacketed reactors are not recommended as the thermal lag in a jacketed system is sufficiently large to permit the system to reach deflagration temperatures. Rather, an immersed cooling coil should be used, or preferably, a jacket and coil system should be used to ensure that the reaction medium is cool and that there are no severe thermal gradients in the polymerization kettle.

The use of additives also plays a role in the removal of the heat of reaction. In large polymerization kettles, there is a noticeable improvement in heat transfer within the reactor if emulsion polymerization is employed (as compared to suspension polymerization) [92].

As described in Section 5.2, solvents other than water may be used as reaction medium. Although TFE is only sparingly soluble in water, it is easily solubilized in fluorinated and partially fluorinated solvents. If the concentration of the TFE in the solvent is sufficiently high, local hotspots may develop even in the presence of proper cooling, leading to runaway reactions and explosions.

Our experience shows that performing batch polymerization reactions (20 g of TFE in a 330-mL autoclave) using perfluorodecalin as a solvent always leads to a runaway reactions and explosions.

For this reason, use of solvents other than water should be avoided when performing batch reactions, and when solvents in which TFE is highly soluble are employed, it should rather be done in a continuous monomer- and initiator-dosing mode, with strict control over the amount of TFE present in the kettle at any given time.

2.6 Conclusions

TFE may be prepared by a variety of methods, not all of them suited to a laboratory setting, and while some synthesis routes are facile and inexpensive, the use of TFE brings with it significant risk to the researcher. Importantly, care should be exercized regarding selection and sizing of gas handling equipment as well as the TFE amount stored and the stockpile location, with a make-and-use strategy being preferred over make-and-store.

3   POLYMERIZATION PROCESS AND EQUIPMENT

TFE is gaseous at standard conditions and is sparingly soluble in water [52]. Thus high pressure equipment must be employed in the polymerization process. Laboratory-scale work may take

place in thick glass ampoules or in stainless-steel autoclaves. However, industrial-scale polymerization primarily takes place in large, high-pressure, stirred-tank reactors.

TFE polymerization can be performed by two distinctly different procedures in aqueous media:

1) The first one, called suspension polymerization, involves contacting TFE with an aqueous medium containing organosoluble initiator and, possibly, small amounts of additives such as pH buffers while stirring the mixture vigorously, obtaining a coarse, stringy or granular product.

2) The second procedure, called dispersion or emulsion polymerization involves contacting TFE with an aqueous medium containing a water-soluble initiator, a dispersion agent, an anti-coagulant, and possibly some additives such as pH buffers and CTAs, usually obtaining a fine suspension of polymer.

Ordinary suspension polymerization is not generally employed in industry as the properties of the product polymer cannot meet the current product specifications. All polymerizations used to date are some form of dispersion polymerization, but with granular PTFE grades produced by a process bordering on the suspension precipitation method, as only a tiny amount (2 to 200 ppm) of dispersion agent is employed.

Furthermore, many of the polymerization processes, as practiced, do not produce true TFE homopolymer, but rather a "modified PTFE". This entails adding a small amount (≤ 0.6 mol %) of a fluorinated comonomer, such as perfluoromethyl vinyl ether, to produce a TFE high polymer containing small amounts of modifier, just sufficient to impart the mechanical properties required for the molding process [93].

The granular grades are employed in powder molding-processes whereas the fine suspensions are used in dispersion coatings of metals and other substrates, impregnation of textiles, fabrics and fibers, the preparation of films, porous sheeting resin (*i.e.*, Gore-Tex) and varnishes, as well as paste-extrusion fabrication processes.

Other polymerization procedures, such as bulk-phase polymerization and supercritical-CO_2 polymerization are possible, but are not known to be of commercial importance at present.

3.1   Polymerization procedures

In theory, polymerization of TFE may be carried out under a continuous regime, but for the most part, it occurs either as a batch or as a semi-batch process, with semi-batch processes being industrially preferred. For the sake of clarity, a semi-batch process is defined in the literature [94] as

a batch-like process in which reagents are fed into the reactor vessel while the reaction is taking place, but without removing any material from the reactor for the duration of the operation.

3.1.1 Batch and semi-batch polymerization

The semi-batch process entails multiple possible dosing regimens, with the continuous dosing of TFE being the most common. Other dosing schemes include the continuous dosing of initiator, continuous dosing of CTA and continuous dosing of dispersing agent [95], usually in conjunction with the continuous dosing of TFE. Examples exist in the literature of stepped dosing as well [96,97]. In most commercial cases, however, the continuous dosing of TFE into the semi-batch reactor is the order of the day, with all the other additives and the initiator being loaded beforehand. Variations on this theme include the loading and dosing of a mixture of TFE and some inert gas, such as N_2 or Ar, with the intent of decreasing the partial pressure of TFE as the reaction proceeds in order to control the of the polymer dispersity [93].

The dosing of TFE typically continues until the reactor contains 30 % to 35 % polymer solids. Examples exist in the literature for polymerization being carried out to solids contents in the range of 15 % to 40 % by mass of the mixture [98]. This is not a hard limit, but a best practice adhered to in order to prevent excessive agglomeration of polymer particles in the reactor. Herisson [99] from the Produits Chimiques Ugine-Kuhlmann company indicates that dispersions in water of up to 50 % can be made if a continuous temperature ramp program is used.

It must also be noted that isothermal polymerization is the rule in the greater majority of industrial operations, although there will be a non-isothermal temperature ramp up period, the length of which is dependent on the size of the reactor as well as safety considerations.

The polymerization process, as practiced by DuPont/Chemours, consists of loading a reactor with the required amount of solvent, initiator, dispersing agent, anti-coagulant, *etc.* and pressuring the reactor with TFE to the desired reaction pressure. Heating is commenced, and the pressure is monitored to determine the start of reaction (evidenced by a pressure drop), after which TFE is dosed into the reactor to maintain a constant pressure while monitoring the mass of TFE dosed into the reactor. When the desired TFE mass has been transferred into the reactor, the TFE line is shut, and the remaining TFE is allowed to react away before the reactor is cooled and opened.

Importantly, under ordinary process conditions, the monomer is gaseous, and at no point in the reaction does the monomer form a liquid phase in the polymerization kettle [2]. The Gore company has disclosed a liquid-phase polymerization process that results in polymer morphologies substantially different from that obtained *via* the usual polymerization methods [100].

3.1.2 Post-polymerization processing

In the case of suspension polymerization, the aftercare entails washing the granular polymer with water to remove any initiator residues as well as any remaining additives. After washing, the polymer may be mechanically processed by grinding to reduce the particle size. The final step involves the drying of the polymer, typically in large air driers [2].

In the case of dispersion polymerization, product ear-marked to be sold as fine powder is coagulated under low-shear conditions and subjected to washing and drying. The washing step for dispersion polymerization requires special attention as all the waste water must be treated before being dumped, in order to remove any perfluorinated surfactants and initiators.

3.2 Polymerization equipment

Free-radical polymerization may be carried out in glass, glass-lined reactors (enameled), platinum- or silver-lined reactors, or directly in stainless steel reactors. Industrial polymerization is carried out with reactors that are baffled and with stirrers that maximize the liquid-to-gas surface area, whereas one will come on any number of configurations in a laboratory setting with baffled and unbaffled systems being equally common. Examples of bench-top and industrial-scale systems are presented in Figure 4 and Figure 5, respectively.

Figure 4:   *Examples of 1-L bench-top type autoclaves (both glass and stainless steel) suited to the polymerization of TFE [Images courtesy of AMAR Equipment PVT. Ltd. Copyright 2017 AMAR Equipment PVT. Ltd.]*

Typically, pitched-blade stirrers are used, with multi-blade arrangements being common in commercial-scale polymerizations. Other configurations reported include unbaffled reactors with anchor-type- [97] and horizontal reactors with paddle type agitators (these are mostly used in copolymerization) . Kim *et al.* [53] investigated the efficacy of various stirrer types for TFE polymerization and found that vortex formation and the maximization of gas-to-liquid surface area are the most important criteria to look at when selecting a stirrer. They recommend the use of an anchor type stirrer with a baffled tank.

Heating of the vessel is carried out *via* a steam-fed heating jacket and internal autoclave cooling is supplied in the form of chilled water circulated through pipes immersed in the reaction medium.

One major difficulty encountered during free-radical precipitation polymerization of TFE is the propensity for polymer to adhere to the walls of the reactor. This seems to occur irrespective of the material of construction. This issue may be overcome by adding a chain transfer agent (CTA) to the polymerization vessel.

Figure 5:   *Head section of an industrial 40-kL polymerization reactor. [Images courtesy of International Process Plants. Copyright 2017 International Process Plants]*

3.3   Reaction mechanisms and kinetics

In the absence of CTAs or other reactants, which may prematurely terminate the growing macroradicals, the only kinetic parameters are the rates of initiation (k_i), propagation (k_p), and mutual termination (k_{td}). The mechanisms and kinetics are dependent on the specific

polymerization system (*i.e.,* free-radical, electrochemical, or coordination-insertion). The mechanisms for the electrochemical and coordination homopolymerization of TFE have not been described, and the publically accessible literature contains limited information on the free-radical process.

3.3.1 Kinetics of suspension free-radical polymerization

Owing to the insolubility of even relatively short PTFE chains, the kinetics of TFE suspension homopolymerization bears a heterogeneous character [86]. The fundamental homopolymerization mechanism is characterized by the linear addition of TFE to the growing macroradical and no radical rearrangement or backbiting can occur within the polymer chain to produce branched structures. The macroradicals are essentially immobile (their thermal motion is limited by the rigid nature of the PTFE chains), and termination of the chain can occur only by recombination or the abstraction (or transfer) of a hydrogen from some non-fluorinated species.

Recombination itself is also not a clear-cut phenomenon. If mobile radical fragments (such as initiator radicals) find the radical chain end, recombination may take place, but, observation of the rate of depletion of active chain ends by electron paramagnetic resonance (EPR) shows that chain recombination occurs slowly in the post-initiation phase (when all initiator radicals have been depleted). The rate of depletion exhibits monomer concentration dependence (as opposed to chain end concentration dependence), and recombination stops entirely after a certain molecular weight has been achieved [86,101]. The current understanding is that, in the post-initiation phase, the macroradical extends by monomer addition until two macroradicals are in close enough proximity to terminate by coupling. If no suitable macroradical is found, termination does not occur.

The use of Tobolsky's equation [102,103] in describing TFE homopolymerization is flawed as the polymerization is not homogenous. A proper, fundamental kinetic expression for the homopolymerization of TFE must differentiate between termination (due to fortuitous termination by initiator radicals, *etc.*) and termination due to mutual recombination of the PTFE macroradicals. Markevich *et al.* [86] made some progress in this matter, and their kinetic expression for the apparent rate constant of mutual termination is supplied in Equation (1),

$$k_t = k_p[M]\lambda a \left(1 + \frac{4\pi\lambda r}{a}\right) \quad \textbf{(1)}$$

where k_t, k_p, λ, a and r stand for the apparent rate constant for mutual termination, the propagation constant, the distance traveled for a macroradical with each monomer addition

(twice the C-C bond length in PTFE), the cross-section of the TFE repeat unit in the polymer, and the radius of the cage around the macroradical in which a mutual recombination reaction can occur, respectively.

The implication of Equation (1) is that, for mutual recombination, there is no independent termination constant and the effective termination constant is a function of the propagation constant, as well as the monomer concentration.

Measurement of the propagation and termination parameters are somewhat difficult, but there are scattered reports in the literature. Plyusnin and Chirkov [104] estimated the elementary rate constants for free-radical suspension polymerization in water at 40 °C by measuring the active chain-end concentrations using 2,2,6,6-tetramethyl-4-piperidinol and found the rates of propagation and dead-end termination (k_p and k_t) to be 7400 and 74 L·mol^{-1}·s^{-1} at 40 °C, respectively. Markevich *et al.* [86] determined an activation energy of 39 kJ·mol^{-1} for the propagation constant (k_p) between 0 and 100 °C. These authors also found that the mutual recombination cage radius for a PTFE macroradical varied from 1 to 5 Å over the range from 0 to 100 °C.

3.3.2 Kinetics of dispersion free-radical polymerization

The intrinsic kinetics of dispersion polymerization is the same as for suspension polymerization, and the polymerization still bears a heterogeneous character. Kim *et al.* [53] reported the effects of the polymerization conditions on the molecular weight of PTFE produced by dispersion under a continuous TFE dosing regimen. The observed kinetics of dispersive TFE homopolymerization is closely tied with the mechanism of polymer- particle formation (discussed in Section 7.2.4) and is divided into a nucleation phase and a particle growth phase:

The nucleation phase is observed as an induction period, which may last as long as 40 minutes (though normally it lasts around 5 minutes) and is dependent on the shear rate and free surface area in the reactor (which in turn is dependent on the agitation speed). During this induction period, the rate of polymerization increases to a plateau value, which is determined by the reaction conditions and the hydrodynamics of the reactor. The plateau area is reached essentially when the formation of polymer nuclei is halted (whether due to initiator depletion or due to depletion of the surfactant). The particle growth phase is noted as a steady, plateaued rate of polymerization, which continues until either monomer diffusion to the macroradical becomes the rate-limiting step, or the mass of polymer in the reactor reaches the threshold where agglomeration takes place. Particle consolidation results in a decreased reaction-surface area, which concomitantly, causes a drop in reaction rate. Kim *et al.* [53,105] demonstrated that, for

dispersion polymerization under non-agglomerating conditions, at least two different kinetic regimes are at play, *viz.* gas-liquid- and gas-solid diffusion controlled reactions, and that the rate of polymerization is a strong function of the number of nuclear polymer particles. These authors did not publish the values for the reaction constants.

Punderson [95] reported that, for dispersion polymerization, the space-time yields are a strong function of both the surfactant concentration and the surfactant dosing regimen. For dispersion polymerization using a single initial dose, the typical space-time yields are around 355 $g \cdot L^{-1} \cdot h^{-1}$ and when using a delayed dosing regimen, the typical space-time yields are below 200 $g \cdot L^{-1} \cdot h^{-1}$.

3.3.3 Kinetics of supercritical CO_2 mediated free-radical polymerization

Xu *et al.* [106] reported that the rates of polymerization of TFE in a supercritical CO_2 medium conforms to the behavior expected from homogenous polymerization (*i.e.*, it follows Tobolsky's law [102,103]). They found TFE polymerization took place homogenously within the supercritical fluid and termination by mutual recombination occured readily, resulting in precipitation of the polymer from the fluid. These authors found apparent $k_p \cdot k_t^{-0.5}$ values of 0.38 (at 35 °C) for the homopolymerization of TFE in supercritical CO_2. These values are markedly lower than those for aqueous polymerization (*ca.* 860).

3.3.4 Gamma radiation induced free-radical polymerization

Tabata and coworkers extensively investigated the radiation induced polymerization kinetics of TFE in solution [107], bulk liquid and in the solid state (*i.e.*, polymerization in frozen TFE). They found that in-source polymerization in bulk liquid and solution proceeds without any noticeable termination step in the initial stages of reaction, with the conversion being a strong function of dose rate. The propagation constants for post-polymerization is a strong function of temperature with the activation energy for post-polymerization being 4 times higher than the in-source activation energy.

3.4 Conclusion

TFE may be polymerized by either suspension-, emulsion-, or supercritical CO_2 modes, and the procedure may be conducted either batch, semi-batch or continuously, with semi-batch using continuous dosing of TFE as the preferred industrial method.

Essentially, in any real-solvent mediated TFE polymerization, the kinetics are governed by monomer diffusion, either into the reaction medium, or through the reaction medium to the PTFE macroradical. Some reaction kinetics have been reported, but there remains a dearth of information on the temperature dependence of the propagation and termination rates.

No articles could be found in the literature that sets down reactor independent correlations for the polymerization rate in terms of fundamental polymerization rate constants of TFE. The polymerization rates reported by Kim *et al.* [53], Xu *et al.* [106], Lai *et al.* [108], *etc.*, as well as all the patent literature, are lumped terms that include reactor hydrodynamics- as well as diffusion effects.

Significant research scope exists for determining the kinetics of polymerization and, in particular, the effects of temperature and pressure on the dispersity of PTFE.

4   POLYMERIZATION INITIATORS

The initiators used in TFE polymerization are all-important as the polymer stability, color, and molecular weight are all, to some extent, functions of the initiator chemistry.

In 1946, the Brubaker patent [19] claimed that the use of peroxy compounds as initiators is preferred for conventional radical polymerization, and in particular, the use of alkali or ammonium persulfate, using thermal activation, is ideal. Redox activation may also be used, but this method tends to contaminate the polymer with metal. However, the redox system does result in a more controlled reaction, and a polymer with a higher M_n [33]. As will be discussed in Section 7.3.3, persulfate initiators introduce discoloration into the polymer and have therefore been superseded by other organic peroxides, such as disuccinic acid peroxide, and, in particular, by perfluorinated peroxide initiators, such as hexafluoropropylene oxide (HFPO) dimer peroxide, [di(perfluoro-2-methyl-3-oxahexanoyl) peroxide][26,109]. Some of the reported initiators are summarized in Table 2, and the individual classes of initiators are discussed hereafter.

4.1   Inorganic free-radical generating initiators

The most common inorganic free-radical generating initiators employed with TFE are the various persulfate initiators, with sodium, potassium, and ammonium persulfate being the most common. Ammonium persulfate is preferred as any residual initiator not washed out of the polymer is decomposed and evaporated during the sintering steps for PTFE, leaving no residual inorganic contamination in the polymer. Typical concentrations of persulfate initiators required to produce high polymers fall in the range of 2 to 500 ppm. Polymerization is typically continued until the reactor contains ~30 % solids [98].

Joyce and others [20,24] indicated that molecular oxygen could also be used to polymerize TFE, but this contradicts other reports [33,85,110]. Oxygen is known to act as a polymerization inhibitor and must be rigorously excluded from the polymerization system. Oxygen difluoride may be used as an initiator, and the polymerization occurs readily and rapidly at temperatures as low as -100 °C [111]. Ozone has also been cited as a possible initiator.

Furthermore, fluorine radicals may be generated by heating certain metal fluorides like CrF_3 and AgF_2 in the presence of TFE, and polymerization may be initiated in this manner to produce a high polymer [112]. At the opposite end of the spectrum, XeF_2 initiates TFE polymerization at 25 °C *via* low temperature release of F• [113].

4.2   Organic free-radical generating initiators

Organic free-radical generating initiators have been the mainstay for commercial PTFE. Organic peroxides are the most common initiators used. Since nearly all PTFE production occurs in aqueous medium, those compounds that can dissolve well in water are most preferred, with disuccinic acid peroxide and diglutaric acid peroxide being the most cited initiators. Water insoluble compounds such has benzoyl peroxide can be utilized in suspension polymerization, but their application is limited to situations where organic solvents or water/organic biphasic systems are employed.

The selection of initiator is based primarily on solubility and half-life, but there are limitations on the chemistry of the initiators owing to the possibility of atom transfer from the initiator to the fluoromacroradicals. Lauroyl peroxide is an example of an organic initiator that also acts as a CTA.

Importantly, azo-initiators have been found ineffective in initiating TFE polymerization. Azobisisobutyronitrile (AIBN) and similar initiators did not produce any polymer at all, irrespective of their concentration or reaction temperature.

Normally, organic peroxydicarbonates, such as bis(*tert*-butylcyclohexyl) peroxydicarbonate do not initiate TFE polymerization. Scoggins and Mahan[114] demonstrated that organic peroxydicarbonates, specifically di(saturated hydrocarbyl)s with carbon atom counts of 1 to 4, can initiate such a polymerization of TFE, either carried on finely divided PTFE powder or as neat powders with no solvent. With diisopropyl and di(sec-butyl) peroxydicarbonates, PTFE was obtained in good yield.

4.3   Free-radical generating redox initiators

Myers [33] indicated that when using a redox initiator with TFE systems, a redox system comprising an organic peroxide, a divalent metal promoter, and a reducing agent gives the highest polymerization rates. While nickel, copper, cobalt, manganese, and iron salts/complexes may be used, iron compounds are the most preferred promoters [115]. Although most inorganic metal salts may be used, organic salts and chelates with the ability to dissolve well in the polymerization medium, as well as the monomer, are ideal. Therefore metal compounds of perfluorocarboxylic acids are preferred. Any of a number of reducing agents may be employed,

with bisulfites being most favored. Other reducing agents include hydrazine, dithionite, or diimines [116].

Other systems also reported include ammonium persulfate/sodium bisulfite with a copper-based accelerator (promoter) such as copper sulfate [116]. Interestingly, Halliwell[116] also mentioned that an excessive amount of copper acts as an inhibitor, so the optimum amount of copper falls between 0.02 and 2 ppm as calculated on the liquid medium. Cobalt and iron show a much more pronounced rate acceleration than silver when silver is used as sole promoter. A copper accelerator is far superior to all three[116].

A variation on this theme includes the additional inclusion of silver ions to the bisulfite, which increase the reactivity of the radicals generated by the divalent metal/bisulfite mixtures towards the polymerization of TFE and TFE/CTFE mixtures [117].

Redox initiated polymerization exhibits one noticeable drawback, *viz.*, discoloration of the polymer due to metal inclusion in the final product powders.

4.4 Fluorinated free-radical generating initiators

Fluorinated dialkyl and diacyl peroxide initiators may be produced beforehand and added into the polymerization reaction in the usual way, but many of these initiators are not thermally stable, even at 25 °C. In example, perfluoropropionyl peroxide is produced by reacting the acid chloride with sodium peroxide using HFC-4310 as solvent. The peroxide is stored at − 80 °C until use. It has been claimed in the patent literature [118] that fluorinated diacyl peroxide initiators may be produced *in situ* during polymerization by introducing the anhydrides of perfluorinated carboxylic acids along with concentrated (~90 %) H_2O_2, although less concentrated H_2O_2 may be used as well. Other fluorinated initiators include [NaOC(CF$_3$)$_2$]-COO [119]. The commercially preferred class of fluorinated initiators are the oligo(hexafluoropropylene oxide) peroxides [26,109], such as bis(perfluoro-2-n-propoxypropionyl) peroxide [106,120]. Perfluoropropionyl peroxide is also widely used in commercial polymerization.

The mechanism of initiation for oligo(hexafluoropropylene oxide) peroxide is rather complicated, as the initiator may undergo decarboxylation as well as internal radical re-arrangement to afford a number of different radical species [120,121]. This is shown in Scheme 6.
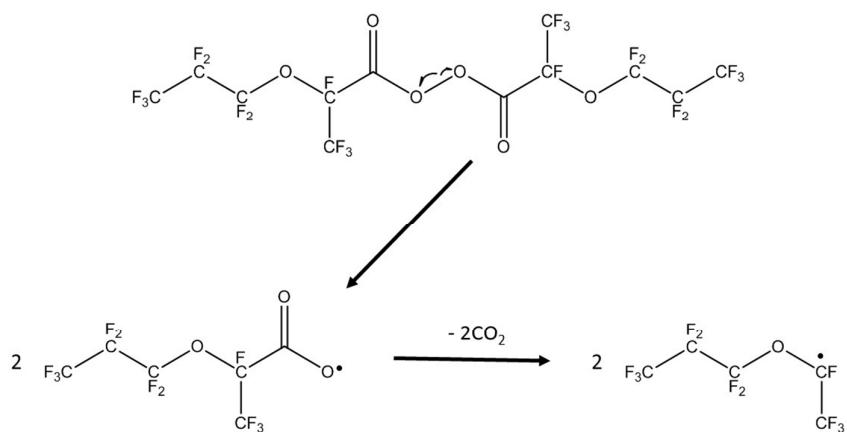
Scheme 6: *Thermal decomposition mechanisms of oligo(hexafluoropropylene oxide) peroxide to yield two fluorinated radical species that initiate polymerization.*

Di(perfluoroacyl) peroxide initiators have a tendency to hydrolyze when used in systems containing water, reducing the initiator efficiency and slowing the polymerization rate [35]. The hydrolyzed initiators may also result in unstable end-groups, thus avoiding depolymerization by unzipping. The use of more sterically hindered initiators tends to overcome this problem. In the example from Nakagawa et al.'s patent[35], $(ClCF_2\text{-}CF_2\text{-}COO)_2$, is the preferred initiator. Di(perfluoroacyl) peroxide initiators are employed extensively in industry because they generate stable end-groups, thus reducing the need to treat the polymer with fluorine in the post-processing step. The claimed instability of di(perfluoroacyl) does not seem to be much of an issue in industry.

Fluorinated disulfides and thio mercury compounds have been reported[122], with bis(trifluoromethyl)-disulfide and bis(trifluoromethylthio)mercury being preferred, achieving high molecular-weight at faster polymerization rates than those noted from the fluorinated peroxides.

4.5   Miscellaneous free-radical generating initiators

Convery [123] indicated that tetravalent lead salts of the perfluorinated or omega-hydrofluorinated carboxylic acids (with carbon count 11 or less) may be used as free-radical initiators in the polymerization of TFE.

4.6   Photoinitiators

UV irradiation has been employed *directly* as an initiation mechanism for TFE and other perfluoromonomers in batch polymerization systems [124]. Gamma radiation, from ^{60}Co, has also

been employed *directly* to effect the polymerization of TFE, both in batch [125], and in a continuous reactor system [126], nominally producing a high-molecular-weight polymer.

More commonly, photo initiation of TFE involves some photoactive species acting as initiator under the influence of UV, or other non-ionizing radiation sources, with elemental mercury being the first example [127]. A report concerns the use of fluorinated azoalkanes like perfluoroazoethane as photoinitiators [128]. Most compounds that produce free-radicals by UV induce bond cleavage may be used as photoinitiators, with salient examples being Cl_2, F_2, SF_5Cl [129], N_2O [130], and short-chain acyl halides [131].

Typically, UV C radiation (280 – 100 nm) and lower energy UV B (300 – 280 nm) radiation are employed, with monochromatic light at 253.7 nm as the wavelength of choice. For gamma irradiation, dose rates of 2.6 kGy·h^{-1} have been reported, with total dosages usually of the order of 700 kGy [125].

Gamma radiation can be used to initiate TFE polymerization in the gas, liquid, or in the solid state, with temperatures as low as -196 °C being feasible [125].

4.7   Other initiators

DuPont/Chemours has published useful data concerning the use of active silica as initiator, prepared from silica gels heated to 400 °C, whereby TFE is polymerized at 1 bar and 25 °C, under anhydrous conditions to yield silica particles coated with a high homopolymer covalently bound to the particle *via* a carbon-silicon, or more likely a carbon-oxygen-silicon linkage [132]. The mechanism is not discussed, but the assumption is that oxygen moieties exist on the reconstructed silica surface, which possesses an unpaired electron that can add onto TFE and initiate polymerization. The rate of polymerization was reported to drop sharply when the PTFE:filler ratio reaches 3:1. Similar claims have been made by the Allied Chemical Corporation [133] regarding activated alumina supported on silica particles. The patent also indicated that the addition of small quantities of metal salts of hexavalent chromic acid (such as magnesium chromate) to the alumina ensure that the polymerization reaction continues at good rate well past the 3:1 TFE to filler ratio limit. The rate of polymerization on activated silica is reported to be 0.07 g of TFE per gram of catalyst per hour and the rate on chromium doped materials as 0.42 g of TFE per gram of catalyst per hour [133].

Furthermore, strong oxidizers, such as $KMnO_4$ in water [93,134] have also been cited as initiators for the low temperature (10–50 °C) polymerization of TFE, both in ordinary- and emulsion polymerization, giving high-molecular weight polymers. The claim was made that any of the salts of permanganic, manganic, and manganous acid can be used in this fashion.

Other inorganic initiators include neat, anhydrous CsF [135] in contact with TFE gas at temperatures in the region of 150 °C. This reaction can produce both PTFE waxes and high polymer with properties comparable to PTFE obtained by free-radical mechanisms.
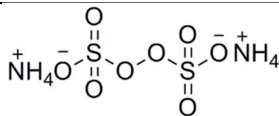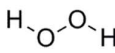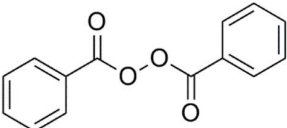
4.8   Ziegler-Natta catalysts
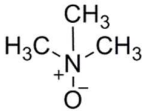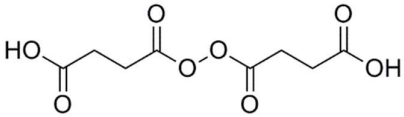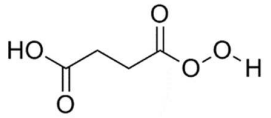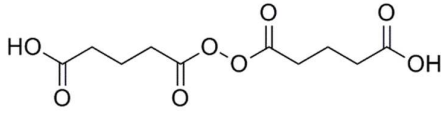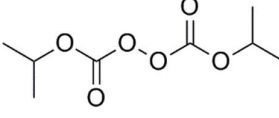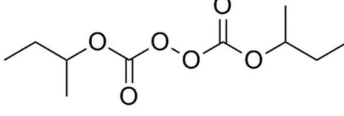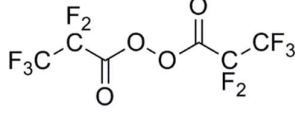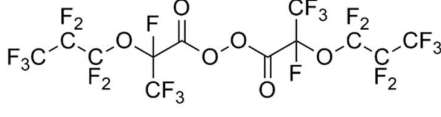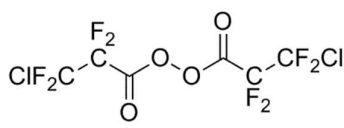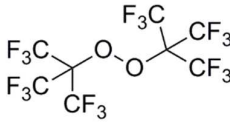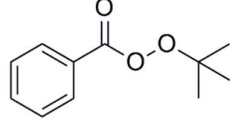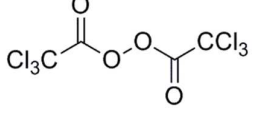
The patent literature[37,136] also reports the co-ordination polymerization of TFE and other perfluorinated monomers using tri-isobutyl aluminum (5 mmol·L^{-1}) and titanium tetrachloride (10 mmol·L^{-1}) in iso-octane.
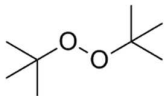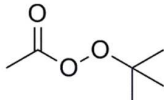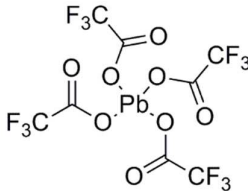
4.9   Conclusions

TFE can be polymerized *via* free-radical, electrochemical, and coordination methods. Free-radical polymerization may be initiated with well-known substances such as persulfates and organic acyl peroxides. In particular, numerous water soluble organic peroxides, such as disuccinic acid peroxide, have been developed. Fluorinated organic initiators have been specially synthesized by commercial entities, permitting polymerization of TFE in fluorinated solvents. Photochemical initiation as well as a variety of special inorganic initiators have also been investigated for use with TFE. Initiator chemistry is all important for the thermal and chemical stability of the end-groups, which in turn, to a large extent determines the thermal and chemical stability of PTFE. Coordination polymerization is under-represented in the literature and presents an interesting avenue for further research.

Table 2:   *Initiators generating rdicals used in the polymerization of TFE.*

Initiator	Structure	CAS No:	Reference
Ammonium persulfate		7727-54-0	19-21,30-32,36,53,108,110
Sodium bisulfite / FeSO$_4$	NaHSO$_3$ / FeSO$_4$	7631-90-5	30,32,108
Potassium persulfate / FeSO$_4$	K$_2$S$_2$O$_8$ / FeSO$_4$	7727-21-1	137
Hydrogen peroxide		7722-84-1	19-21
Benzoyl peroxide		94-36-0	22

Trimethylamine oxide		1184-78-7	[23]
Disuccinic acid peroxide		123-23-9	[25,31,101]
Monosuccinic acid peroxide		3504-13-0	[25]
Diglutaric acid peroxide		10195-54-7	[25]
Diisopropyl peroxydicarbonate		105-64-6	[114]
Di(*sec*-butyl) peroxydicarbonate		19910-65-7	[114]
Perfluorodipropionyl peroxide		356-45-6	[27]
Di(perfluoro-2-methyl-3-oxahexanoyl) peroxide		56347-79-6	[26,109]
bis(3-chloro-2,2,3,3-tetrafluoro-1-oxopropyl) peroxide		88505-66-2	[35]
Bis(perfluorotert-butyl)peroxide		927-84-4	[138]
t-butyl peroxybenzoate		614-45-9	[33]
Bis(trichloroacetyl) peroxide		2629-78-9	[139,140]

Di(*tert*-butyl) peroxide		110-05-4	[110]
Tert-butyl peracetate		107-71-1	[110]
Oxygen difluoride	$F \diagup O \diagdown F$	7783-41-7	[111]
Pb (IV) tetrakis(trifluoroacetate)		16656-82-9	[123]
SF_5Cl		13780-57-9	[129]
$KMnO_4$	$KMnO_4$	7722-64-7	[134]
CsF	CsF	13400-13-0	[135]
AgF_2	AgF_2		[112]
CrF_3	CrF_3		[112]
PbF_4	PbF_4		[112]

5   REACTION CONDITIONS

5.1   Monomer purity

TFE used in polymerization should be as pure as possible, with a 99.99 % pure material classified as "polymerization grade". In industry TFE is routinely purified to 99.99 % and higher to ensure no telogens are present in the gas stream. Impurities usually come from the production process, with substances such as HCl, CF_4, HFP, $C_2F_3H_3$, $C_2F_2H_4$, and C_2F_6 being the typical contaminants. The contaminants affect the solubility of TFE in the reaction medium, the reactivity of TFE or act as CTAs. These have deleterious effects on the reaction rate, product yield, molecular weight, and thermal stability of the final product. Specifically in the case of HFP, the contaminant may co-polymerize with TFE. However, the reaction rate is so low that most of the HFP simply remains unreacted, crowding the TFE out of the reaction medium and blanketing the gas-liquid interface, thereby forming an additional layer through which TFE must diffuse before it reaches the actual reaction zone.

As TFE is usually stored in the presence of a radical scavenger, the TFE must be cleaned before it can be used in polymerization. In a laboratory setting, the stabilizer can be removed simply by

slowly passing the gas stream through a silica gel column [141]. The silica column may be regenerated under vacuum at 250 °C.

Furrow [142] disclosed an industrial 3-step method for the scrubbing of impurities from TFE, in which TFE is first contacted with 98 % sulfuric acid (*via* bubbling or a counter-current gas scrubber), then with molecular sieves having an 8 Å pore size, and finally with pyrophoric copper to remove any trace oxygen from the gas stream.

5.2   Solvent environment

TFE may be polymerized either in the gas- or liquid phase, both autogenously [110], or in the presence of a suitable radical source, but as this bulk reaction cannot be easily controlled, it is preferred to polymerize TFE in the presence of a liquid carrier. As pointed out by Brubaker [19], the choice of solvent depends on the initiator used, heat transfer considerations, and inertness to the polymerization process as well as the solubility of the monomer. These criteria are repeated in nearly all polymer chemistry textbooks [143-151].

The term "carrier", rather than solvent, should be used as PTFE does not dissolve in anything, including hot fluorinated solvents [47]. The polymerization process is classed as precipitation polymerization [152] owing to the fact that even relatively short PTFE chains crash out of the solvent [153]. Naturally, if a non-fluorinated comonomer is used, it becomes possible to solubilize the polymer, depending on the amount of comonomer incorporated in the final polymer [154].

Discussions in the literature regarding the selection of polymerization solvents are centered on monomer solubility and chain-transfer properties. In the case of TFE, and all fully fluorinated monomers, the main criterion for a solvent is its atom transfer ability.

While it has been mentioned that per halogenated monomers can be polymerized in bulk *a la* ethylene or styrene, the low temperatures and rather high pressures required make it an uneconomical process. Besides this, control of the polymerization reaction in bulk medium is challenging at best and process safety cannot be guaranteed [118]. Hence, to the best of our knowledge, bulk polymerization of fluorinated monomers is not employed in industry today.

Solvents may be completely avoided if gaseous photoinitiators are used in conjunction with UV light, but, as with bulk free radical polymerization, removal of the heat of reaction is an issue that limits the commercial feasibility.

The solvent should be a fluid at polymerization conditions, but the solvent needs not be a liquid at ambient conditions, as is the case with CO_2. More importantly, the solvent should not exhibit excessive vapor pressure at polymerization conditions lest it contribute to the process equipment

cost, and it should not boil at such a high temperature that it cannot be readily removed from the product polymer. The polymerization of TFE, as practiced by DuPont/Chemours, prefers the use of solvents with a boiling point no higher than 150 °C, but preferably no higher than 100 °C, and no lower than 20 °C [109].

5.2.1 Solvents for free-radical polymerization of TFE

Radical telomerization of fluorinated monomers have been extensively reviewed by Ameduri and Boutevin [7], and they indicate a large number of solvents may be employed. However, owing to the electron-withdrawing effects of fluorine, the radical chain ends of the fluoromacroradical are highly electrophilic and proton transfer occurs readily between the macroradical and conventional polymerization solvents [101]. Therefore, hydrocarbon solvents cannot be used for the synthesis of perfluorinated high polymers by free radical mechanism.

Of the conventional solvents employed in polymer synthesis, only water seems to be completely inert toward the radicals of fully fluorinated monomers.

Other solvents that are inert toward fluorinated monomers include various liquid perfluorocompounds, such as perfluorohexane, perfluorocyclohexane and perfluorodecalin as well as various chlorofluorocarbons (specifically chlorofluoroalkanes of 1 to 2 carbons in length). The most preferred chlorofluorocarbon solvent is $Cl_2FC-CClF_2$ (Freon 113 or R113) [27].

Hydrofluorocarbons (such as HFC-4310) or hydrochlorofluorocarbons may also be employed, and hydrofluoroethers [26], hydrofluoropolyethers [155], and perfluoropolyethers are currently being investigated as polymerization media for polyfluorinated monomers.

Another option to be considered is the use of biphasic systems of fluorinated solvent (such as R113) and water (done in conjunction with emulsion polymerization using fluorinated surfactants). In particular, it has been reported [155] that fluoropolyethers with hydrogenated end-groups may be used as the hydrophobic solvent. The Ausimont company (now Solvay Specialty Polymers) has also indicated that highly-branched, short-chain hydrocarbons such as 2,2,4-trimethylpentane will not act as a CTA if used in a biphasic system with water [156]. However, the examples given in the patent are not sufficiently convincing.

Other fluorinated solvents, which may be used by themselves, or as part of a biphasic system, include perfluorinated cyclic tri-substituted amines without any N-F bonds, such as perfluoro-N-methylmorpholine [157], and linear and cyclic perfluoroalkyl sulphides [109].

Furthermore, liquid inorganic fluorides have also been used in their lower oxidation state as solvents for the polymerization reactions [112], with arsenic trifluoride and anhydrous HF being the

most prominent. Such solvents are not safe, environmentally friendly, nor economical and thus are not used anywhere in commercial production of fluoropolymers.

DuPont/Chemours has published extensively on the solvents used in the polymerization of fluoromonomers [26,27]. These reports indicate that in order to avoid the transfer of protons to the fluorinated macroradicals from a hydrofluorocarbon, the solvent structure should not contain:

- Methyl groups (-CH$_3$), except as part of a fluoroether group (*i.e.* CF$_2$-O-CH$_3$) [26];
- More than two adjacent CH$_2$ groups (*i.e.* –CH$_2$-CH$_2$-);
- Hydrogens on a carbon adjacent to two CH$_2$ groups (*i.e.* CH$_2$-CH$_2$-CHF-);
- Not more than two hydrogens adjacent to ether oxygens apart from a methyl group (*i.e.* CH$_2$-O-CF$_2$, or CHF-O-CHF, but not CH$_2$-O-CHF, *etc.*); and
- Oxygen may be present in the solvent only as an ether or an alcohol unit.

It is preferred, though, that the solvent compound contains no more than one hydrogen and that this hydrogen be on the difluoromethyl group (*i.e.* –CF$_2$H) [27].

DeSimone pioneered recent developments in fluorocarbon polymerization with the use of supercritical CO$_2$ as solvent [28,29,106,120]. The optimal (1:1) ratio of TFE to CO$_2$ can be directly generated *via* the vacuum pyrolysis of alkali metal salts of perfluoropropanoic acid [57], so the supercritical CO$_2$ method has been facile in a laboratory setting for some time already. TFE is fully miscible in sc-CO$_2$, but PTFE is not, so the polymer will precipitate as the reaction continues, generating two distinct phases.

As was mentioned in Section 2.5, the use of solvents other than water is not generally recommended due to safety considerations. Besides safety, the commercial use of chlorofluorocarbons and hydrochlorofluorocarbons has been banned under the Montreal Protocol [63], and CO$_2$ and hydrofluorocarbons as well as their derivatives are coming under increasingly strict control from the Kyoto Protocol. Subsequently, the use of these compounds as solvents for the commercial synthesis of fluoropolymers may not be commercially viable in the near future. Even in a laboratory setting, the use of these compounds is being phased out, and it may not be possible to employ these compounds for solvents in any setting in the near future. Prior to the implementation of the Montreal Protocol, fluorinated solvents superseded water as the solvent of choice for free radical polymerization of perfluorinated monomers, but were rarely used commercially due to cost.

Currently, water is the only environmentally benign and green solvent suitable for the synthesis of high- molecular-weight PTFE by free radical polymerization.

Brubaker mentions that the polymerization can be performed in either acidic, neutral or alkaline aqueous environments, but that alkaline conditions are preferred as acidic environments could leach metals from the reactor into the polymer, causing discolorations. This claim has been repeated by a number of other authors [20-22,24,25]. The Brubaker patent[19] indicates the use of borax as the most desirable buffer, but other alkaline compounds such as sodium phosphate and NaOH may also be employed. Other literature indicates that acid environments are preferred for obtaining high M_n PTFE [33], with the pH ranging between 3.5 and 4.5. The pH of the solvent is seen to be immaterial to the actual polymerization reaction, and pH only plays a role with respect to the stability of the initiator, additives, reactor apparatus, and any comonomers.

It is vital that any solvent employed in the polymerization of TFE be rigorously deoxygenated (into the sub-ppm levels) as oxygen will inhibit the polymerization reaction and may form an explosive mixture with TFE. Some of the solvents so far employed in the polymerization of TFE are summarized in Table 3.

5.2.2   Solvents for coordination polymerization of TFE

The coordination polymerization of TFE may be carried out in any non-aromatic hydrocarbon solvent, with iso-octane being preferred [37].

5.2.3   Solvents for electrochemical polymerization of TFE

Electrochemical polymerization may be carried out in the liquid monomer, in anhydrous HF or in a mixture of fluorinated carboxylic acids, or in hexafluorodimethylcarbonate [38,39].

5.2.4   Solvent pre-treatment

As stated previously, the polymerization process is sensitive to the presence of oxygen, so care must be taken to remove oxygen from the solvent as well as the monomer.

Typically in industry, large reservoirs of demineralized water are sparged with nitrogen (with or without stirring) to liberate the dissolved oxygen, ensuring the reservoir to remain under a slight positive pressure to frustrate any oxygen back diffusion into the reservoir.

On a lab scale, the same method may be employed, but nitrogen, argon or even TFE itself may be used to sparge. Alternatively, the unsparged water may be charged into the reactor, and the entire reactor de-oxygenated *via* the freeze-thaw method.

5.3   Pressure and temperature

The temperature and pressure conditions inside the polymerization kettle are of utmost importance, as they determine kinetics of reaction, and thus, polymer yield and molecular

weights. Furthermore, operating temperature and pressure need to be taken into account when designing the reactor system in order to ensure the process operates within safety limits.

Table 3:   *Solvents employed in the free-radical polymerization of TFE.*

Solvent	Structure	CAS No.:	Reference
Water	$H-O-H$	7732-18-5	[19]
HF, anhydrous	$H-F$	7664-39-3	[112]
CF_2ClH		75-45-6	[107]
Perfluoro-1,2-dimethylcyclobutane		28677-00-1	[118]
Perfluoro-1,3-dimethylcyclohexane		335-27-3	[112]
Perfluoro-N-methylmorpholine		382-28-5	[157]
Bis(perfluoro-n-butyl) sulfide			[109]
Formic acid		64-18-6	[158a]
Acetic acid		64-19-7	[158a]
Sulfuric acid (97 %)		7664-93-9	[158a]
AsF_3	AsF_3	7784-35-2	[112]

[a]See the section on CTAs for more details.

5.3.1 Pressure

In general, the TFE concentration in the reaction medium is determined by the partial pressure of the gas and the reaction pressure has little direct effect on the properties of the final polymer other than those which may be influenced by concentration. The operating pressure is determined by the equipment employed, but, as discussed in Section 2.5, TFE may spontaneously decompose under pressure, resulting in a pressure spike in the reactor that may cause a deflagration and possibly an explosion. The upper pressure limit is determined by temperature and the vessel size, but is generally set at 90 bar.

TFE can polymerize even at low pressures, but, in the case of gas-phase polymerization (*i.e.* photo initiation by UV and SF_5Cl [129]), the kinetics and therefore, the molecular weight of the PTFE obtained, as well as the yield, is determined by the partial pressure of TFE. The higher the pressure, the greater the yield and molecular weight.

5.3.2 Temperature

In free-radical polymerization the operating temperature is selected based primarily on the decomposition kinetics of the initiator, but other factors, such as solvent boiling point and kinetic considerations also influence the choice of temperature. Generally, the polymerization temperatures do not exceed 150 °C. For example, Brubaker [19] reported that, for optimal results, free-radical polymerization should be carried out at 20 bar TFE or higher and at temperatures around 80 °C to give yields in the range of 80 to 100 %.

The patent literature indicates that proton transfer is a strong function of temperature and by lowering the polymerization temperature to between -40 °C and 0 °C, a TFE high polymer may be obtained even in the presence of significant amounts (≥10 %) of CTAs [158].

Polymerization may be performed at ambient temperatures using photo initiation methods such gamma or UV light, with the temperature of a UV-photo initiated polymerization reaction being determined by the temperature required to keep the initiator and other additives in the gas phase. For coordination polymerization the recommended reaction temperature falls between 30 °C and 40 °C [37], and for electrochemical polymerization, the temperatures ranges between -80 °C and ambient.

The greater majority of polymerization operations are isothermal in nature, with the reactors starting at some ambient temperature, being ramped up to the reaction temperature and then maintained at this temperature for the duration of the operation. The Kuhlmann company has disclosed a dispersion polymerization process [99] that entails the continuous increase of the temperature during the operation in order to maintain the stability of the emulsion, which in turn

permits a higher final solids loading to be achieved. The temperature ramp rate (defined here as $\Delta T/\Delta t$) should not be less than 1/6 °C·min^{-1} and they place an upper limit of 120 °C on the reaction temperature. This scheme does not appear to be followed in any commercial setting.

5.4 Agitation

Importantly, the shear rate plays a role in determining the size of the PTFE particle agglomerates in dispersion polymerization, so there is an optimum shear rate that must be maintained if a fine dispersion is to be produced. The literature indicates that a power number to discharge coefficient ratio greater than 1.4, but preferably 3.4, should be used and that the power input of the stirrer should be in the region of 0.0004 to 0.0020 kg·m·s^{-1}·mL^{-1}, preferably around 0.001 kg·m·s^{-1}·mL^{-1} [159]. In supercritical CO_2 mediated polymerization, the agitation plays a major role in determining the particle size distribution [106].

5.5 Polymerization additives

Brubaker [19] mentioned that filler materials, such as glass, carbon black, copper, and bronze may be added to the polymerization kettle to produce "filled" PTFE in-situ. More common additives include pH controlling agents, dispersants, anti-coagulants, and CTAs.

5.5.1 Buffering agents

As previously stated, pH controllers include borax [19,116], NaOH, HCl, acetic acid, K_2CO_3, NH_4CO_3 [134], or buffer mixtures. The role of the pH controller is primarily to ensure that the aqueous polymerization medium does not adversely affect the initiator performance and that metals from the materials of construction are not leached into the reaction mixture, with typical pH values ranging from 7 to 11 [119]. In non-aqueous media, buffering agents are not required.

The choice of buffering agent must be carefully considered as it not only adds to the cost of the polymer, but may contaminate the polymer and cause problems in the end application, and using buffering agents that may undergo proton transfer lead to premature termination and low-molecular-weights.

5.5.2 Dispersants for emulsion polymerization

In aqueous polymerization, production of fine PTFE powder requires the use of a dispersing agent (*i.e.* a surfactant). This process is commonly referred to as emulsion polymerization. It should be noted here that when using fluorinated solvents or supercritical CO_2, a dispersing agent is not required.

Initially, alkaline buffers, which may act as detergents (such as borax), were employed. Longer chain hydrocarbon peroxides (such as diglutaric and disuccinic acid peroxide) [25] as well as long-chain saturated hydrocarbons (such as tetradecane, cetane, paraffin wax, and heavy mineral oil) [31]

were also used to disperse the polymer. In the abovementioned, the peroxides acted as both initiator and dispersing agents.

The primary issue with using hydrocarbon dispersants (surfactants) is the probability of the formation of low molecular weight-polymers due to hydrogen abstraction by the growing fluoromacroradical [36,95]. Furthermore, the affinity of hydrocarbons for TFE and its polymers is limited, so the dispersive effects of hydrocarbon agents are not satisfactory. However, Bankoff [31] claimed that hydrocarbons may be used as dispersive agents in aqueous polymerization without significant chain transfer, provided the hydrocarbon is greater than 12 carbon atoms in length. The rationale for this is the extremely low solubility of the hydrocarbon in water as well as the low solubility of TFE, initiator, or macroradical in the hydrocarbon, thus limiting the contact between the hydrocarbon and the macroradical. The implication here is that the active polymerization occurs in the aqueous phase. Examples in the literature exist for the use of "paraffin" as a dispersant [160].

Instability of the dispersion is a further disadvantage of hydrocarbon-based dispersants. It is exceedingly difficult to obtain a dispersion of a perfluorinated polymer that may be stored for prolonged periods using such dispersants. Also, the dispersion particle size is, in general, undesirably large when using a hydrocarbon dispersant with perfluoropolymers.

Imperial Chemical Industries (ICI) reported that the difficulty of chain transfer of hydrocarbon surfactants (in particular, aliphatic sulfonic acids and derivatives, *i.e.* sodium lauryl sulfate) onto TFE macroradicals and may be overcome if said dispersant is introduced to the reaction mixture after polymerization has started, but before the mass of polymer produced exceeds 7 % of the total mass of the reaction mixture (polymer + everything else), with the addition occurring as either a batch- or a staged addition [161]. However, it appears this method has not been taken up by other commercial manufacturers of PTFE as this method does not provide sufficient control over the particle size distribution. Punderson [95] reported a refinement of the ICI method, where a low initial dose of surfactant is used (as little as 0.015 mass %) followed by a continuous addition of surfactant until the reactor reached 35 mass % solids content. This method provides particle size distributions substantially similar to those obtained from fluorinated surfactants.

Berry[32] introduced the use of fluorinated species as dispersive agents, employing perfluorodimethylcyclohexane as dispersing agent. Chlorofluorocarbons and perfluorinated oils may also be used as dispersing agents. However, perfluorinated monocarboxylic acids, or their salts [98,110,115,116,141] have traditionally been the best and most widely used dispersant. Typical concentrations of dispersing agent range from 2 to 200 ppm based on the mass of water.

Prior to Berry, attempts were made by Benning [36] to modify existing anionic surfactants for use with fluoropolymers, employing fluorinated aliphatic phosphate surfactants. Similar work was carried out by ICI, with various perfluorosulfonic acids and their salts [162]. Other compounds employed as dispersive agents included keto acids and their derivatives (particularly the metal salts) [124], hexachlorobicyclo-5-heptene-2,3-dicarboxylic acid (chlorendic acid) and its salts [163], tertiary perfluoroalkoxide [96], and perfluoropolyether-based carboxylic acid salts [97]. The patent literature also claims that tertiary perfluoroalkoxide provide an increase in instantaneous polymerization rates over the ordinary monocarboxylic acid salts. It is evidenced from the patent literature (*e.g.* [96,99,100,164]) that the preferred method for emulsion polymerization of TFE consists of water as solvent, perfluorooctanoic acid (PFOA) as dispersant, and a water-insoluble aliphatic hydrocarbon as anti-coagulant (as opposed to using the hydrocarbon by itself as the dispersant). Some of the compounds used as dispersive agents in the aqueous emulsion polymerization of TFE are summarized in Table 4. However, PFOA and PFOS are toxic, persistent and bioaccumulative.
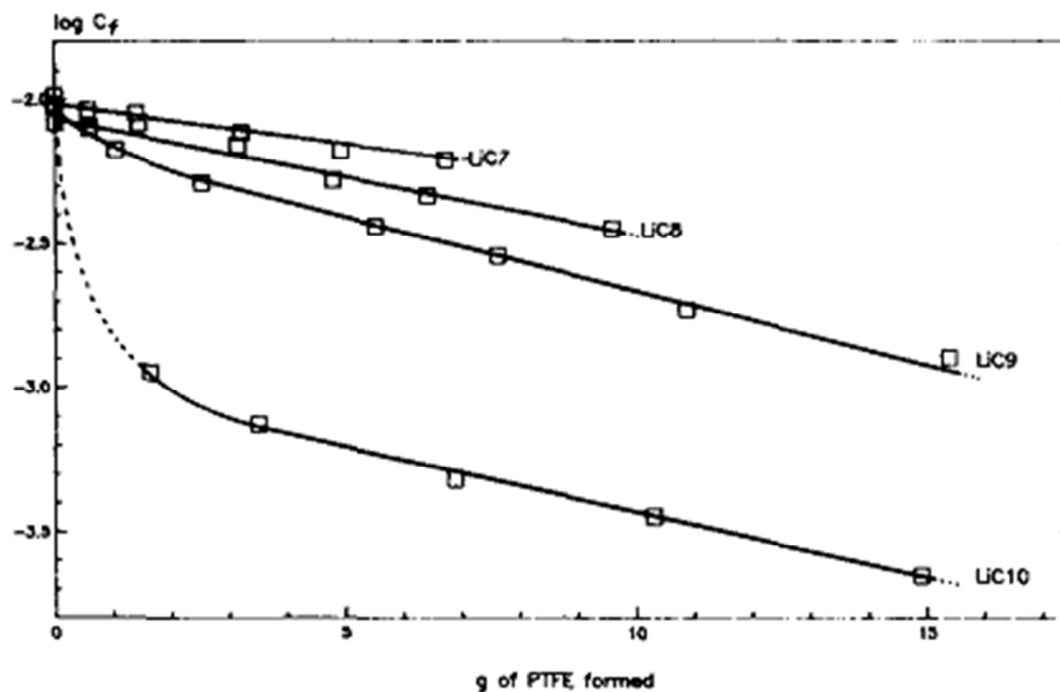
Figure 6: *Free surfactant concentration (in mol·L^{-1}) of the lithium salts of the homologous series of perfluorinated carboxylic acids from 7 to 10 carbons in length [141].*

The fluorinated surfactants are not a "renewable" resource within the reactor and the concentration of free surfactant decreases with polymer yield (that is, reaction time). Depending on the starting concentration, an initial, rapid drop in concentration to below the critical micellar

concentration (CMC) is seen to occur, followed by a nearly linear concentration decrease with time. This behavior is illustrated for the lithium salts of carboxylic acids in Figure 6. This behavior is primarily due to the sequestering of the surfactant *via* incorporation into the developing polymer particles [95].

The CMC values for ammonium perfluorooctanoate ($C_7F_{15}COONH_4$) have been reported as 0.5 to 1.422 %, depending on the measurement technique and the temperature[105,165-167]. Kissa[166] provided a comprehensive summary of the CMC values for number of fluorinated surfactants.
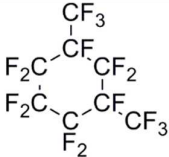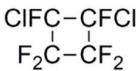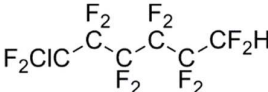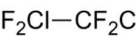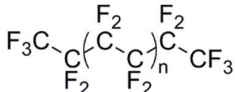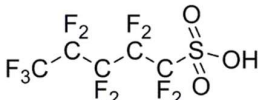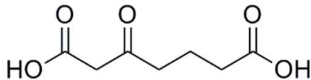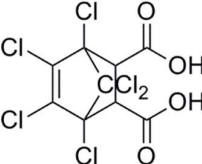
The long-chain perfluorocarboxylic are being phased out due to health-[168] and environmental concerns, with 3M having ceased production of perfluorocarboxylic acids (PFCAs) and its phosphonate and sulfonate analogues. W.L. Gore & Associates Company stopped using PFCAs altogether. Though Gen-X surfactants, $C_3F_7OCF(CF_3)CO_2H$, has been marketed DuPont/Chemours, this company has also stopped using PFCAs and, in 2017, they reached a settlement regarding a class action lawsuit resulting from the use of PFCAs in the polymerization process.

In recent years, considerable effort has gone into developing safer and more environmentally benign surfactants [169,170].

5.5.3   Stabilizers

While hydrocarbons are undesirable as surfactants, they have found use as stabilizers in the dispersion polymerization of TFE. Long-chain aliphatic hydrocarbons are added to the dispersion to prevent the premature agglomeration of the dispersed particles. Mixtures of hydrocarbon compounds under the generic name of "paraffin" have been employed, as have pure hydrocarbon compounds such as n-hexadecane [32,53,105,160].

Table 4: *Dispersive agents used in the aqueous emulsion polymerization of TFE.*

Surfactant	Structure	CAS No:	Reference
Perfluorodimethylcyclohexane		355-02-2	32
1,2 - Dichlorohexafluorocyclobutane		356-18-3	32
1-Chloro-6-hydroperfluorohexane		307-22-2	32
1,2 - Dichlorotetrafluoroethane	F_2Cl-CF_2Cl	76-14-2	32
Perfluorokerosene			32
Perfluorocarboxylic acids and salts			34,53,101,108,110,116,141,160, 171
Chlorofluorocarboxylic acids			172
Perfluoropolyether-based carboxylic acids			97
Perfluoro-n-pentane sulfonic acid			162
3-Keto pimelic acid			124
Chlorendic acid		115-28-6	163

5.5.4 CTAs in TFE polymerization

CTAs are generally undesirable in TFE polymerization as the electrophilic fluoromacroradicals will do its utmost to abstract any atom it can (hydrogen most particularly) to terminate the chain, which may result in a low molecular weight polymer *sans* the thermal- or mechanical properties of a TFE high polymer. Ameduri and Boutevin [7] provided some transfer constants for methanol

and dialkyl phosphite onto various fluoromonomers, but the works cited do not determine transfer-constants for CTAs onto TFE.

However, the patent literature [101] indicates that, if TFE can be polymerized up to very high-molecular-weights ($\sim 10^7$-10^8 g·mol^{-1}), a significant portion of the macroradicals may become entrapped in the polymer matrix and be immobilized such that they cannot terminate by mutual recombination. As discussed in Section 7.3.2 this results in lower polymer thermal stability. To overcome this, addition of H_2, methane, ethane, *etc.* may be added to the polymerization kettle in order to "cap" the growing macroradical before it reaches too high a molecular weight. The addition of a CTA may be continuous, or may be done batch-wise, with the available literature indicating batch addition to be preferable owing to more accurate concentration control.

CTAs are also employed to reduce the adhesion of PTFE to the walls of the reactor and the stirrer mechanism. Examples of such CTAs include citric acid. The CTAs used with TFE and their typical quantities (based on TFE) are summarized in Table 5.

Table 5:   *CTAs employed in aqueous free-radical polymerization of TFE.*

CTA	CAS No:	Monomer relative quantities (Mol %)	Reference
H_2	1333-74-0	0.01 – 2.5	[101]
CH_4	74-82-8	0.0008 – 0.4	[101]
CH_2F_2	75-10-5	0.01 – 2.5	[101]
CHF_3	75-46-7	0.01 – 10	[101]
CH_3-CHF_2	75-37-6	0.01 – 0.5	[101]
C_2H_6	74-84-0	0.01 – 0.05	[101]
CH_3OH	67-56-1	0.01	[171]
CH_3CH_2COOH	79-09-4	0.05	[171]
Citric acid	77-92-9	0.01	[98]

As would be expected, the addition of a CTA to a TFE polymerization strongly affects the rate of polymerization: for example, an addition of 0.15 mol % of H_2 only results in a 20 % reaction rate decrease [101].

The patent literature indicates that the kinetics of chain transfer are strong functions of temperature, and chain transfer may be suppressed completely for aliphatic carboxylic acids such as formic acid, acetic acid, as well as sulfuric acid, if the temperature is brought to between -40 °C and 0 °C [158].

It is important to mention that there is a vast body of literature [7,12] on the telomerization and oligomerization of TFE and other fluoromonomers, and these processes extensively employ CTAs. The CTAs mentioned here are those that are employed specifically in the processes, which result in polymers of TFE and do not amount to the whole gamut of CTAs used with fluoromonomers [7].

5.6   Conclusions

TFE may be polymerized *via* free-radical, electrochemical, and coordination methods. The PTFE-synthesis process is highly sensitive to factors such as monomer purity and the presence of CTAs and one is restricted to a narrow range of solvents. For any kind of polymerization, perfluorinated liquids are the solvent of choice, but also water as the most stable and "green" solvent. The future of PTFE production may reside in supercritical carbon dioxide as this solvent negates much of the problems associated with perfluorinated surfactants as well as the concerns over water wastage.

PFOA and its sodium and ammonium salts are the premier dispersing agent for emulsion polymerization if aqueous systems are used, although there are numerous other surfactants available. However, these surfactants are bioaccumulative, toxic and persistent[170] and have been banned in 2015. Hence, research into more environmentally benign surfactants, such as partially fluorinated polyethers, is undergoing a fast development, but it remains to be seen if there will be any implementation of these surfactants in industry.

6   TELOMERIZATION   AND   REVERSIBLE-DEACTIVATION RADICAL POLYMERIZATION OF TFE

6.1   Telomerization of TFE

The preceding discussion focused on the conventional free radical polymerization of TFE to produce high-molecular-weight PTFE. The telomerization of TFE is not strictly related to the production of high-molecular-weight PTFE, but the radical chemistry for both processes are nearly identical, and an understanding of telomerization may aid in elucidating the reaction mechanisms of TFE polymerization.

Ameduri and Boutevin[7] have reviewed the telomerization of fluorinated monomers. Telomerization of TFE has been extensively studied in the context of the initiation pathways, *viz.*, redox-, photochemical-, thermal-, electron beam-, and free radical initiation; the last one being the most used by far.

Many CTAs, or telogens, have been employed and 1-iodoperfluoroalkanes (such as CF_3I [173,174], C_2F_5I and IC_2F_4I) were the primary telogens for TFE telomerization. Other halogenated CTAs include HBr, CH_2Cl_2 [175], $CHCl_3$ [176,177], CCl_4 [178], and CF_2Cl-$CFClI$ [179]. In the last case, the reaction was initiated by ^{60}Co gamma rays, while when CF_3CCl_2I [180] was employed, thermal activation was preferred. For radical telomerization involving alcohols as CTAs, the chain-transfer constants for methanol, ethanol, and isopropanol were determined as 0.036, 0.085, and 017, respectively [181].

The telomerization of TFE may be improved by the use of a suitable catalyst. Fielding [182] obtained TFE telomers containing more than ten TFE units using CCl_4 as CTA in the presence of tetraethylammonium fluoride catalyst. This evidenced a lower chain-transfer constants (*ca.* 10^{-2}) than either 1-iodoperfluoroalkanes or HBr. The catalytic redox telomerization of TFE with carbon tetrachloride was reported by Battais *et al.* [183] using $FeCl_3$/benzoin catalytic complex. They evaluated the rate constant k_1 of the reaction rate between the telogen and the metal at its lowest oxidation state, as well as the structure of low-molecular-weight telomers by gas chromatography (Figure 7). The low chain-transfer constants mentioned above obviously led to rather high-molecular-weight telomers. However, by redox catalysis, lower-molecular-weight chains were produced. Telomerization of C_2F_4 using CCl_4 catalyzed by $CuCl_2$, copper powder [184] and by $Fe(CO)_5$ [185] was also reported. Telomers obtained by these processes always exhibited a Cl_3C-$(C_2F_4)_n$-Cl structure with yields for the mono-, di-, tri-, and quaternary adducts being 11, 16.6, 15, and 6.5 %, respectively. The yield of telomers with n greater than 4 was reported as 41 %. Hanford [186] utilized C_2H_5SH to telomerize TFE using a peroxide initiation pathway and claimed to have obtained H-$(CF_2CF_2)_n$-C_2H_4SH telomers. However, the real structures were H-$(CF_2CF_2)_n$-SC_2H_5. When disulfides such as H_3CS-SCH_3 were used, the resulting telomers exhibited H_3C-S-$(CF_2$-$CF_2)_n$-S-CH_3 structure, showing that hydrogen atoms were not leaving groups.
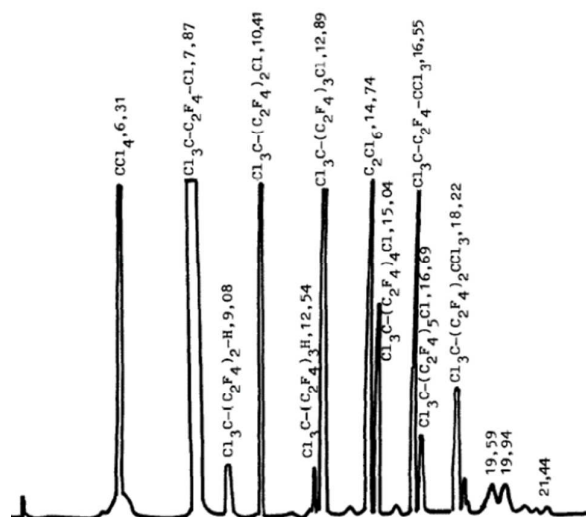
Figure 7: *Gas chromatogram of the total product mixture from the redox telomerization of TFE with CCl₄ (the numbers on the top of each peak stand for the retention times in min)*

6.2   Reversible-deactivation radical polymerization of TFE

Controlled-radical (or reversible-deactivation radical polymerization) of TFE is underreported in the literature. The publically accessible literature contains reports only on the iodine transfer polymerization- (ITP)[7] and one only on the RAFT/MADIX[187] of TFE. The ITP polymerization of TFE is closely related to the telomerization of TFE where 1-iodoperfluoroalkanes are employed as CTAs. These two techniques differ mostly in the target molecular weight of the polymer. The work on ITP of TFE was pioneered by Tatemoto at the Daikin Industries, basically on the production of PTFE-*b*-soft block-*b*-PTFE thermoplastic elastomers [188-191], with later contributions from Ausimont S.p.A. [192-194]. Techniques such as RAFT/MADIX have been applied to the homo- and copolymerization of VDF [195-197], CTFE [198], and HFP [199]. With the exception of the RAFT copolymerization of TFE with iBuVE controlled by a xanthate[187], to the best of our knowledge, no work on RDRP of TFE has been reported.

7   PROPERTIES OF PTFE

PTFE (CAS No: 9002-84-0) is a white, hydrophobic solid, whose properties depend strongly on its molecular weight. High-molecular-weight PTFE is chemically inert and insoluble in all known solvents, including hot fluorinated liquids. The polymer also exhibits an exceptionally low frictional coefficient and superb thermal stability. The salient properties of PTFE are summarized in Table 6. These properties are divided into two broad categories, *viz.,* properties of the as-polymerized or "virgin" PTFE, and properties of the processed PTFE. The molecular weight, polymer morphology as well as the chemical, electrical, and thermal properties are

dependent on the chemistry of the polymer and count among the properties of as-polymerized PTFE, whereas the mechanical and tribological properties can only be studied with processed PTFE and are, to a large extent, a function of the processing condition; therefore they count among the properties of processed PTFE.

Table 6:   *Physical and chemical properties of PTFE.*

Property	Value			Measurement standard	Reference
As-polymerized PTFE					
Melting point		335	(°C)	D3418	[200]
Glass transition		-103	(°C)	-	[201]
Decomposition point		590	(°C)	-	[65,66,74]
Phase transition		19	(°C)	-	[202]
Processed PTFE					
Theoretical density	at 23 °C	2.16	(g·cm^{-3})	ASTM D4895	[203]
Tensile strength	at 23 °C	31	(MPa)	ASTM D4894	[203]
Compressive strength	at 23 °C	4.4	(MPa)	ASTM D695	[203]
Hardness		55	(Shore D)	ASTM D2240	[203]

The polymerization process is highly sensitive to the purities of the monomer and the additives, the level of oxygen in the system as well as the fluctuations of pressure in the reactor. Hence, the polymerization process is difficult to reproduce exactly and no two batches of product will have the exact same properties in terms of yield, molecular weight, and particle size. Nevertheless, the polymer properties will fall in a narrow range and some properties, such as thermal stability, will vary so minutely between batches as to be undetectable.

This section discusses the properties of PTFE in relation to the polymerization conditions. Some of the properties covered here, such as the mechanical properties, have received detailed discussion in the literature [2,4] and will be touched on only briefly.

7.1   Molecular weight

Aqueous free-radical polymerization (both precipitation and emulsion) may yield molecular weights anywhere from 300 g·mol^{-1} to 10^7 g·mol^{-1}, depending on the initiator concentration, temperature and reaction pressure. Higher TFE partial pressures, low initiator concentrations

and low temperatures generally result in higher molecular weights. Commercial PTFE is marketed with a reported number-average molecular weight range of $10^6 - 10^7$ g·mol^{-1}. Table 7 compares the number-average molecular weight reported in the literature from various techniques.

Table 7: *Comparison of the molecular weights obtained for commercial PTFE resins by various techniques.*

Number-average molecular weight (g·mol^{-1})	Technique	PTFE grade	Reference
1.10×10^7	End-group analysis	Teflon® 6	[204]
1.27×10^7	Rheology	Teflon® 6	[204]
9.60×10^6	Standard Specific Gravity	Not stated	[200]
4.55×10^6	DSC (Suwa equation)	Not stated	[200]

Liquid medium photo initiation usually produces a waxy, low-molecular-weight polymer. However, the Ausimont corporation indicated that high polymers with thermal and mechanical properties similar to those produced by conventional free-radical methods can be obtained at low temperatures (~ 15 °C) when combining photo initiation of peroxide initiators with emulsion polymerization techniques [92]. Provided the heat of reaction can be removed sufficiently quickly, gaseous photoinitiators (*i.e.* SF$_5$Cl) can be used to initiate polymerization in the gas phase (that is, without any solvent or liquid carrier in the polymerization vessel), with the resulting polymer exhibiting a range of molecular weights ranging from telomeric liquids to waxes to high polymers with thermal and mechanical properties indistinguishable from polymers prepared by conventional techniques.

Claims have been made in the patent literature [171] that, when polymerizing TFE in the presence of a dispersing agent, the number-average molecular weight of the polymer comprising the spherical particles varies with the radius of the particle, having a lower molecular weight in the core than on the surface of the shell. Furthermore, proper choice of CTA added to the polymerization mixture permits tailoring of the ratio of the shell and core molecular weights as well as affecting the particle size distribution [97] (see Section 7.2.4 for the mechanism). This core/shell structure may be continuous, or may be discrete, depending on the monomer, initiator and CTA dosing regimen [97]. Noda *et al.* claimed a shell molecular weight ranging from 10 to 800 kg·mol^{-1} [97].
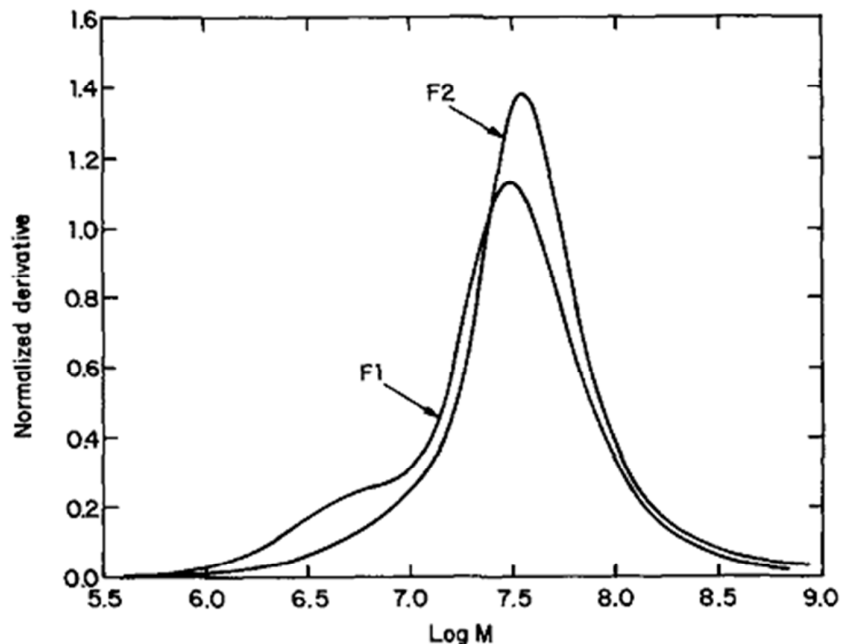
Figure 8: *Differential-molecular-weight-distribution curves for Teflon® 6 and 7A, obtained by viscoelastic spectroscopy [204].*

Little is known in the literature about the weight-average molecular weight (M_w) of PTFE. Wu [204] reports the M_w of commercial and specially synthesized PTFE determined using rheological methods, indicating that Teflon® 6 and 7 resins, both having a M_n of $\sim 10^7$ g·mol^{-1}, exhibit a dispersity of 3.58 and 2.76, respectively. Tuminello *et al.* [205] reported M_w values for specially synthesized PTFE, but does not give details of the synthesis method, so a comparison of dispersities as a function of polymerization conditions cannot be made.

Felix *et al.* [93] indicates that the dispersity of PTFE may be controlled to a certain extent by playing with the partial pressure of TFE during the polymerization reaction and by decreasing the partial pressure during the run, the dispersity may be broadened significantly. As stated in Section 3.3, there is a dearth of literature on the reaction kinetics and the effects of temperature and pressure on the dispersity of PTFE. Figure 8 compares the differential-dispersion curves obtained from rheology for commercial PTFEs.

7.2   Morphology

The discussion here summarizes the structure of PTFE as polymerized in terms of the chain arrangements, the microparticle structure, and the structure of bulk particles. The micro- and macrostructure of PTFE post-sintering and post-shaping, that is, the morphology of bulk

51

articles, has already been discussed in several reviews [2,4,206], particularly relating to the effects thereof on the mechanical properties of PTFE.

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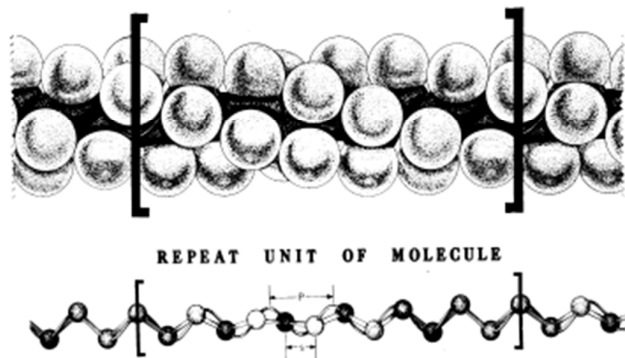
Figure 9: *Helical chain structure of PTFE in phase II crystal form (reprinted with permission from Elsevier) [207].*

7.2.1 Microstructure of PTFE

PTFE synthesized *via* free radical polymerization is always obtained as a linear chain. There are no branches and no loop structures as backbiting cannot occur with a fully fluorinated polymer backbone [21,153]. The PTFE chain adopts a helical structure (shown in Figure 9), and the polymer crystallizes in a hexagonal crystal arrangement. The helical structure itself is due to lone pair – lone pair repulsion between the fluorine atoms on adjacent CF_2 units. The helical conformations seem not to be a function of polymerization conditions, but rather a function of the temperature and pressure under which the polymer is studied [2,207].

PTFE may exist in one of four crystal phases (the phase diagram is shown in Figure 10), with phase I being the most common, followed by phase IV and then phase II. In phase I, the PTFE helix adopts a 13/6 conformation (this means 13 CF_2 units taking part in 6 full rotations about the carbon axis to return the fluorine atoms to the starting coordinates), and it adopts a 15/7 conformation in phase IV. Phases I and IV are the commonly observed crystal phases for PTFE as they occur at atmospheric pressure and ambient temperatures. Phase II is encountered usually at sub-ambient temperatures, while phase III is encountered only at high pressures.
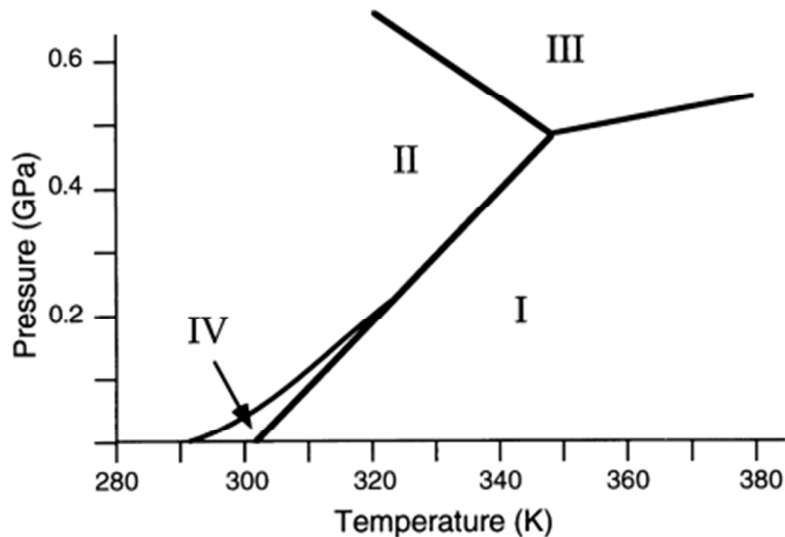
Figure 10: *Pressure-temperature phase diagram for the crystal structure of PTFE (reprinted with permission from Elsevier) [207].*

Importantly, the helical structure imparts a stiff, rod-like character to the polymer chain, and, as a result, the polymer crystallites are expected to consist of an assemblage of large regions of long, straight, and ordered chain packing. Diffraction studies have shown that this is indeed the case, and that all PTFE crystallites adopt this arrangement [208]. This is the main reason for the high crystallinity observed in both virgin and sintered PTFE. PTFE produced by other methods of initiation may differ in microstructure, with PTFE synthesized *via* gamma radiation initiation of TFE in the solid state exhibiting branching similar to what is observed in electron-beam irradiated PTFE [125,209-212].

7.2.2   Mesostructure of PTFE

PTFE exhibits an unusual particle structure in that the polymer is composed of microparticle in the form of both spherical- (or cobblestone shaped) and rod-like structures, with the rod-like structures consisting of long ranged, highly ordered, directionally oriented crystallite packing (being virtual single crystals), and the spherical structures appear to consist of more randomly oriented, smaller crystallites (Figure 11) [141,213]. Ribbon-like structures [208,214] and hexagonal platelets [215] have also been observed.
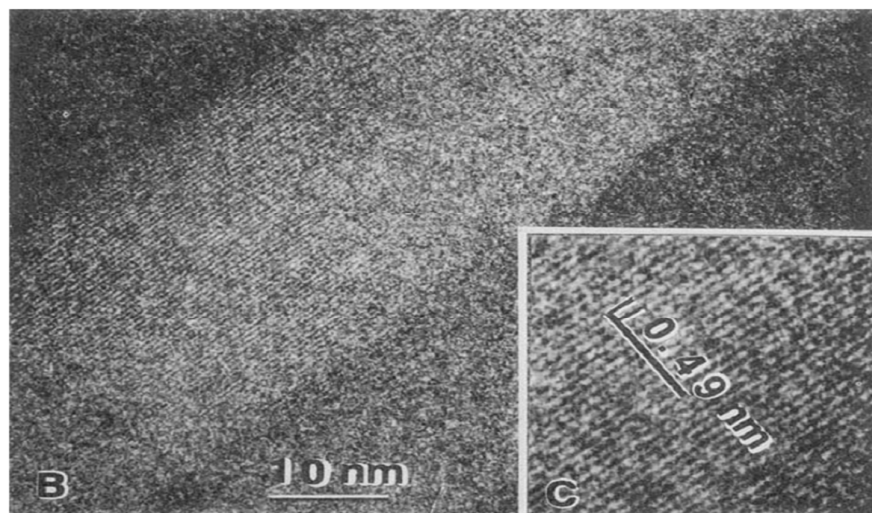
Figure 11: *Low dose, high resolution, negative contrast electron micrograph of rod-like PTFE particles showing the linear nature of the PTFE chains and their ordered long distance packing [213] (reprinted with permission from John Wiley and Sons).*

These features were first reported by Berry [160], and they are present in both suspension and dispersion polymerization products. Berry also indicated that the ratio of rod-like- to spherical particles can be tailored by adjusting the concentration of dispersant and initiator, with higher concentrations of surfactant delivering a higher percentage of rod-like particles. Furthermore, Punderson[95] indicated that the charging regime for the surfactant strongly affects the ratio of rod-like- to spherical particles, with a polymerization carried out using only a total initial charge of surfactant producing more rod-like particles than spherical particles, whereas the continual dosing of surfactant produces a higher proportion of spherical particles.

Kim *et al.* [105] shed some light on the exact effect the surfactant has on the microparticle morphology, indicating that spherical particles predominate when the surfactant is present in concentrations below the CMC and that the morphology gradually shifts to predominantly rod-like particles as the concentration approaches the CMC. Rod-like particles form the vast majority of the polymer at concentrations above the CMC.

Micrographs detailing the particle- and chain structure for the rod-like particles are shown in Figure 11, for the spherical particles in Figure 12, and for the ribbon structures in Figure 13. The rod-like structures exhibit an approximately triangular cross-section [216] made up of closely packed elementary fibrils with an approximate diameter of 6 nm [217]. Using the chain diameter of 0.49 nm obtained by Chanzy *et al.* [213], the fibrils are seen to be made up of approximately 12, closely

packed, PTFE chains. The preceding arrangements are shown in Figure 14. Luhmann and Feiring[141] reports that the length-to-width ratio of the rods can vary from unity to well over 100:1, with the ratio generally increasing with increasing the surfactant concentration.

The ribbon like structures range is length and width, but appear to be 6 nm in thickness, exhibiting an average length of 500 nm and an average width of 250 nm [208]. The thickness seems to be invariant of the source of the polymer (*i.e.* the manufacturer). The implication is that, if the rod structures are considered as 1D structures or as lines, the ribbon structures are 2D extensions, in essence a stacking of rods. The study by Rahl *et al.* [208], Luhmann and Feiring[141] and the electron micrographs of Chanzy *et al.*[213] (Figure 12) indicate that the spherical particles are nothing more than folded ribbon structures rolled up in a ball. This is illustrated in Figure 15, as first proposed by Rahl *et al.* [208].
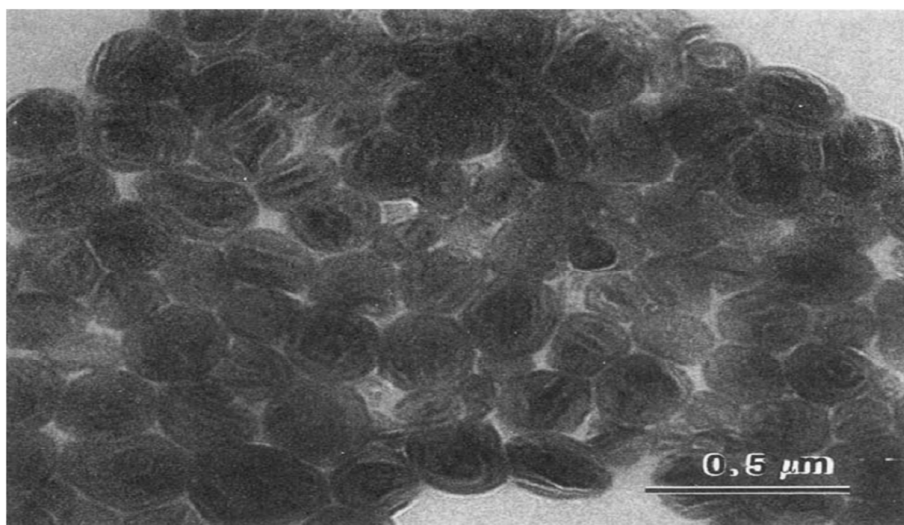
Figure 12: *Transmission electron micrograph of spherical PTFE particles that has been beam etched at 200 kV with a cumulative dose of 40 electrons.Å⁻² [213] (reprinted with permission from John Wiley and Sons).*

Examples of the hexagonal platelets are given in Figure 16. PTFE formed from the monomer in the solid state (by gamma irradiation[125]) exhibits an irregular, flaky morphology. The hexagonal platelets are observed only in PTFE with very low-molecular-weight or early on in emulsion polymerization, but virtually never in suspension polymerization, and they are completely different from the other structures observed in PTFE as the polymer chains are arranged perpendicular to the basal plane of the platelet.
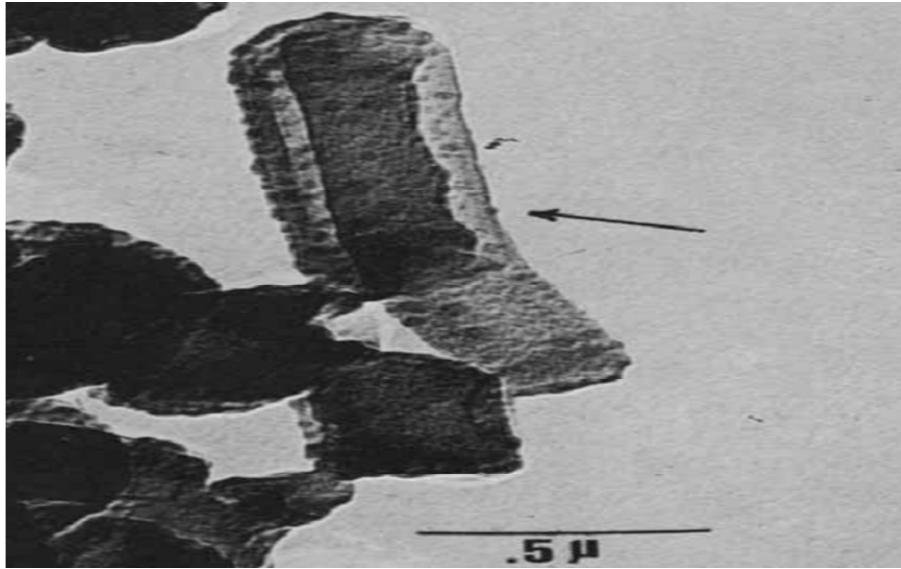
Figure 13: *Transmission electron micrograph of a PTFE ribbon taken from emulsion polymerization of TFE [208] (reprinted with permission from John Wiley and Sons).*

In essence, the hexagons are merely oversized rod structures that have been permitted to expand radially by addition of more chains as opposed to the lengthwise expansion *via* growth of the chain [141].

PTFE Chain arrangement in a fibril   Fibril arrangement in a rod-like particle

0.49 nm

6 nm

Single PTFE chain
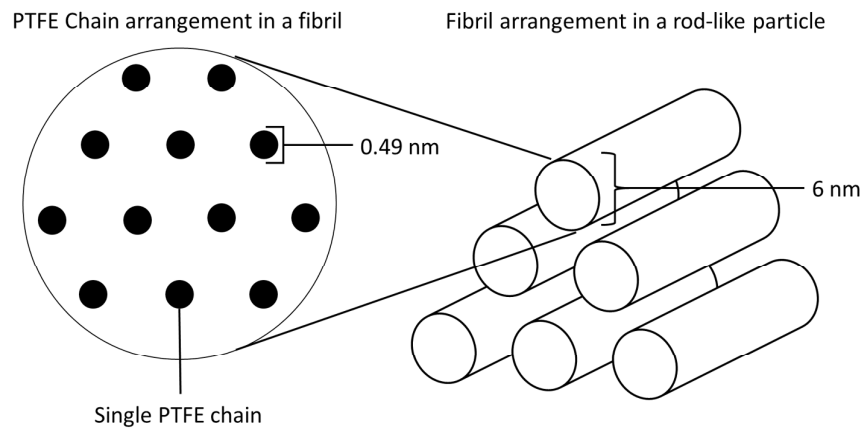
Figure 14: *Chain arrangements of PTFE in an elementary fibril and fibril arrangement in a rod-like particle for PTFE in phase II crystal form (see Figure 10).*

When PTFE is subjected to a sudden tension while at temperatures near its melting point, PTFE elongates rather than breaks. This elongation results in a microporous PTFE commonly known as expanded PTFE (or ePTFE). The mesostructural morphology of ePTFE is shown in Figure 17. Essentially, the expanded polymer mesostructure is composed of partitioned elementary fibrils [4].
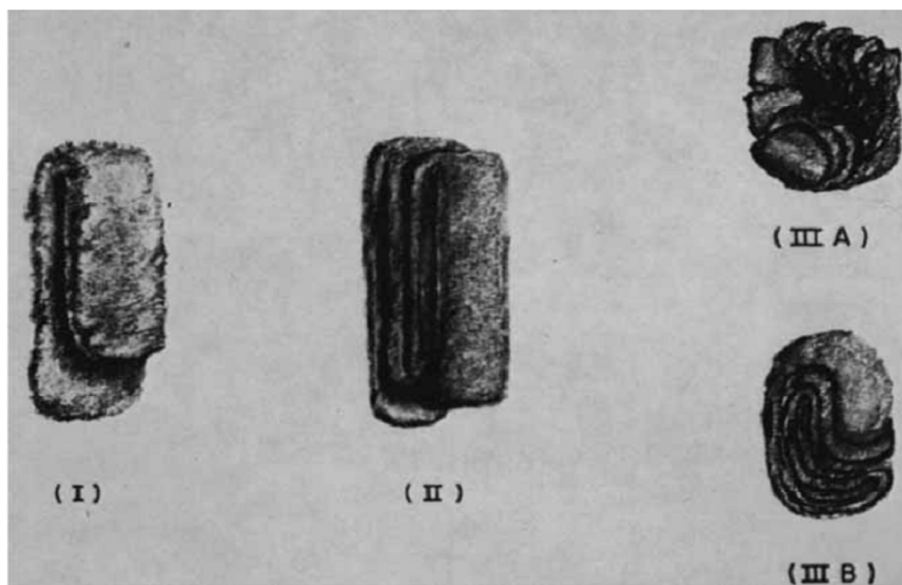
Figure 15: *Spherical PTFE particle formation by roll-up of a PTFE ribbon structure* [208] *(reprinted with permission from John Wiley and Sons).*
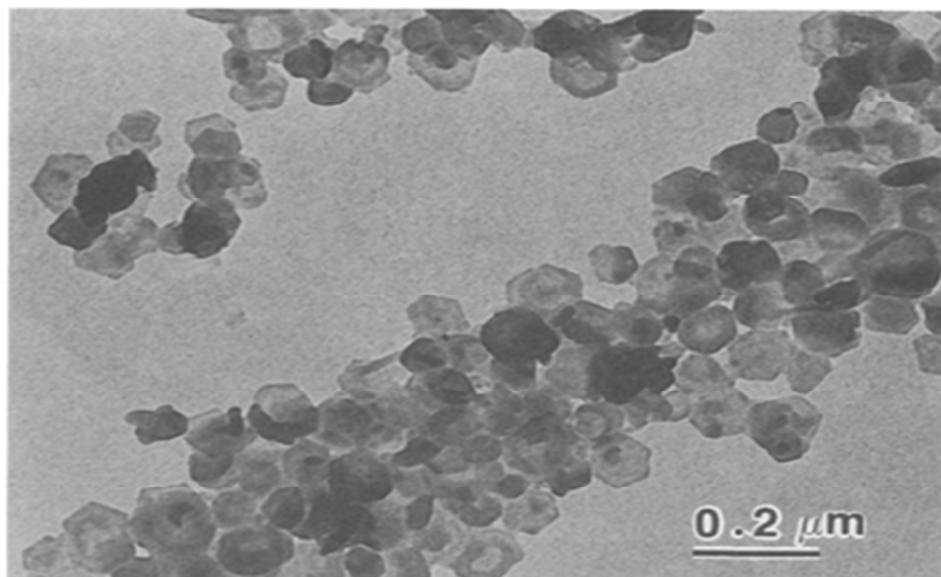
Figure 16: *Hexagonal platelets typically observed dispersion polymerized oligomeric PTFE [215] (reprinted with permission from Springer Nature).*

7.2.3 Macrostructure of PTFE

In aqueous, free-radical suspension polymerization, the polymer is usually isolated from the reactor as clumps of coarse, compacted, granular material of irregular shape or as stringy particles. The degree of clumping and the size of granules depends on the vigorousness of the agitation in the reactor [105]. It also depends on the molecular weight of the polymer and the level of solids reached in the reactor, but not on the temperature or the pressure [93,116,159]. If a dispersing agent is employed, the polymer is isolated as a fine powder when coagulated under low-shear conditions. Uncoagulated dispersions of PTFE in water are also commercially available.

The mesoscale structures (rods, spheres, ribbons) tend to both grow and consolidate during polymerization, giving rise to the large particle structures observed for the bulk polymer, similar in shape to their constituents, but ranging into the micrometer scales for the rod-like structures. In ordinary suspension polymerization, the spherical particle size can vary drastically with agglomerate d_{50} particle sizes in excess of 1.5 mm [93], but in the case of PTFE high polymer ($M_n \sim 10^6$ g·mol^{-1}) prepared with a dispersing agent, spherical particle size ranges from 0.05 to 0.50 µm, and a d_{50} ranging from 0.12 to 0.35 µm has been reported [171]. Still other literature claims an average d_{50} of 0.1 µm [97,161]. If the dispersions are coagulated and dried, the agglomerates exhibit a particle size between 100 and 1000 µm [97]. The use of the continuous TFE partial pressure drop method in ordinary suspension polymerization results in a decrease of agglomerate d_{50} particle sizes to the sub-millimeter range [93].
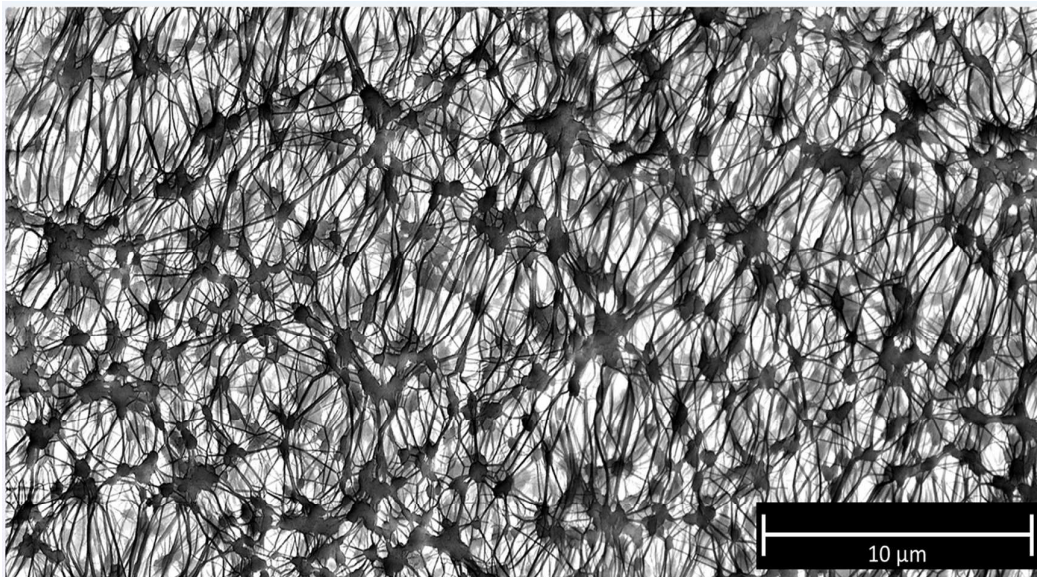
Figure 17: *Picture of GORE-TEX® Membrane by SEM (copyright © 2009 by W. L. Gore & Associates, Inc. Used by permission).*

When the polymerization process is carried out using liquid-phase TFE, the bulk morphology and microstructure differ substantially from the norm, with the polymer isolated from the reaction vessel as a foam or as a clear to slightly opaque, stable dispersion that does not coagulate under shear stress [100]. This material, when dried, becomes a sponge-like PTFE consisting of layers of polymer sheets. These sheets are porous and exhibit a continuous, randomly oriented three-dimensional fibrous microstructure with the fibrils having a sub-micron diameter. In some instances, the microstructure consists of platelets of highly crystalline PTFE.

The flaky microparticle isolated from solid-state polymerization usually range from 2 to 5 μm and form irregular clumps with no definitive size [125].

If water is not the reaction medium, the morphology may vary considerably, depending on the molecular weight obtained and type of termination reaction, with the polymer isolated as granular powder, finely dispersed powder, or gummy goo.

In the case of supercritical CO_2, the polymer is isolated as a fine, free-flowing powder with particle sizes dependent on the agitation within the reactor. Xu *et al.* [106] indicated the particle size distribution of PTFE from an unstirred polymerization ranges from 400 μm to well over 2 mm, with a d_{50} of 240 μm, while for a stirred reaction, the particle size distribution ranged from 20 to 800 μm, with a d_{50} of 135 μm.

Besides the aforementioned bulk morphologies, PTFE may also be deposited onto a substrate *via* admicellar[218] polymerization [108]. This produces a thin films of PTFE coating on the surface of whatever substrate was employed with examples from the literature including alumina chips and alumina powders[108].

7.2.4   Mechanisms of particle growth

Suspension and emulsion polymerizations are differentiated in terms of particle growth by the mechanism of particle nucleation: In the former, particle nucleation occurs homogenously, throughout the liquid phase, with short-chain, elementary fibril crystallites containing active end-groups crashing out of "solution" to form microscopic, local fluorous phases within the solvent [153]. Polymerization continues in this fluorous region to form the initial rod structures, some of which aggregate to form ribbons and finally spherical particles.

The available literature [53,95,105,141,159,171,219] indicates that, during emulsion polymerization, the initial stage of polymerization is dominated by nucleation in micelles according to the same mechanism found in suspension polymerization, followed by the formation of small, water-wetted polymer particles composed of a mixture of microparticle geometries and sizes, which depend strongly on surfactant chemistry and concentration. The processes of chain growth and agglomeration into particles is summarized in Scheme 7.

During the course of the reaction, the particles grow until they cannot be wetted any longer and become a distinct, hydrophobic bulk phase in the reactor. At this point, fluoromacroradicals are deposited from the aqueous medium onto the solid particles and come into direct contact with the gaseous TFE, which results in a great increase in reaction rate with the concomitant generation of high molecular-weight polymers.
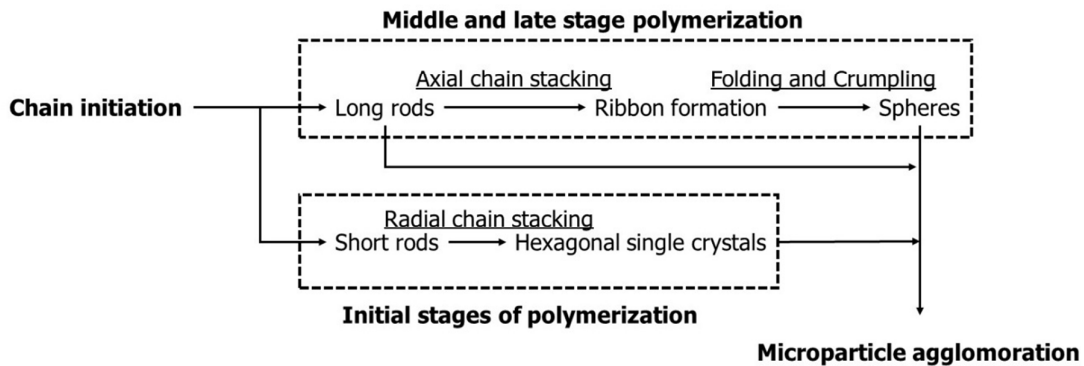
Scheme 7: *The formation of the various microparticle types found within PTFE produced by dispersion polymerization.*

If the agitation in the reactor is such that these growing particles collide and consolidate into larger particles, then the gas-contacted polymerization occurs both on the surface and in the interstices of the consolidate particles. The increased rate of reaction on the particles surface draws TFE away from the liquid medium, resulting in a decrease in the number of new "nucleation particles" with the concomitant increase in particle size, but narrowing in particle size distribution.

Hence, the particle size and the particle size distribution can be controlled by altering the agitation regime to ensure low-shear mixing, which promotes the formation of new nuclei over the consolidation of existing particles, or by adding CTAs to cap any fluorinated macroradicals at a certain molecular weight (and thus chain length) to prevent particle growth due to gas-contacted polymerization. However, the use of a CTA leads to lower molecular weights and is not ordinarily preferred. Changing the monomer concentration in the liquid phase or the initiator concentration will not promote the formation of new nuclei as the number of particles and the particle size is seen to be nearly independent of initiator [105].

It is possible to seed the polymerization medium with small particles (specific surface area greater than 9 $m^2 \cdot g^{-1}$ is ideal), but this contaminates the polymer with residues, so altering the shear rate to ensure *in situ* PTFE nuclei production is the preferred method by which the particle size is controlled. Also, the higher the shear rate, the stringier the particle agglomerates tend to be.

The aforementioned nucleation stage cannot last forever as the dispersing agent is slowly incorporated into the growing polymer particles and optimization of the shear rates will only prevent the premature termination of the nucleation phase. Under optimal shear conditions, polymerization carried out with a batch loading of dispersing agent will transition smoothly from a nucleation dominated regime to a particle growth dominated regime when the polymer solids content of the reactor has reacted 4 to 10 mass % [95], depending on the initial dispersing agent concentration.

7.3   Chemical and thermal properties
7.3.1   Chemical stability

The chemical stability of high-molecular-weight PTFE is ostensibly due to the high strength of the C-F bond (~460 kJ/mol) [220]. PTFE is attacked by neither acids nor bases. In particular,

PTFE is inert in boiling sulfuric, nitric, hydrofluoric, and hydrochloric acids, and in boiling solutions of aqueous bases [2,47]. PTFE does not dissolve in any solvent and is not even swollen by any solvent.

Only nascent alkali- and alkali earth metals, as well as a small selection of other metals and metal oxides are known to attack PTFE below its thermal decomposition temperature, generating metal fluoride and carbon. Aluminum and magnesium mixtures with PTFE are the most salient examples of reactive mixtures [221]. Steam may also attack very finely divided PTFE, generating HF and CO_2[47].

Oxygen attacks PTFE by forming CF_2O from the radical degradation products of PTFE thermal decomposition, and not by any intrinsic mechanism of attack. This CF_2O then undergoes further reaction to CO_2, CO, and CF_4, or to HF if moisture is present.

7.3.2 Thermal stability

PTFE also exhibits excellent thermal stability, being inert to over 400 °C even under pure oxygen. Pure PTFE will display nearly the same degradation temperature under air and nitrogen, while modified and filled PTFE will generally have a lower oxidative stability due to catalytic effects. The mechanism of PTFE breakdown has been discussed in detail [6]. In summary:

A PTFE macroradical may unzip [74], that is, depolymerize, giving back the monomer species. Ordinarily, the forward polymerization reaction dominates at low temperatures and in an excess of TFE. As the temperature increases, or the partial pressure of TFE decreases, the depolymerization reaction starts to dominate. The fully terminated PTFE polymer chain may decompose by undergoing chain scission at temperatures in excess of 590 °C, followed by unzipping of the new radically terminated chain segment. This chain scission is intrinsic to the polymer structure and cannot be improved upon by simple tweaking of the polymerization conditions. Alternatively, the fully terminated chain may unzip from the end-group and the more prone the end-group toward elimination, the less thermally stable the polymer becomes. The mechanism of breakdown is presented in Scheme 3.

In the particular case of PTFE initiated by persulfate, the sulfate group is hydrolyzed to OH in the aqueous polymerization medium [30,222]. The unstable 1,1-difluorocarbinol end-group reacts to form carboxyl groups, so ultimately, PTFE produced from persulfate initiators are terminated by fluorocarboxyl end-groups. These end-groups may eliminate CO_2 and HF, even at moderate temperatures, to form unsaturated end-group structures. The end-groups, being much less stable than the PTFE backbone, are eliminated first at elevated temperatures, followed by the unzipping of the chain from the end. Furthermore, the presence of unsaturated chain ends

produces a discoloration of the polymer. Initiation using sodium bisulfite does not produce hydrolyzable end-groups, with the chain being terminated by a more stable bisulfite end-group and, concomitantly, the chain is more thermally stable [30].

One caveat should be kept in mind: While the intrinsic thermal stability of PTFE is determined by the end-group or the CF_2 backbone, any real TFE homopolymer exhibits a pseudo-thermal stability. Low-molecular-weight PTFE or PTFE with a wide dispersity tends to evaporate off the low-molecular-weight chains from 300 °C to the bulk breakdown temperature. In these cases, thermogravimetric experiments may show a total polymer weight loss before the bulk breakdown temperature, even though no chain breakage has occurred.

In aqueous or fluorinated solvents, TFE polymerization is terminated by recombination. However, if a high-molecular-weight PTFE is produced, the polymer may undergo a thermal breakdown quicker than lower-molecular-weight PTFE. This has been attributed to the existence of unterminated macroradicals in the bulk polymer [101]. Essentially, the macroradicals become so large that the chain ends become immobile and polymerization is conducted by diffusion of monomer into the bulk polymer. But, when the polymerization is completed, these chain ends are not at liberty to terminate by recombination, remaining as macroradicals until contacted with air, producing unstable peroxide end-groups. This difficulty is overcome by adding minute quantities of specific CTAs to the polymerization that permit the radical to be capped by a hydrogen, and so ensuring the stability of the polymer chain towards unzipping from the unterminated macroradical chain end [101].

7.3.3 End-groups in PTFE

It is generally accepted that end-groups have no significant effect on the macroscopic properties of most polymers. This is because of their negligible weight when compared to the whole mass of polymer and because energy values for the bonds in end-groups and those in the constitutive units are practically equal [223]. However, this is not true for perfluoropolymers where hydrogen containing end-groups (produced by, *e.g.* persulfate initiators) do have definite influences on the performance and stability, ascribed to the difference in bond strength of C-H and C-F (410 and 460 kJ·mol^{-1}, respectively).

With hydrogen- and fluorine- containing polymers, such as PVDF, it has been shown that thermal stability and fire resistance are influenced by the end-groups generated in the presence of different initiators [224-226]. In this case, the relative strength of C-H to C-F bonds cannot be the determining factor. This unexpected behavior was attributed to different degradation mechanisms induced by the nature of the end-groups [223,227]. In addition to the thermal stability,

other properties such as fluidity and electrical conductivity have been demonstrated to be significantly influenced by end-groups.

Knowledge of the type and number of chain ends can reveal information about the mechanisms and relative rates of chain transfer and termination processes [228]. End-groups can also determine the crystallization kinetics from the melt of thermoplastic fluoropolymers, and hence the processing and end-use properties.

There is a dearth of literature on the subject of end-groups in PTFE, or more specifically, the end-groups produced by different initiators. Madorskaya and co-workers[227] reported the end-groups and subsequent effects on properties of the polymer for PVDF, but a similar, rigorous treatment of the end-groups in PTFE has not been published. Pianca *et al.* [223] supplied an overview of some of the end-groups present in fluoropolymers as well as their mechanisms of elimination, with the most studied initiator type being the ammonium and metal persulfates [222] and bisulfites [30]. The end-groups produced by these initiators include: $(C=O)OH$, $(C=O)NH_2$, $C{\equiv}N$, CF_2H, $(C=O)F$, $CF{=}CF_2$, $S(=O)_2OH$ and $(C=O)O^- X^+$, where X is a metal (such as Na, K, Li) or an ammonium group [223]. Of these, the amide, carboxylic acid, carboxylates, and sulfonates are the primary end-groups. Xu *et al.*[106,120] treat the end-groups generated by perfluorinated initiators.

$$-CF_2-CF_2-O-SO_3^- + H_2O \rightarrow [-CF_2-CF_2-OH] + HSO_4^-$$

$$[-CF_2-CF_2-OH] \rightarrow [-CF_2-COF] + HF$$

$$[-CF_2-COF] + H_2O \rightarrow -CF_2-COOH + HF$$
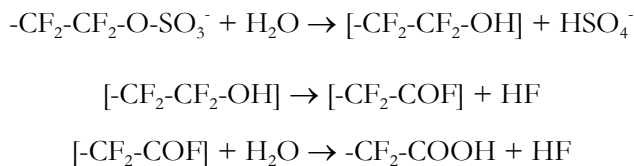
Scheme 8: *Mechanism of carboxylic acid end-group formation by persulfate initiators[223].*

Little has been mentioned in the literature on the mechanisms of formation of the end-groups from the initiator. Sometimes, the mechanisms are similar to those observed in non-fluorinated polymers, but for the case of PTFE, the end-groups differ significantly from hydrocarbon polymers. The reported mechanism by which a persulfate forms a carboxylic acid end-group is shown in Scheme 8.

The primary end-groups may decompose *in situ* during polymerization or under post-polymerization thermal treatment, leading to mixtures of end-group functionalities in the final polymer. For a carboxylic acid and carboxylic acid salt terminated PTFE chain, the reported elimination reactions are summarized in Scheme 9. Path (a) is observed when the sample is treated at 380 °C and delivers perfluorovinyl end-groups as well as carbon dioxide and hydrogen

fluoride. Path (b) occurs when the polymer is treated with water at 210 to 250 °C. This mechanism gives rise to difluoromethyl groups and carbon dioxide. Path (c) is noted during industrial extrusion of perfluoropolymers manufactured by aqueous emulsion polymerization with potassium persulfate as initiator and causes acyl fluoride groups, as well as hydrogen fluoride and carbon monoxide to be formed.

(a) $-CF_2-CF_2-COOH \rightarrow -CF=CF_2 + CO_2 + HF$

(b) $-CF_2-CF_2-COOH \rightarrow -CF_2-CF_2H + CO_2$

(c) $-CF_2-CF_2-COO^- X^+ \rightarrow -CF_2-COF + XF + CO$

(d) $-CF_2-COF + H_2O \rightarrow -CF_2CO_2H$
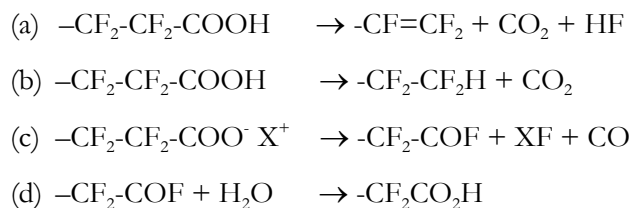
Scheme 9: *Decomposition pathways of carboxylic acid end-groups in PTFE to produce various secondary end-groups.*

The proposed mechanism for the formation of an acyl fluoride is a carboxylate thermolysis with carbon monoxide elimination similar to the method described by Pellerite [229] and is shown in Scheme 10. The cyclic zwitterionic intermediate loses CO upon heating to form the acyl fluoride group. This acyl fluoride will hydrolyze on contact with atmospheric moisture to lead back to a carboxylic acid.
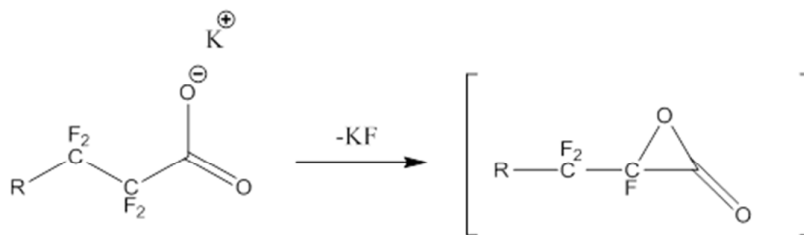
Scheme 10: *Unimolecular reaction mechanism proposed for formation of zwitterionic intermediate that leads to formation of acyl fluoride groups [223,229].*

The elimination reactions of the other end-groups have not been reported in the literature. In particular, how a nitrile group could be produced from an amide group is not discussed. Furthermore, PTFE synthesized with persulfates tend to undergo discoloration during thermal treatment, but the proposed mechanisms do not elucidate how an end-group with a sufficient number of conjugated p-orbitals can be generated to effect the aforementioned discoloration.

Markevich *et al.* [86] indicated that, if the PTFE macroradicals are not terminated by mutual recombination with some other radical fragments or capped *via* atom abstraction (usually a proton), then the PTFE macroradicals may persist indefinitely under inert conditions. In

practice, the PTFE macroradicals have been shown to be stable for days if kept at temperatures below 100 °C [86]. Upon exposure to atmospheric oxygen, these macroradicals form peroxides, which are stable at ambient conditions, but are prone to easy elimination upon heating (see Section 7.3.1).
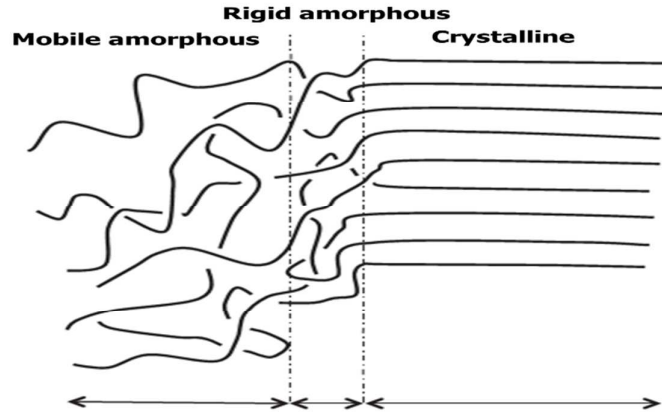
Figure 18: *Polymer chain arrangements in PTFE at the amorphous to crystalline transition, showing the different types of amorphous region (reprinted with permission from Elsevier) [201].*

7.3.4   Melting point and glass transition

PTFE does not exhibit a melt phase like PE does. Rather, PTFE has a first order transition point at ~335 °C where the chains start to move more freely. PTFE composites manufactured by powder processing techniques are "sintered" at or slightly above this temperature in order to coalesce the agglomerate particle. This melting point is a strong function of the molecular weight and the crystallinity of the polymer, with the melting point usually falling in the range 300 to 330 °C (usually 327 °C), depending on the initial crystallinity of the polymer [230,231].

PTFE produce *via* solid-state polymerization [125] exhibits a sharp drop in melt temperature with increasing radiation dose as the crystallinity decreases, with the initial, highly crystalline material exhibiting a melting point in the region of 335 °C.

Table 8: *Reported glass-transition temperatures (T_g) for PTFE, indicating the scope of the controversies regarding this property of PTFE.*

Technique	T_g (°C)	Reference
Positive glass-transition temperatures		

Dynamic mechanical analysis	+130	[232,233]
	+116	[201]
Rheometry	+110	[234,235]
Dilatometry	+123	[236]
Thermally stimulated currents	+130	[237]
Negative glass-transition temperatures		
Dynamic mechanical analysis	-110	[238]
	-103	[201]
Various mechanical measurements	-110	[239]
Calorimetry	-110	[240]
	-50	[241]
Calculational methods	-75	[242]

The origin of the glass-transition temperature is not as simple to explain as the melting point in terms of a molecular mechanism. There are numerous contradictions in the literature regarding the glass-transition temperature, with some results indicating a low T_g (*ca.* -100 °C) while others claim a high value (*ca.* +100 °C). The various reported values for the glass transition temperature are summarized in Table 8. More recent investigations using rheometry and dynamic mechanical analysis [201] indicate that PTFE exhibits two transitions, one relating to the mobile amorphous regions and the other one to the rigid amorphous regions (detailed in Figure 18), with the "true" glass transition being at -103 °C.

7.4   Mechanical properties

PTFE chains have little propensity for polarization and ionization and do not engage in hydrogen bonding. This results in a minimization of the polar and non-polar forces between PTFE chains and between PTFE chains and other molecules. Besides this, and, as already discussed, PTFE adopts a ridged, linear chain conformation. Consequently, the PTFE chains can slip easily past each other, rendering the polymer soft and ductile.

The mechanical properties of PTFE (such as tensile and compressive strength, flexural modulus, hardness, and impact toughness) have been extensively investigated under a variety of temperatures and loading conditions and numerous summaries exist [203,239,243-249]. Both the tensile and compressive properties are strong functions of the temperature and the strain rate, but are

weak functions of crystallinity. The modes of failure of PTFE articles differ significantly, depending on whether PTFE is above or below its glass-transition temperature [249].

In general, the mechanical properties of finished PTFE articles are strongly affected by the processing conditions, with air inclusions being the most common molding defect.

The molecular weight of the PTFE also plays an important role in its mechanical properties. The long chains of high-molecular-weight PTFE are to some extent prevented from moving. If shorter chains are present, they may act as lubricants for the long chains, increasing the rate of chain slippage. Hence, the higher the number-average molecular weight and the lower the dispersity of the polymer, the stronger the final molded article in tension environments, and vice versa.

For the aforementioned reasons, PTFE is also highly susceptible to cold flow (creep) and exhibits a large elongation-to-break, with 300 to 500 % elongation being common. Numerous manufacturers of finished and semi-finished PTFE articles have taken to incorporating filler materials into PTFE in order to combat the propensity of the polymer for cold flow. These filler materials include glass fibers, silica, brass, amorphous carbon, graphite, MoS_2, and a host of metal- and metal oxide powders [250,251]. These fillers also affect the hardness of PTFE resin.

To date, there have been no rigorous studies published on the mechanical properties of PTFE as a function of the dispersity since PTFE cannot be subjected to the usual methods employed to determine the molecular-weight distribution. Each manufacturer of PTFE resin provides the mechanical properties of their polymers under standard testing conditions (*i.e.* Section 8), and these properties may vary greatly between grades.

7.5   Hydrophobicity and surface properties

Items made from pure PTFE are hydrophobic and non-adhesive. Hydrophobic polymers are characterized by a static water contact angle of >90° and smooth PTFE surfaces exhibit a contact angle of 108 to 114 ° [252], reaching up to 118 ° if the polymer is unmodified [253]. Zhang *et al.* [253] indicated that PTFE articles could be made super hydrophobic by extension (pulling) of the substrate, with contact angles of up to 165° possible. Ion-plating is another method by which the hydrophobicity of PTFE coatings may be increased [254].The hydrophobicity of smooth PTFE is due to the lack of polarizability of the PTFE chain, which stymies the interaction of water with the surface of the polymer by hydrogen bonding.

Recent studies on the wettability of non-polar surfaces have shown that smooth, clean PTFE surfaces may be wetted to a significant extent by water if the interfacial surface tension is lowered with a surfactant [255-269] and contact angle values as low as 8 ° have been reported [263]. For

example, non-ionic- (Triton X100, Triton X165), cationic- (cetyltrimethylammonium bromide, pinacyanol bromide), anionic- (Sodium dodecyl sulfate), and zwitterionic surfactants have all been investigated (this includes both hydrocarbon and fluorocarbon compounds). The extent to which surfactant containing water can be made to wet PTFE is dependent on the surfactant chemistry, but for the first three classes of surfactants the effect is noticeable only up to the CMC and there is very little increase in the wetting of aqueous solutions of these surfactants beyond the CMC. The CMC acts as a turning point: Initially there is little change in the contact angle between the water and PTFE, but as the surfactant concentration approaches the CMC, the contact angle drops rapidly with concentration until a plateau is reached, where the contact angle is invariant of surfactant concentration. The same effect is observed with zwitterionic surfactants, but the point where there is a drop in the contact angle is found at surfactant concentrations far in excess of the CMC.

The use of static water contact angle measurements to determine hydrophobicity was questioned by Gao and McCarthy [270]. They indicated that advancing and receding contact angle hysteresis provides a much clearer picture of hydrophobicity and hydrophilicity. Their experiments show that a PTFE thin film will wrap itself around any water droplet place on its surface. Essentially PTFE shows a strong affinity for water. Based on this, PTFE should be considered a hydrophilic material, as opposed to a hydrophobic material. However, their definitions have not received much consideration in the surface science community, and PTFE is still regarded as a hydrophobic material.

The lack of any significant van der Waals interactions between PTFE and other molecules negates the climbing ability of species like ants and geckos, which make use of van der Waals interactions in their feet [271]. This lack of interaction is also the reason why adhesives do not stick to PTFE.

The surface properties of PTFE may be altered by including small amounts of modifier monomers or by treatment of the PTFE surface by electron beam- [272-277], UV-radiation- [278], glow discharge- [279-283], jet plasma- [284-287], wet chemical- [288-290], and grafting techniques [291].

The surface properties of PTFE are not known to be a function of the molecular weight or the as-polymerized polymer microstructure, and therefore, of the polymerization conditions. Nearly all surface property tests are conducted on a sintered sheet or a film of PTFE and under these testing conditions, imperfections in the shaping of the film or sheet play a much larger role in the measured surface property that the as-polymerized microstructure or molecular weight.

However, there have been no rigorous investigations into the effects of the ratio of rod-like to spherical particles or the dispersity on the surface properties.

7.6   Tribology and friction coefficients

The dynamic coefficient of friction ranges from 0.05 to 0.10 [203]. The dynamic friction coefficient and the static coefficient are both nearly independent of operating temperature up to the melting point of PTFE. The coefficient of friction is also dependent on the pressure, with the coefficient decreasing with increasing pressure, as well as the filler material and filler loading [2,4,250,251,264]. PTFE will undergo rapid mass loss under abrasive conditions if the PV value is exceeded[264].

PTFE exhibits interesting self-lubricating behavior: When rubbed against metal surfaces, the PTFE chain undergoes scission to produce various radical fragments, some of which form metal-carbon bonds with the surface of the metal substrate. These surface-bonded radical fragments create a continuous PTFE-like transfer film, which effectively results in the PTFE on the metal mimicking a PTFE on PTFE system [264]. The lack of significant interaction between PTFE chains results in an extremely low coefficient of friction, and hence the exceptional tribological properties.

Depending on the metal substrate, the formation of a layer of metal fluoride on the metal surface due to abstraction of fluorine from any nascent mental sites may also occur[292]. The surface fluorination competes with the formation of a transfer layer, resulting in an increase in wear between the polymer and the metal surface. Iron and aluminum are particularly susceptible to the formation of metal fluorine, whereas copper is less susceptible. Hence, PTFE exhibits much less wear when rubbed against copper than aluminum or iron [292,293].

The effects of PTFE wear due to surface fluorination cannot be mitigated by simple oxide layer passivation as the conditions at the polymer metal interface are such that PTFE will strip oxygen from the metal surface [292]. Hence, control of PTFE wear requires a detailed control of the surface chemistry of the underlying substrate.

As for the mechanical properties, no rigorous study has been reported on the tribological properties of PTFE as a function of the molecular-weight distribution.

7.7   Electrical properties

PTFE is non-conductive and possesses an excellent dielectric strength due to the non-polarizability of the polymer chains [2,4]. The dielectric strength is almost invariant with frequency up to 10 MHz and remains nearly constant with temperature as well [2,294]. Weathering has minimal effect on the dielectric strength of PTFE.

7.8   Conclusions

PTFE exhibits a range of useful properties, many of which are strong functions of temperature and molecular weight. The molecular weight is dependent on both the initiator chemistry, the reaction temperature as well as the chemistry of additives present in the reaction. The polymerization process is sensitive to impurities and any materials that can donate a proton will result in a reduced molecular weight.

PTFE may exist as rods, spheres, ribbons, or hexagons. The macrostructure of PTFE is dependent on the polymerization technique employed: dispersion polymerization produces mostly spherical particles with smaller d_{50} while suspension polymerization leads to mostly rod like particles with larger particle d_{50}, but with severe agglomeration.

Thermal and chemical stabilities of the initiator is a determining factor in the stability of the PTFE chains, and the more prone the end-group is to elimination, the lower the chemical and thermal stability of the polymer. Currently, the use of sterically hindered, perfluorinated peroxide initiators is preferred as the presence of the perfluoroend-groups imparts an increased stability to the polymer.

The mechanical- and tribological properties are dependent on the molecular weight, the crystallinity and the size of the particle agglomerates in addition to the testing temperature. Imperfection, such as voids, contribute greatly to premature mechanical failure of PTFE finished articles.

PTFE is hydrophobic and exhibits a low coefficient of friction, but suffers from low mechanical strength and is severely susceptible to creep and to abrasion. It also displays excellent dielectric strength for key applications for insulation.

Indeed, the determination of the dispersity of PTFE is onerous and a rigorous treatment of the mechanical properties of PTFE in relation to the dispersity is lacking in the literature. The use of rheological techniques [204,295] to characterize the dispersity and compare the mechanical behavior of PTFE with differing dispersities presents an interesting avenue for further research.

8   POLYMER ANALYSIS TECHNIQUES

The most important physical properties for the characterization of PTFE include thermal stability, melting point, chemical purity, crystallinity, molecular weight, and dispersity [1,2]. As PTFE is not soluble in any solvent, gel-permeation chromatography, viscosimetry, and osmotic pressure methods cannot be used for the determination of the number-average molecular weight

or the dispersity of the polymer. Non-solubility also implies that conventional light scattering techniques cannot be employed to determine the M_w of the polymer.

8.1   Spectroscopic techniques
8.1.1   Gamma-ray spectrometry

Berry and Peterson[30] determined the M_n of PTFE for the first time using radioactive end-group analysis. These authors used ^{36}S containing potassium persulfate and sodium bisulfite, with the ^{36}S obtained from Oak Ridge National Laboratory. The technique involved direct measurement of the radio decay of the end-groups using a Geiger counter.

8.1.2   Infrared

End-group analysis, either by FTIR [296] or UV/Vis or by NMR spectroscopy, permits the determination of M_n. For FTIR analysis, the ratio of the end-group to the CF_2 units is correlated to the film thickness and the absorbance at wave numbers specific to the expected end-group, shown in Equation (2).

$$\frac{[CF_2]}{[End\ Groups]} = \frac{A \cdot \delta}{d \cdot 10^{-6}} \quad \textbf{(2)}$$

where *A, δ* and *d* stands for the absorbance, the end-group specific correction factor and the film thickness of the sample, respectively.

For this correlation, the end-groups COF, COOH^free and COOH^bound are used (1883 cm^-1, 1815 cm^-1 and 1809 cm^-1, 1777 cm^-1). The calibration factor δ differs for each end-group, being 406 for COF, 335 for CO_2H (free), and 320 for CO_2H (bound) [297]. A detailed description of the end-groups and their IR absorbance bands was published by Pianca *et al.* [223].

8.1.3   Nuclear magnetic resonance

Liquid-state NMR spectroscopy is not possible for PTFE as even low-molecular-weight PTFE waxes that are not soluble in any solvent, including solvents commonly used for recalcitrant samples in NMR spectroscopy (*e.g.* deuterated DMF and DMSO). Chemical analysis of PTFE or other perfluoropolymers must rely solely on solid-state magic angle spinning (MAS)- or on molten state NMR spectroscopy. Several textbooks and articles on the solid-state NMR spectroscopic analysis of polymers are in circulation [298-303] that discuss the available methods for solid-sate NMR spectroscopy of fluoropolymers, such as MAS and, both with and without decoupling. For perfluoropolymers, high-speed MAS is used, with 50 kHz spin rates giving satisfactory results. It is known from personal communication that DuPont/Chemours conducts molten state NMR spectroscopy, but the details of the operation are unknown.

Chemical purity is determined by solid-state NMR spectroscopy, using MAS to record the ^{19}F and ^{1}H NMR spectra for the polymer. For pure high molecular weight PTFE, only the signal assigned to $-CF_2-\mathbf{CF_2}-CF_2-$ should be observed (found at ~ -122 ppm) and no signals should be noted in the proton NMR spectrum [106]. In reality, some minor signals attributable to end-groups are present in the spectra and typical ^{19}F NMR side signals include CF at ~ -143 ppm and CF_3 at ~ -80 ppm. A sample solid state ^{19}F NMR spectrum of PTFE synthesized in sc-CO_2 with a fluorinated initiator is presented in Figure 19.

As an example of collection parameters: Lappan *et al.* [296] collected ^{19}F NMR spectra using a CRAMPS probe with 2.5 mm MAS rotor. Single pulse excitations were performed with a MAS spin rate of 32 kHz and a $\pi/2$ (90 °) pulse duration of 3 µs, accumulating 1024 scans for each spectrum.

Note: Solid-state NMR spectroscopy is not a ubiquitous technique, and those research groups who do own such an instrument often do not have a MAS rotor capable of 50 kHz spin rates. Spinning bands can be reduced or deleted by increasing the rotor speed. Compared to the data available for PVDF[195-197,304,305], data for the homopolymers of highly fluorinated monomers (such as CTFE and TFE) are sparse.
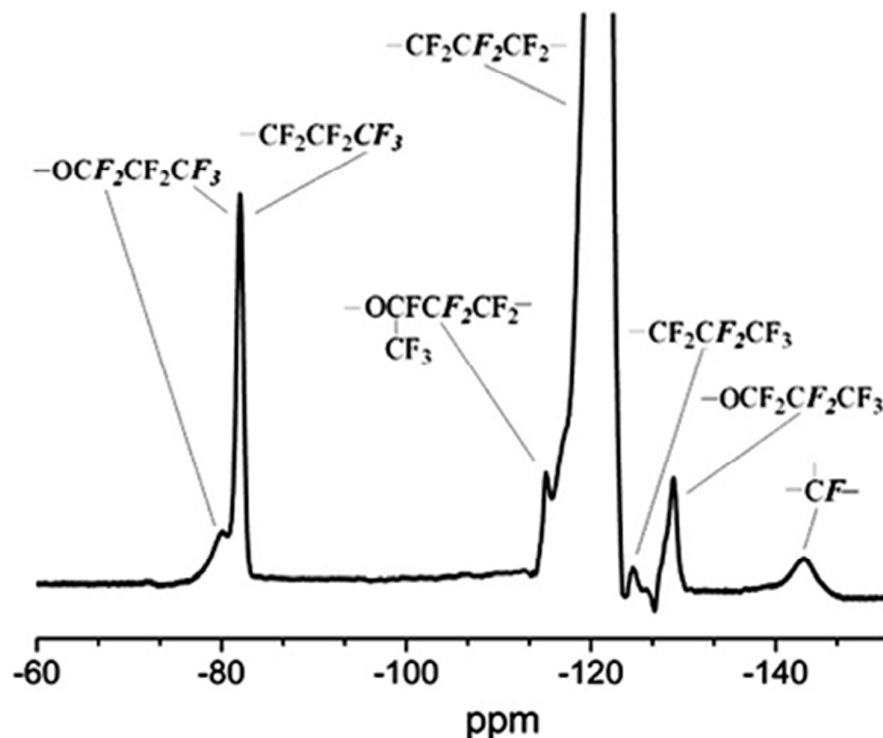
Figure 19: *^{19}F NMR spectrum of PTFE synthesized in sc-CO$_2$ using bis(perfluoro-2-n-propoxypropionyl) peroxide as initiator (reprinted with permission from Wiley) [106].*

8.2   Microscopy and particle analysis

The ratio of spheroidal to rod-like micro-particles, the average spheroidal micro-particle diameter, and the distribution of micro-particle diameters may be accomplished by direct inspection of SEM micrographs of the polymer. However, care should be taken when using an electron microscope as PTFE is highly susceptible to electron-beam-induced chain scission [209-213,272-275,306-316].

Sample preparation for PTFE dispersions require dilution to approximately ~0.02 mass % in demineralized water and dripped onto a metal grid suitable for SEM or TEM analysis. To ensure the PTFE is conductive, the polymer can be stained with phosphotungstic acid (PTA) and this is best effected by adding 1 mol % of PTA to the diluent water [141]. Non-dispersed polymers can simply be immobilized on some conductive adhesive film and then sputter coated using gold or carbon [106].

The distribution of agglomerate particle diameters may be determined by sieve tray analysis, but depending on the size of the agglomerates, readings will vary considerably due to electrostatic effects causing the particles to adhere to the sieves. The average particle diameter may also be

determined *via* Mie-light scattering analysis of a dilute dispersion (~0.02 mass% solids in water) with 550 nm light as well as by a sedigraph, using an ultra-centrifuge technique [171]. Particle surface areas per mass of sample are determined by the BET method [98].

8.3 Diffraction and light scattering

8.3.1 X-ray diffraction

Crystallinity of the polymer is usually determined by powder X-ray diffraction (XRD), but other methods, such as FTIR and DSC can also be used [317-319]. The most reliable methods is XRD, and fractional crystallinity is determined by dividing the peak area under the crystalline peaks by the total peak area of the spectrum. Numerous software packages are capable of performing the integration and crystallinity calculations, with TOPAS [320] being the most salient example.

8.3.2 Light scattering

Chu *et al.* [321] managed to perform high-temperature light scattering on low-molecular-weight PTFE using CTFE oligomers as a "solvent" at temperatures above the melting point of the polymer (~ 330 °C), using a specific equipment. These authors determined, among other properties, the M_w and the radius of gyration (18 ± 2 nm) of a PTFE chain.

8.4 Rheology

In the late 1980s, Wu [204], Tuminello *et al.* [205], and Starkweather and Hu [295] developed a method to characterize PTFE by rheology, employing the viscoelastic spectroscopy technique. In the case of "low-molecular-weight" PTFE, the dynamic modulus was used, whereas stress relaxation modulus enabled to determine "high- molecular-weight" PTFE.

They claimed to be able to extract a dispersity for PTFE from the rheological data. Wu [204] indicated that the M_n values obtained by rheology do not significantly differ from the M_n values obtained by end-group analysis. For example, with commercially available Teflon® 6 resin he found a M_n of 1.1 x 10^7 g·mol^{-1} by end-group analysis and a M_n of 1.27 x 10^7 g·mol^{-1} by rheology.

The accuracy of the dispersity determined by rheological techniques is not dependent on the exactness with which the molecular weights of a series of calibration compounds are known. Viscoelastic spectroscopy provides an assessment of the molecular weights of PTFE independent of the calorimetric and standard specific gravity methods, which are reliant on the accuracy of the end-group analysis technique. However, these is a paucity of literature on the application of viscoelastic spectroscopy in research on the synthesis of PTFE.

8.5   Thermal analysis

8.5.1   Thermogravimetric analysis

The intrinsic thermal stability of PTFE is measured *via* thermogravimetric analysis (TGA) [6], using the standard ASTM method for polymer analysis, which follows a heating program from ambient (~25 °C) to 850 °C at a rate of 10 °C·min⁻¹ under a nitrogen atmosphere flowing at 50 mL.min⁻¹. Oxidative thermal stability follows the same method, substituting oxygen or air for nitrogen. Depending on the reaction conditions in the instrument, mixtures of PTFE with certain metals may undergo runaway reaction and care must be taken to ensure that these compositions do not destroy the instrument [221].

8.5.2   Differential scanning calorimetry

Melting point is determined using either a DTA or a DSC, running approximately 5 mg of polymer at 10 °C·min⁻¹ from ambient to 400 °C and back again under a nitrogen atmosphere flowing a 50 mL·min⁻¹ [125]. Typically, aluminum or platinum pans are used for the melting point determination. Accuracy requires that the polymer be cycled through at least one, but preferably two thermal cycles to remove any thermal history, with the melting point determined from the data of the third thermal cycle.

Heat of crystallization (determined by DSC) has been correlated to M_n by Suwa *et al.* [200] and by Weigel *et al.*[296] These correlations are presented in Equation (3) and Equation (4), respectively, with ΔH_c in cal·g⁻¹. Re-examination of the literature [296] indicates that the equation of Weigel is preferred over Suwa's correlation. It must be noted that these correlations can be trusted only if the calculated M_n falls between 10^5 and 10^7 g·mol⁻¹.

$$\bar{M}_n = 2.1 \times 10^{10} \times \Delta H_c^{-5.16} \qquad \textbf{(3)}$$

$$\bar{M}_n = 3.5 \times 10^{11} \times \Delta H_c^{-5.16} \qquad \textbf{(4)}$$

Typical collection parameters require the use of a closed lid aluminum pan and ~ 5 mg of polymer sample. The heat of crystallization is, as far as is known, independent of heating rate (at least between heating rates of 5 to 35 °C·min⁻¹).

Suwa *et al.* [200] used custom-synthesized PTFE as standards. The number-average molecular weight of these polymers were determined by standard specific gravity techniques based on the methods presented by Sperati *et al.* [322,323].

8.6 Standard specific gravity techniques

Specific gravity measurements have also been used to determine the number-average molecular weight [322,323], but this method is not generally used as defects generated during sample preparation, such a voids and gas bubbles, can seriously affect the accuracy measurement. For high-molecular-weight PTFE, or TFE polymers where a simple CTA was employed (*i.e.* no branching or pendant groups), the standard specific gravity (SSG) is correlated to the number-average molecular weight by Equation (5) [171]. Variations on this equation have been published in subsequent literature [53,97], and the equation used by Kim *et al.* is given in Equation (6).

$$SSG = 2.612 - 0.582 \log_{10} \bar{M}_n \qquad \textbf{(5)}$$

$$\log_{10} M_n = 31.83 - 11.58 \times SSG \qquad \textbf{(6)}$$

The SSG was correlated to the number-average molecular weight using end-group analysis [30,222,322,323] and this method is only as accurate as the end-group analysis. The SSG is defined by the ratio of the mass of a sample plate to the mass of water, at 23 °C, of an equal volume of pure water. Sample plates are typically prepared by molding 3.5 g of polymer in a 1-" diameter cylindrical die *via* gradually increasing the pressure (minimum time is 30 s) to ~352 kg.cm^{-2} and held there for ~2 minutes to permit stress equalization. The preform is sintered at 380 °C, typically for 30 minutes, before being slow cooled (~1 °C.min^{-1}) to 300 °C . The plate should be conditioned at 23 °C for 3 hours after removal from the furnace to ensure that the entire volume is isothermal.

8.7 Conclusions

PTFE may be subjected to a range of analyses techniques. The structure of PTFE is typically studied using infrared spectroscopy while the molecular weight is usually determined *via* calorimetric means. However, owing to the complete insolubility of PTFE, it cannot be subjected to the critically important analyses such as gel-permeation chromatography (GPC) or viscosimetry. Furthermore, the solid-state NMR spectroscopic analysis of PTFE is non-trivial and can be challenging even to the best equipped laboratories.

The routine methods (DSC and SSG) employed in the determination of the molecular weight of PTFE are all ultimately calibrated against data obtained from end-group analysis. The accuracy if this data is questionable by today's standards and the values obtained for number-average molecular weight from Suwa's equation and the SSG correlations are subjective. In particular, Suwa's equation should be used with extreme caution, as the heat of crystallization is a function

of the entire dispersity, not just the number-average molecular weight. Using Suwa's equation with PTFE sample having dispersities significantly different from the calibrant samples may result in gross errors in M_n values.

There is significant scope for the re-investigation of the DSC correlations for molecular weight (M_n) using well defined polymers whose M_n are corroborated independently by techniques such as NMR spectroscopy and rheology.

Figure 20:   *PTFE insulated co-axial cable (image courtesy of Bhuwal Cables Company).*

9   APPLICATIONS OF PTFE

PTFE finds use in a vast number of technical fields, with applications ranging from electrical- to medical equipment, clothing, and even pyrotechnics. The information provided here is not meant to be an exhaustive catalogue of all the current and past application fields of PTFE, but rather to illustrate the contemporary importance of PTFE as well as the recent trends in the utilization of PTFE.

9.1   Electrical and electronic applications

Since its first appearance on the market, PTFE has been employed in the electrical industry as cable insulation and as dielectric in capacitors. The electrical and electronic applications are made possible by the high dielectric strength and the invariance of the dielectric constant over a wide frequency range. In particular, PTFE is applied as insulator in radio and microwave frequency communication cabling (co-axial cables, *etc.*), insulator in Wi-Fi antennas and medical instrument cables [324]. PTFE is especially employed in the military-, automotive-, and aerospace electronics sector [325] where electrical insulation material is required to perform under extreme temperatures.

PTFE insulation is also employed in cable coatings in the oil and gas industry, particularly in deep well settings owing to the excellent chemical resistance, low permeability, and thermal stability. Figure 20 and Figure 21 show examples of electrical products made with PTFE.

Figure 21:   *Cut-open film capacitor showing the PTFE dielectric roll (image courtesy of RuTubes Audio Components Company).*

9.2   Pipes, tubing, gaskets, seals, filters, and machined parts

PTFE may be ram extruded to form pipes and tubes, which find application in the fine chemical, petrochemical, nuclear, and food processing industries. Numerous types of connectors, nozzles, valves, and filter membranes are produced for chemical industry and laboratory applications are produced the world over (*cf.* [326-330]). Figure 22 provides an example of filter cartridges made with PTFE membranes.

PTFE has also been used as gasket material [331,332], as O-rings and other seals (such as plumber's tape) as well as valve seats in ball valves and needle valves [333]. PTFE sealing tape is probably the most ubiquitous application of PTFE in daily life. Industrially, the most commonly encountered PTFE are PTFE valve seals and gaskets.

It is a historical fact that the first major uses of PTFE were in the nuclear industry as gasket- and pipe liner material in the uranium enrichment plant operating during World War II.

Figure 22: *PTFE filter cartridges showing the PTFE membranes (image courtesy of the American Melt Blown & Filtration Company).*

9.3   Tribological applications

PTFE is employed as a dry lubricant [334,335] and as a release agent, with the most common household applications being the lubrication of bicycle and motorcycle sprockets and chains as well as door and window hinges [336] (PTFE dry lubricant is most well-known under the brand name WD-40 [337]). PTFE is also employed as the contact surface in slider bearings[335] (such as the structural bearings in bridges and expansion sliders for piping systems [338]). The low-friction properties of PTFE was used to good effect during the construction of the Millau viaduct in France [339], where PTFE slider bearings were used to jack the pre-assembled roadway across the pylons. Figure 23 provides a detailed cutaway of a PTFE slider bearing.

Lai *et al.* [108] have indicated that PTFE surface coatings could be used as a non-magnetic dry lubricant for high-speed magnetic storage devices used in the electronics industry (such has hard disk drives).

9.4   Chemically resistant, hydrophobic coatings and textiles

PTFE is most widely recognized as the non-stick coating on frying pans and PTFE has been employed as a non-stick, easy-cleaning, chemically inert coating in the food industry for many years [340]. Other uses of PTFE coatings include release coatings on molds, pipe liners (example shown in Figure 24), vessel- and thermocouple coatings in the pharmaceutical and chemical

industries [327,341] (including pipe liners in acid plants, non-fouling coatings in heat exchangers *etc.*) as well as anti-corrosion coatings for machinery housings [325]. One cannot enter a chemistry laboratory without finding, at minimum, PTFE coated magnetic stirring bars.
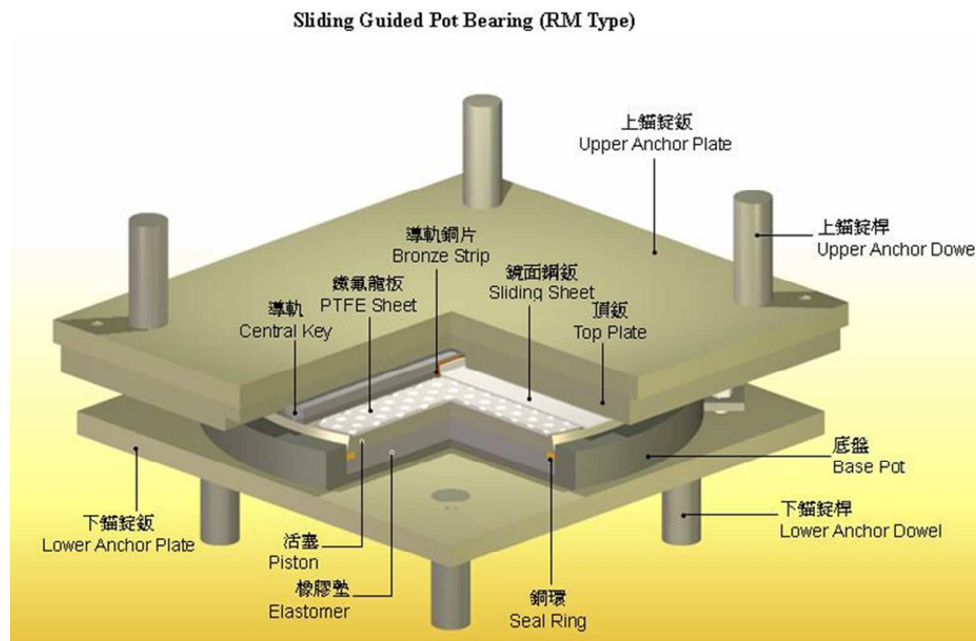
Figure 23: Diagram of a *PTFE sliding expansion bearing for road bridge applications (image courtesy of Nippon Pillar Singapore).*

PTFE is also used to coat textiles for water proofing [342]. In particular, expanded PTFE has been used as water proof, breathable membranes in clothing (known commercially as Gore-Tex [343]).

Figure 24: *PTFE lined pipe reducer (image courtesy of JCS Line Piping Products).*

9.5   Medical applications

Medical applications of PTFE (used mainly as expanded PTFE) include vascular grafts [344-346] and as surgical meshes, stents[347], catheters, scaffolds for ligament and tendon repair, and facial augmentation material in plastic surgery [348-350]. PTFE was also used in early replacement heart valves. The medical uses for PTFE primarily exploit the chemical inertness and hydrophobicity of the polymer and, in addition to the above-mentioned *in vivo* uses, are also used to coat various medical devices and tools. Figure 25 shows an example of ePTFE vascular grafts.

Figure 25:   *Example of an ePTFE vascular graft (image courtesy of the Terumo Corporation).*

9.6   Pyrotechnic applications

PTFE finds a niche use as the fuel in some metal/fluorocarbon pyrotechnic formulations. PTFE mixed with various metals, such as magnesium, aluminum, calcium, and silicon are used in missile counter measures, thermal lances, and signal flares [221]. PTFE based pyrotechnics are often known as MTV (Magnesium/Teflon/Viton) formulations.

Fluoropolymers are not widely employed in thermal lance technology and most fluorocarbon based pyrotechnics are used in military applications. These technologies are under reported due to the sensitive nature of missile counter measure feature. For example, it was not until 1997 that the US government permitted publication on the topic, despite a patent being filed as early as 1958 [351].

The pyrotechnical applications of PTFE are still active fields of research, as evidenced by the number of recent publications on this topic[352-355].

Figure 26: *Magnesium/Teflon/Viton (MTV) countermeasure flare cartridges mounted in a C-130 Hercules (image courtesy of Staff Sergeant David W. Richards).*

9.7   Conclusions

PTFE has found applications in numerous fields, ranging from electrical insulation and pipe liners to coated fabrics and medical applications (vascular grafts, stents, and items for plastic surgery). A combination of exceptional chemical and thermal stability, as well as hydrophobicity, sets PTFE at the top of the list of extreme polymers.

10   CONCLUSIONS AND PERSPECTIVES

The bulk fluoropolymer trade is estimated to grow to 94 ktons in 2018[17]. Figure 27 details the bulk fluoropolymer market valuation for the period 1998 to 2018. Even through the economic downturn of 2008 and the years thereafter, growth has been steady. The fluoropolymer type distribution, Figure 28, indicates that PTFE remains the predominant product amongst the vast array of fluoropolymers in use.

Recently, a global shift has been noted towards using sustainable materials, such as bio-sourced polymers, in order to reduce the impact of the plastics industry has on the environment. Commodity plastics such as high density polyethylene and polypropylene are being replaced with bio-derived polymers made from corn starch, and similar feedstock. Despite the global drive towards bio-derived plastics, the exceptional properties of fluoropolymers ensure that they cannot be replaced with more benign materials in high-tech applications. However, the fluorochemical industry, and by extension, the fluoropolymer industry, arguably has a poor environmental track record, though only 3 % of overall polymers can be recycled. The lack of innovation on the environmental aspects by large industry players has resulted in class-action lawsuits and significant reputational damage to these enterprises. DuPont has recently spun off

their fluoropolymers division into a separate company, Chemours. While DuPont officially maintains this was done for business related reasons, there is significant reason to believe the spin-off was done to mitigate any legal and public relations fallout over the environmental pollution generated by their fluoropolymer related activities.
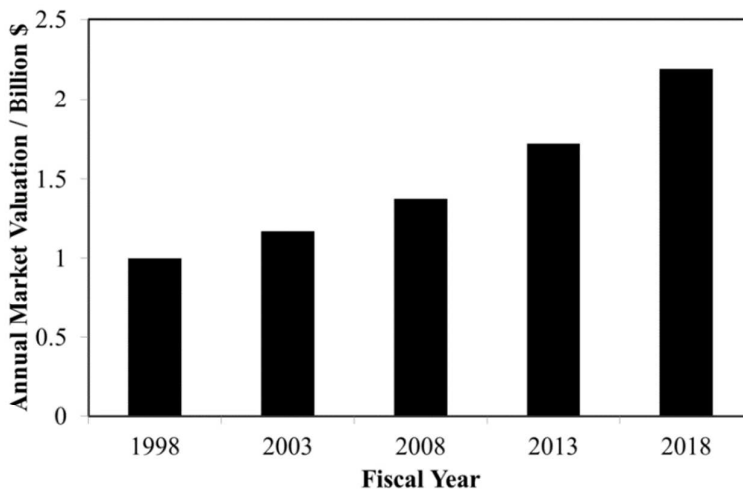
Figure 27: *Bulk fluoropolymer market value for the period 1998 to 2018. The 2018 value is an estimate (Data taken from Wood[17]).*

There clearly are economic opportunities in this market. Some of these may lie in the recent phase-out of perfluorinated surfactants. DuPont/Chemours stopped using PFOA in 2013, and the rest of the industrial industry followed suit by 2015. Evidently the replacements have been short-chain, partially fluorinated acids. Proven, but dormant, technologies such as super-critical-CO_2 synthesis may have to be resuscitated.
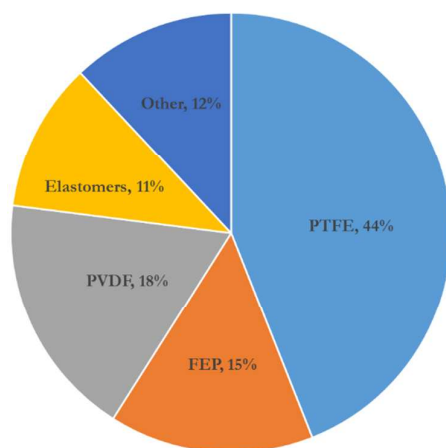
Figure 28: *Distribution of fluoropolymer market share by polymer type in 2013 (Data taken from Wood [17]).*

The full characterization of PTFE dispersity and the effects of the dispersity on the physical properties of PTFE are aspects that appear underexploited. Significant research scope exists for the evaluation of these properties as a function of the dispersity, and incorporation of these relationships into new product development. Control of the dispersity will enable primary producers to better tailor their PTFEs to the applications [356,357], reducing material wastage and the concomitant negative environmental impact.

Spent PTFE cannot be recovered by the ordinary methods used for plastics recycling and the material ends up on landfills or other disposal sites where it persists nearly indefinitely. Vacuum pyrolysis is one of the few methods available to recover the fluorine content in PTFE. When properly executed, TFE may be recovered from waste PTFE in high yields and good purity, adopting a cradle-to-cradle approach. Dyneon seems to be the only large PTFE producer doing this. Undoubtedly, other producers will follow in time, with increasing pressure on them to commit to higher degrees of environmental accountability. Much research is still in progress and it can be anticipated relevant findings in the coming decades.

11 ACKNOWLEDGMENTS

12 LIST OF SYMBOLS AND ABBREVIATIONS

ATR-FTIR	attenuated total reflection Fourier transform infrared spectroscopy
Δ	heating
ΔH_c	heat of crystallisation
AIBN	azobisisobutyronitrile
APS	ammonium persulfate
BET	Brunauer–Emmett–Teller
CMC	critical micellar concentration
CSM	cured site monomer
CTA	chain transfer agent
CTFE	chlorotrifluoroethylene
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
DP_N	number average degree of polymerization
DSC	differential scanning calorimetry
E	ethylene
EB	electron beam
FTIR	Fourier transformed infrared spectroscopy
G	spacing group
GPC	gel permeation chromatography
HFP	hexafluoropropylene
HFPO	hexafluoropropylene oxide
IR	infrared
ITP	iodine transfer polymerization
KPS	potassium persulfate
M	monomer (or comonomer)
MADIX	macromolecular design by interchange of xanthate
MAS	magic angle spinning
M_n	number average molecular weight
M_w	weight average molecular weight
NMR	nuclear magnetic resonance
OFCB	octafluorocyclobutane
PCTFE	poly(chlorotrifluoroethylene)
PDI (Đ)	dispersity
PFCA	perfluorocarboxylic acid
PFIB	perfluoroisobutene
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonic acid
PFPE	perfluoropolyether
PMVE	perfluoromethyl vinyl ether
PTA	phosphotungstic acid
PTFE	poly(tetrafluoroethylene)
PVDF	poly(vinylidene fluoride)
R	alkyl group
RAFT	reversible addition-fragmentation chain transfer
R_f	perfluorinated group
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SSG	standard specific gravity
TEM	transmission electron microscopy
TFE	tetrafluoroethylene
T_g	glass transition temperature
TGA	thermogravimetric analysis
T_m	melting temperature

UV	ultraviolet light
UV/Vis	ultraviolet light/visible light
VDF	vinylidene fluoride (or 1,1-difluoroethylene)
XRD	x-ray diffraction

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