A Kinetic and Mechanistic Study of the Low-Temperature Fluorine-Initiated Copolymerization of Tetrafluoroethylene with Oxygen

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ABSTRACT: The fluorine-initiated reaction of tetrafluoroethylene with oxygen, in a liquid phase at low temperature, leads to almost quantitative yields of polymeric perfluoroethers made by CF_2CF_2O and CF_2O units and containing variable amounts of peroxy bonds. This chain reaction is studied in a series of semibatch experiments, and the results are interpreted on the basis of a rather simplified reaction mechanism involving a sequence of elementary steps of different free-radical species. A most unexpected experimental finding is the positive action exerted by the oxygen pressure on the initiation rate; this effect is attributed to a competitive reaction of fluorine atoms with molecular oxygen to form FO_2 reactive species which are able to produce a substantial number of chain-initiating biradicals. The kinetic relationships deduced from the overall reaction model are proved to fairly describe, in a quantitative way, the correlation between the operating variables and the various polymer structure indexes. The values of the typical kinetic parameters of the process are estimated; they appear to be consistent with an emerging general picture of the reactivity characteristics of the different perfluorinated oxygenated radical species in the condensed state.

1. Introduction

On the oxidation of fluorinated olefins, and more specifically on the reaction of tetrafluoroethylene (TFE) with molecular oxygen, there is a fairly wide literature that goes back a good many years. Several papers have been published on the oxidation of TFE in the gas phase, either under purely thermal activation at elevated temperatures, or under the action of free-radical initiators, UV, γ, and laser radiation.[1,2] Other studies have been performed in the condensed phase at low temperatures, where the reaction appeared to follow a notably different pathway.[2,3] The nature and proportion of the various reaction products from TFE and O_2 were greatly influenced by the adopted experimental conditions, and this caused a somewhat discordant interpretation of the main mechanistic features of the reaction. A quite common fact, however, was that when one was working in the gas phase the main reaction products were of micromolecular nature, such as CF_2O and the oxirane, while when the reaction was carried out at relatively low temperatures, particularly in the condensed phase, the formation of polymeric products became important and even prevailing. The nature of these macromolecular substances varied between two extreme types, having the same chemical composition but very different properties. One was a highly unstable polyperoxide, $[C_2F_4O_2]_n$, clearly resulting from a simple alternate copolymerization process of the two reagents; the other was a notably stable polyacetal, $[CF_2O]_n$, whose origin could only be ascribed to a far more complex chain process. In general, however, the structures of the polymers obtainable under photochemical activation were of intermediate nature, since they contained different ratios of the two perfluoroalkylene units (CF_2 and CF_2CF_2) linked to each other by ether or peroxide bridges.[2] Working under well-chosen reaction conditions, it was however possible to selectively direct the low-temperature liquid-phase photochemical combination of TFE with oxygen toward the formation of polymers having polyether structure with only a minor content of peroxy linkages. Stimulated by the market interest in perfluoropolyethers, many studies have been devoted, particularly in these laboratories, to this singular "oxidative polymerization" process, which proved to be quite a common feature for fluoroolefins and to be one of the most direct, efficient, and versatile methods for the synthesis of such a class of compounds. These studies clarified the most important mechanistic aspects of this complex photochemical reaction and allowed us to successfully scale-up the process for the industrial production of a series of perfluorinated polyethers.[4]

It was later ascertained that even some specific chemical initiators could be employed to activate the same reaction, affording significant practical and technological advantages over the photochemical method.[5] In particular, the low-temperature reaction of TFE with oxygen, in an inert solvent, activated by elemental fluorine, was proven to be a most efficient way to produce almost quantitative yields of valuable perfluoropolyethers, whose general structure is expressed by the formula $R_FO(CF_2CF_2O)_n(CF_2O)_m(O)_pR_F$, where (O) represents a peroxide oxygen and R_F is a CF_3 or a C_2F_5 group.[6] Since the feasibility of the use of a chemical initiator also offered a good opportunity to obtain a better insight into the basic features of this complex reaction, a systematic study of the fluorine initiated process has now been performed. The key issue addressed by this study was the correlation between the structure of the obtainable polymer and the operating variables of the process; a more general aim, however, was to validate and substantiate the basic reaction model already proposed for the chain reaction between fluoroolefins and oxygen and to identify the main kinetic relationships that govern the process. Knowledge of reaction kinetics was deemed to be important, indeed, not only to confirm certain mechanistic beliefs but also to gather useful process information enabling prediction of the behavior of the same system in less explored reaction conditions.

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Some preliminary results of this study have been already anticipated:[6] in the present paper a wider range of experimental findings are reported and discussed. The data are derived from a set of systematic experiments made in a batch reactor at a fixed temperature, and the polymer structures are measured as a function of the reaction variables. The results are interpreted on the basis of a reaction mechanism that is similar to that already assumed for the corresponding photochemical reaction. To explain the experimental facts, however, some additional elementary steps are introduced into the scheme and a more comprehensive reaction mechanism is proposed, which, even if necessarily rather simplified, allows one to obtain a fairly good correlation and interpretation of the various experimental findings.

2. Experimental Section

2.1. Setup of the Experiments. The extremely high tendency of TFE toward free-radical polymerization, even at low temperature, makes it impractical to study its reaction with O_2 employing a substantial concentration of the fluoroolefin in the liquid phase; under the action of an effective free-radicals source, it would be difficult, indeed, to ensure enough dissolved oxygen to prevent a fast homopolymerization to PTFE. On the contrary, by reducing to a minimum the rate of initiation, a substantial concentration of C_2F_4 would essentially produce the dangerous polyperoxide. The reaction has been necessarily studied by adopting a semibatch methodology, where known amounts of the gaseous reagents (TFE, O_2, F_2) were continuously fed into a well-stirred inert liquid phase. The main reaction products were dissolved into the medium, which was homogeneous up to the end of the experiment; the excess oxygen leaving the reactor carried out at least part of the unreacted C_2F_4 and part of the low molecular weight side products (i.e., CF_2O, C_2F_6, C_2F_4O). Under these conditions, it has been ascertained that from the very beginning of the reaction a relatively small concentration of C_2F_4 built up in the liquid phase, which then remained practically constant during the course of the experiment. This stationary “equilibrium” concentration of monomer, $[C_2F_4]$, was strictly related to the other operating variables and was in the range $10^{-1}-10^{-2}$ mol L^{-1}.

A preliminary investigation on the reaction conditions allowed us to optimize the TFE conversion (which was nearly quantitative), selectivity in polymeric products (generally over 90%), and the structure of the polymer. As to this last point, it was considered preferable to obtain a relatively high content of enchained CF_2CF_2 units as well as a reduced presence of peroxide bonds, two somewhat conflicting requirements that needed a rather restricted and well-balanced choice of reaction conditions.

The key investigated factor was the ratio F_2/TFE of the feed; reactions were performed varying the amount of fluorine for a fixed amount of TFE feed into a fixed volume of solvent. While the amount of O_2 continuously introduced into the reaction medium proved to be unimportant, provided of course it was well in excess over the amount consumed during the reaction, a key factor turned out to be the oxygen pressure. Consequently, a set of measures were specifically executed to know the equilibrium concentration of dissolved oxygen under various oxygen pressures in the employed reaction medium at the chosen reaction temperature.

2.2. Experimental Procedure. Caution! Many hazards are associated with the reagents and the chemistry described here. TFE/O_2 mixtures are thermodynamically unstable and, within a large gamut of compositions, can explode by thermal or chemical activation. The use of elemental fluorine, particularly under pressure, requires skilled operators, with appropriate equipment and procedures. Polymeric polyperoxides of the type here described become heat and shock sensitive whenever their content of active oxygen exceeds about 4 wt %.

Table 1. Assignment of the ^{19}F NMR Characteristic Signals of the Polymer

structure	chemical shift (ppm)[a]
$-\mathrm{OCF_2CF_2O}\mathit{CF}_2\mathrm{OCF_2CF_2O}-$	−52.0
$-\mathrm{OCF_2O}\mathit{CF}_2\mathrm{OCF_2CF_2O}-$	−53.6
$-\mathrm{OCF_2O}\mathit{CF}_2\mathrm{OCF_2O}-$	−55.3
$-\mathrm{OCF_2CF_2O}\mathit{CF}_3$	−56.3
$-\mathrm{OCF_2O}\mathit{CF}_3$	−58.0
$-\mathrm{CF_2OO}\mathit{CF}_2\mathrm{OCF_2CF_2O}-$	−64.6
$-\mathrm{CF_2OO}\mathit{CF}_2\mathrm{OCF_2O}-$	−66.3
$-\mathrm{CF_2OOCF_2}\mathit{CF}_2\mathrm{OCF_2CF_2O}-$	−84.8
$-\mathrm{CF_2OOCF_2}\mathit{CF}_2\mathrm{OCF_2O}-$	−86.2
$-\mathrm{CF_2OCF_2}\mathit{CF}_3$	−87.7
$-\mathrm{CF_2OCF_2}\mathit{CF}_2\mathrm{OCF_2CF_2O}-$	−89.0
$-\mathrm{CF_2OCF_2}\mathit{CF}_2\mathrm{OCF_2O}-$	−90.7
$-\mathrm{CF_2OO}\mathit{CF}_2\mathit{CF}_2\mathrm{OOCF_2}-$	−90.7
$-\mathrm{CF_2OO}\mathit{CF}_2\mathrm{CF_2OCF_2}-$	−95.2
$-\mathrm{CF_2OOO}\mathit{CF}_2\mathrm{CF_2OCF_2}-$	−95.6

[a] With reference to $CFCl_3$.

The reactions were performed in a 1 L stainless steel reactor filled with 750 mL of CF_2Cl_2 (Ausimont, A 12) as solvent in which constant flows of the monomers (TFE and oxygen) and the initiator (F_2) were fed under vigorous mechanical stirring (Rushton turbine at 1000 rounds/min) at constant pressure and temperature.

Each reactant flow was measured and controlled by a thermal mass flowmeter (Bronkhorst, HI-TEC) calibrated with the specific gas; fluorine (Matheson Inc., used after removal of residual HF on sodium fluoride traps) was mixed with oxygen before entering the reactor through a feeding pipe dipped into the solvent; tetrafluoroethylene (Ausimont, polymerization grade) was fed from a pressurized cylinder (10 bar) through a separate feeding pipe.

The reactor was cooled by cold nitrogen flowing into a pipe tightly wound around the external surface; the temperature of the liquid reacting mixture was measured by a thermoresistance and kept within ±1 °C by an electronic device controlling an electric resistance immersed in the liquid phase.

All the experiments were performed using constant TFE and oxygen flows, while the initiator flow was changed; oxygen was always in 2-fold excess compared to TFE. Temperature was kept at −83 °C in all the experiments. The duration of the reaction was always maintained at 2 h.

Pressure was measured at the off-gas line and controlled by an automatic valve. Because of the low vapor pressure of the solvent at the reaction temperature and since TFE nearly quantitatively converted into polymer, the total pressure was approximated to the partial pressure of oxygen (P_o). A P_o value lower than 1 absolute bar was obtained by diluting the oxygen flow with nitrogen.

The typical procedure was the following: the reactor was cooled and charged with dichlorodifluoromethane; under stirring, the oxygen flow was started and the pressure set to the desired value. Because of the relatively short reaction time, it was important to minimize the concentration transients, especially for TFE. For such a reason, before starting the reaction TFE and O_2 were fed for the time (generally 1−3 min) necessary to reach a $[C_2F_4]$ value close to the supposed steady-state value; afterward the initiator feeding was started.

Four samples from the off-gas stream and two samples from the liquid reaction mixture were taken during each run.

The off-gas stream was traced with a known nitrogen flow and analyzed by gaschromatography using both a Fluorcoal column (isotherm, room temperature) and a molecular sieves column (to separate oxygen from nitrogen). The two combined analyses gave absolute flow and composition of the off-gas stream (oxygen, CF_2O, C_2F_6, C_2F_4, C_2F_4O, CF_2Cl_2).

Samples of the liquid reacting mixture were taken using a cooled glass trap; the samples were weighed, and after distillation, the volatile fraction was analyzed by gaschromatography (Fluorcoal) in order to quantify byproducts and TFE dissolved in the reacting mixture. The mean value of TFE concentration during the experiment has been considered as steady-state concentration $[C_2F_4]$.

Table 2. Experimental Results (for Symbols and Definitions See Text)

run	P_o	$F \times 10^4$	$[C_2F_4] \times 10^2$	η	f	DP_n	X_1	X_p	X_{1E}	X_{1P}	C_2F_4	CF_2O	C_2F_6	C_2F_4O
1	0.4	3.45	5.5	0.858	0.737	31.9	0.151	0.221	0.178	0.054	0.064	0.01	0.007	0.020
2	0.5	3.09	7.6	0.845	0.720	35.9	0.112	0.281	0.143	0.032	0.098	0.02	0.007	0.017
3	0.5	3.45	5.7	0.859	0.705	33.4	0.149	0.220	0.179	0.040	0.073	0.02	0.007	0.012
4	1.0	3.47	4.0	0.929	0.700	37.6	0.230	0.130	0.252	0.084	0.044	0	nd	0.002
5	1.0	3.10	6.7	0.871	0.656	42.0	0.138	0.220	0.164	0.045	0.074	0.02	nd	nd
6	1.0	2.98	9.0	0.892	0.705	42.0	0.110	0.272	0.138	0.033	0.100	0.03	nd	nd
7	1.0	3.09	5.3	0.899	0.689	40.0	0.158	0.182	0.183	0.044	0.045	0	0.002	0.001
8	2.0	2.74	3.8	0.957	0.594	55.9	0.243	0.119	0.268	0.063	0.028	0.03	0.009	0.007
9	2.0	2.62	4.8	0.924	0.662	50.7	0.198	0.131	0.218	0.060	0.046	0.02	0.007	0.007
10	2.0	2.38	8.2	0.878	0.642	54.6	0.113	0.244	0.140	0.064	0.086	0.03	0.006	0.011
11	2.9	2.38	3.1	0.982	0.642	60.9	0.295	0.091	0.317	0.077	0.014	0	0.007	0.006
12	2.9	2.26	5.2	0.930	0.637	61.2	0.189	0.147	0.213	0.048	0.045	0.02	0.006	0.007
13	2.9	2.14	7.4	0.892	0.626	63.0	0.129	0.215	0.155	0.033	0.073	0.03	0.006	0.010
14	4.0	2.08	3.3	0.961	0.622	70.3	0.252	0.120	0.278	0.059	0.018	0.01	0.006	0.006
15	4.0	2.02	4.5	0.938	0.692	63.6	0.216	0.125	0.238	0.063	0.030	0.01	0.005	0.006
16	4.0	1.96	7.3	0.888	0.640	66.9	0.129	0.215	0.154	0.036	0.061	0.03	0.005	0.010
17	4.0	1.85	9.7	0.880	0.632	71.4	0.083	0.298	0.108	0.079	0.089	0.03	0.004	0.012
18	3.7	2.26	3.7	0.996	0.638	65.3	0.273	0.114	0.300	0.061	0.011	0.01	0.006	0.005
19	3.7	2.14	6.7	0.933	0.627	65.6	0.143	0.197	0.171	0.036	0.047	0.01	0.004	0.008
20	4.5	2.14	3.6	0.996	0.637	68.8	0.299	0.116	0.330	0.060	0.002	0	0.005	0.005
21	4.5	1.90	7.9	0.934	0.652	71.3	0.116	0.224	0.142	0.052	0.058	0.03	0.004	0.009
22	4.5	1.79	11.2	0.933	0.634	78.1	0.079	0.312	0.103	0.026	0.096	0.03	0.004	0.014
23	5.0	1.67	2.9	0.960	0.731	74.8	0.312	0.085	0.333	0.082	0.018	0.02	0.005	0.004
24	5.0	1.55	6.3	0.886	0.732	74.1	0.159	0.184	0.186	0.039	0.061	0.05	0.004	0.008
25	5.0	1.43	8.5	0.866	0.799	71.9	0.109	0.253	0.136	0.062	0.086	0.08	0.003	0.015
26	6.0	1.43	4.5	0.934	0.806	76.9	0.222	0.136	0.249	0.052	0.036	0.03	0.004	0.006
27	6.0	1.43	6.1	0.951	0.795	79.2	0.170	0.172	0.196	0.049	0.054	0.06	0.005	0.009
28	6.0	1.31	8.9	0.897	0.785	82.5	0.103	0.267	0.130	0.030	0.086	0.06	0.003	0.011
29	7.0	1.31	7.5	0.894	0.760	85.1	0.127	0.215	0.154	0.030	0.073	0.06	0.003	0.009
30	7.0	1.37	2.8	0.870	0.703	85.7	0.359	0.089	0.387	0.067	0.001	0.01	0.004	0.004
31	7.0	1.25	8.3	0.857	0.750	86.6	0.104	0.256	0.132	0.023	0.075	0.05	0.002	0.009
32	8.0	1.16	4.1	0.896	0.760	96.2	0.264	0.114	0.291	0.053	0.010	0.01	0.003	0.005
33	8.0	1.10	4.2	0.854	0.773	95.4	0.238	0.135	0.267	0.044	0.012	0	0.002	0.004
34	9.0	0.92	7.3	0.861	0.826	107.0	0.122	0.217	0.148	0.028	0.060	0.02	0.002	0.007
35	9.0	0.86	11.3	0.847	0.891	104.4	0.066	0.327	0.091	0.015	0.099	0.02	0.002	0.010

At the end of the reaction, after distillation of the volatiles, the polymer was discharged, degassed and weighed. Iodometric titration of the peroxide content [2] and ^{19}F NMR analysis (Varian XL instrument operating at 200 MHz) were performed.

Table 1 lists the characteristic ^{19}F NMR signals for each kind of enchained CF_2 group and for the terminal groups which allow one to determine the structure and the microstructure of the polymer (molar fraction of the different units and bonds), its molecular weight and degree of polymerization (DP_n). Only CF_3O- and C_2F_5O- groups have been found as chain ends of the polymer. Trioxide bonds $-CF_2CF_2OOO-$ have been also detected, in very low amounts (their molar fractions ranging between 0.005 and 0.01); for structural characterization, they have been considered as peroxides.

Gel permeation chromatograms of polymer samples were obtained working at 30 °C in perfluorohexane, using a pump (model 590) and a refractive index detector (model 401) by Waters, and two mixed-bed 100% divinylbenzene polymer columns (250 mm × 10 mm). Fractions of analogous nonperoxidic polymers obtained by solvent−nonsolvent fractionation, whose molecular weight was measured by NMR spectroscopy, were used for calibration.[7]

On the basis of gas chromatographic and NMR analyses and on the basis of the amount of polymer obtained, balances on TFE, F_2, and oxygen have been done and conversions calculated. TFE conversion to polymer is expressed as the molar fraction of TFE converted to polymer units. TFE conversion to C_2F_4O was generally lower than 1%, while the amount of CF_2O produced was strongly dependent on the reaction conditions, being related to the amount of the one-carbon units of the polymer.

F_2 conversion was always quantitative; its selectivity to form polymer chain ends was calculated from the amount and molecular weight of the obtained polymer. Mass balance confirmed that C_2F_6 was the only byproduct of fluorine.

The same equipment and analytical procedures have been used to measure the equilibrium concentration of oxygen dissolved in CF_2Cl_2 under various pressures. The results, shown in Figure 1, proved that the relationship between dissolved O_2 and its partial pressure satisfactorily obeys Henry's law.

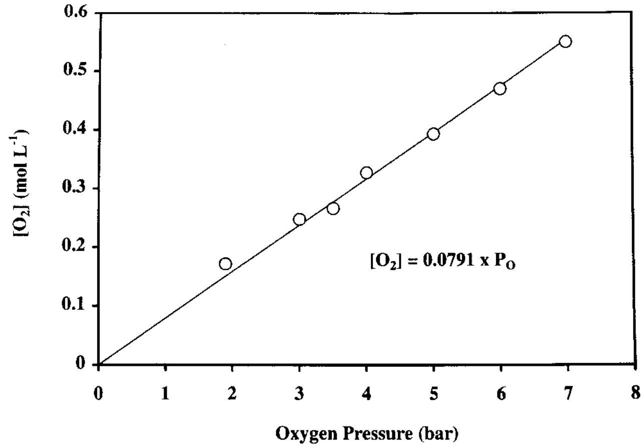

Figure 1. Molar concentration of dissolved oxygen, in CF_2Cl_2 at − 83 °C, vs O_2 partial pressure.

2.3. Results. Table 2 collects the results of all the experiments: the 2 h reactions have been performed at a temperature of −83 ±1 °C in a volume of 750 mL of CF_2Cl_2 with a constant flux of 160 N mL min^{-1} of C_2F_4 (9.5×10^{-3} mol L^{-1} min^{-1}).

The following symbols and definitions are used in the Table: P_o is the partial pressure of oxygen (absolute bar); F is the flux of fluorine (mol L^{-1} min^{-1}); $[C_2F_4]$ is the equilibrium concentration of the monomer in the liquid phase (mol L^{-1}); η is the fraction of monomer incorporated into the polymer (CF_2 + CF_2CF_2 units + end groups/mol of monomer fed); f is the "efficiency" factor of fluorine (moles in the polymer end groups/moles of fluorine fed); DP_n is the number-average polymerization degree (enchained units plus end groups/ polymer

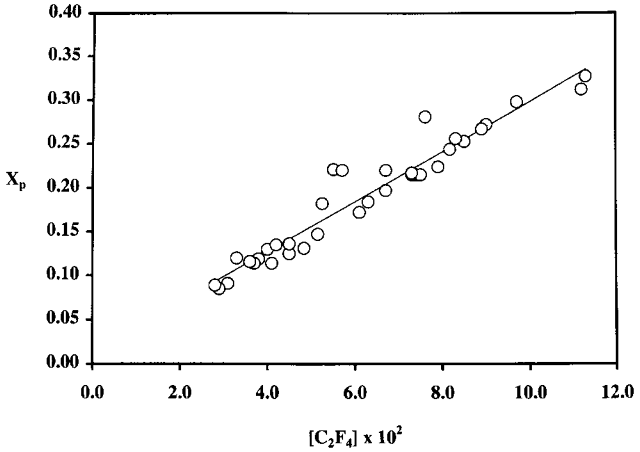

Figure 2. Relationship between the peroxide content of the polymer and the equilibrium concentration of the monomer.

molecule); X_1 is the molar fraction of CF_2 units in the polymer over the sum $CF_2 + CF_2CF_2$ units; X_p is the molar fraction of peroxide bonds in the polymer over the sum of ether and peroxide bonds; X_{1E} is the molar fraction of CF_2 units which are linked to an ether oxygen with respect to the sum of ether-bonded $CF_2 + CF_2CF_2$ units; X_{1p} is the molar fraction of CF_2 units which are linked to a peroxide bond with respect to the sum of peroxide bonded $CF_2 + CF_2CF_2$ units; C_2F_4, CF_2O, C_2F_6, and C_2F_4O are the molar fractions of the unreacted monomer and of the main side products formed in the reaction. The data concerning CF_2O refer to the "excess" carbonyl fluoride, i.e., the measured total CF_2O produced minus the amount expected on the basis of the number of CF_2 units that are present in the polymer.

Some points of interest may be put into evidence from a first glance at the trend of the data given in Table 2.

There is little, if any, systematic change of the overall reaction results in terms of conversion of the monomer and selectivity to polymer, on changing the experimental conditions over the range explored. This suggests that, at least to a first approximation, the formation of micromolecular reaction products could be regarded as the result of side reactions that are essentially unrelated to the main factors that govern the polymer structure.

As expected, there is a notable variation of the polymer structure indexes (X_1, X_p) with the operating variables. In general, the variation trend matches what one would have expected on the grounds of the results and of the general reaction model already discussed in the case of the same reaction photochemically activated[2]. For example, as shown in Figures 2 and 3, there is a nearly linear relationship between the peroxide content and $[C_2F_4]$, as well as an inverse correlation linking X_p to X_1. At constant oxygen pressure, by increasing the rate of initiation, i.e., the fluorine flux, there results a clear lowering of the peroxide content of the polymer, as well as an increase of its content of CF_2 units. Moreover, since the fluorine efficiency is practically constant and fluorine atoms constitute the polymer end groups, by increasing the ratio F_2/TFE there occurs a proportional decrease of DP_n. As regards the polymer fine structure, the expectation is confirmed that ether bonds tend to be mainly associated with the one-carbon units, that is $X_{1E} > X_1 > X_{1p}$.

The experimental results, however, also indicate a strong effect exerted by the pressure of oxygen over the polymer structure. This is a new and unpredictable result since, according to the behavior and the model of the photochemical process, one would not expect that oxygen concentration in the medium could exert any detectable kinetic influence on the overall reaction.

For a better understanding of all these results and for the purpose of interpreting and correlating in a more quantitative way the various interrelated factors that operate in determining the polymer structure, it appears now to be appropriate to have a brief discussion about this chemistry and to adopt a modeling approach to the reaction.

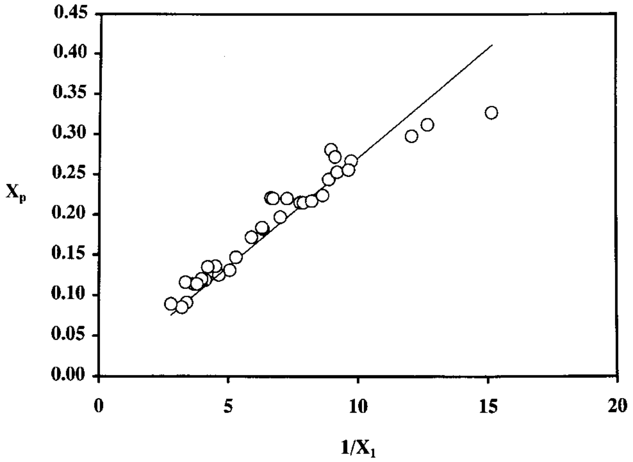

Figure 3. Polymer composition: inverse relationship between the content of one-carbon atom units (X_1) and of peroxide bonds (X_p).

3. The Reaction Model

The formation from TFE and O_2 of a polymer substantially having a polyether structure is the result of a chain process involving three types of reactive free-radical species:[2] R, perfluoroalkyl; RO, perfluoroalkoxyl; RO_2, perfluoroperoxyl. All these radicals belong to two different classes: one (C) in which the R group is a one-carbon atom group (CF_3, $\sim OCF_2$), and the other (M) in which R contains two carbon atoms (C_2F_5, $\sim OCF_2CF_2$). The most simplified kinetic model of the process involves at least six different types of elementary reactions of the above radicals. A convenient simplification results from expressing all the reaction rates of each kind of reactive species, in the various elementary steps, by a single constant, irrespective of the very nature and molecular mass of the R group. (It is obviously recognized that this can be a very rough approximation and that a particularly significant error might be committed assuming that all the growing radicals are kinetically equivalent, whatever their chain length, and particularly in the very first stage of chain propagation.)

On account of this simplification, the reaction model could be reduced to the six elementary reactions shown in Scheme 1,

Scheme 1. Elementary Steps of the Reaction Model

chain propagation

$$R + O_2 \rightarrow RO_2 \qquad K_1$$

$$RO_2 + C_2F_4 \rightarrow M \qquad K_2$$

$$RO + C_2F_4 \rightarrow M \qquad K_3$$

radical reactions

$$2RO_2 \rightarrow 2RO + O_2 \qquad K_4$$

$$MO \rightarrow C + CF_2O \qquad K_5$$

chain termination

$$2RO_2 \rightarrow ROOR + O_2 \qquad K_6$$

$$R = \text{perfluoroalkyl radical C or M}$$

$$C = CF_3 \text{ or } -OCF_2$$

$$M = C_2F_5 \text{ or } -OCF_2CF_2$$

where initiation, which is going to be specifically discussed in the next paragraph, is not included.

Basic steps are as follows:

1. The addition of O_2 to the carbon centered radicals.
2. The chain propagation with monomer of the peroxyl radicals.
3. The chain propagation with monomer of the oxyl radicals.
4. The self/cross reaction of peroxyl radicals leading to oxyl radicals.
5. The unimolecular fragmentation of the tetrafluoroethylenoxy radicals.
6. The coupling of two peroxyl radicals leading to chain termination.

This set of free-radical reactions is as classical as that already described for the same synthesis photochemically initiated. Only a few comments appear here to be appropriate.

The quenching by oxygen of a fluorocarbon radical is an extremely fast, diffusion-controlled reaction: it is indeed the only possible reaction that can be considered for the R radical. Under the adopted conditions, for example, the presence of enchained units bearing more than two difluoromethylene groups has never been detected, thus excluding the occurrence of some R + C_2F_4 propagation steps; the addition of a perfluoroalkyl radical to monomer is expected, indeed, to be orders of magnitude slower than its reaction with oxygen. Reaction 1, therefore, as well as the very existence of free perfluoroalkyl radicals, will not be further considered in the following kinetic treatment of the process.

Both peroxyls, $\sim OCF_2O_2$ (CO_2) and $\sim OCF_2CF_2O_2$ (MO_2), can react in two different ways: they can add to an olefin molecule (reaction 2) to propagate the chain with insertion of a peroxide bond, or they can undergo bimolecular self- or cross- reaction, either to be transformed into the corresponding oxyl radicals (reaction 4), or to terminate the chain by a coupling reaction that leaves a peroxide bond into the chain (reaction 6). Their preferred reaction will clearly depend on their actual concentration and on the concentration of the monomer.

Oxyl radicals, produced via reaction 4, are of two different types; difluoromethylenoxy radicals (CO) can only propagate the chain by addition to the monomer (reaction 3); tetrafluoroethylenoxy radicals (MO), however, in addition to the same chain propagation reaction, can undergo β scission (reaction 5), breaking their C−C bond to give CF_2O and one-carbon radicals (C), that will be eventually inserted into the chain either as difluoromethylenoxy or as difluoromethyleneperoxy units. The preferred reaction path for the key MO intermediate will depend on the monomer concentration, which clearly favors chain propagation over unimolecular fragmentation (here also temperature exerts a great effect, favoring fragmentation).

The chain structure of the polymer will clearly be the result of a complex interplay of alternative and competing reaction pathways of the two intermediate species (RO_2 and MO); it is not surprising, therefore, that a simple pattern does not emerge of the relationships between polymer structure and operating variables, which basically are the equilibrium concentration of the monomer and the concentration of the peroxyl radicals.

As far as chain termination is concerned, recombination of two peroxyls (reaction 6) is considered to be the dominant termination reaction. In this chain process, therefore, a very critical factor for determining kinetic chain length should be the ratio K_4/K_6, related to the probability that the encounter of two peroxyls will result in their reduction to chain propagating oxyl radicals instead of causing termination of the growing chains.

As said before, the kinetic model that is being considered is certainly a rather simplified one; only a few radical reactions, believed to be a substantial part of the mechanism, are included into the scheme, while numerous other reactions are ignored that possibly can occur within such a complex reaction system. For example, as chain termination is concerned, other self- and cross-couplings of the different radical species (R, RO, RO_2) that are present in the reacting system could be taken into consideration. On the basis of known kinetic and thermodynamic parameters, all these recombination reactions are indeed thermodynamically favored, very fast reactions. However, provided that enough C_2F_4 and O_2 is present in the system, coupling reactions such as

$$\mathrm{RO} + \mathrm{RO} \rightarrow \mathrm{ROOR} \qquad \mathrm{RO} + \mathrm{R} \rightarrow \mathrm{ROR}$$
$$\mathrm{R} + \mathrm{R} \rightarrow \mathrm{R{-}R}$$

are not expected to play a significant role because of the extremely low stationary concentration of these reactive species due to their great tendency toward different reactions. This is not totally true, however, for the coupling

$$\mathrm{RO_2} + \mathrm{RO} \rightarrow \mathrm{ROOOR}$$

as proven by the very small fraction of trioxide bridges that has generally been detected in the polymers (far less than one trioxide for each polymer molecule); one should therefore admit that there is also a small probability of chain termination via an effective cross-encounter of peroxyl and oxyl radicals.

Furthermore, the simplified reaction model does not include those reactions that might be responsible for side products, i.e., the excess CF_2O over the amount equivalent to the number of CF_2O units inserted into the chain and the oxirane C_2F_4O. Among various possible reactions leading to such side products, the following might be particularly considered:

$$\sim\mathrm{ROCF_2O} \rightarrow \sim\mathrm{RO} + \mathrm{CF_2O}$$
$$\sim\mathrm{ROOCF_2O} \rightarrow \sim\mathrm{RO_2} + \mathrm{CF_2O}$$
$$\sim\mathrm{ROOCF_2CF_2O} \rightarrow \sim\mathrm{RO_2} + \mathrm{C_2F_4O}$$
$$\sim\mathrm{RO_2} + \mathrm{C_2F_4} \rightarrow \sim\mathrm{RO} + \mathrm{C_2F_4O}$$
$$\sim\mathrm{ROOCF_2O} \rightarrow \sim\mathrm{RO} + \mathrm{CF_2O_2}$$
$$\sim\mathrm{OCF_2CF_2O_2} \rightarrow \sim\mathrm{OCF_2} + \mathrm{CF_2O_2}$$
$$\mathrm{CF_2O_2} + \mathrm{C_2F_4} \rightarrow \mathrm{CF_2O} + \mathrm{C_2F_4O}$$

Some of these reactions describe irreversible "chain depropagation" processes that have indeed to be considered possible, even if only likely at more elevated temperatures; the last reactions involve the formation of difluorodioxirane, already hypothesized as intermediate in a study of TFE oxidation,[1d] and its great epoxidizing power toward fluoroolefins.[8] Interestingly, such a reaction sequence would also equate the formation of the epoxide to the excess of carbonyl fluoride, a result that is roughly in accord with most of the experimental findings.

All the listed reactions would be intrinsically part of the chain growing mechanism, and their occurrence would obviously affect the correctness of the kinetic scheme deriving from the simplified mechanism. As already observed, however, it is also possible that both side products are formed via reaction pathways independent from the main chain growing mechanism. Due also to the fact that, under the adopted reaction conditions, the formation of side products has been always kept to a minimum, the occurrence of the above-reported reactions has been ignored in the simplified model.

A question that could be raised is whether some chain-transfer or disproportionation reactions can occur that might affect the polymer molecular weight. They look very unlikely, indeed, because for said reactions to take place there should always occur a C−F bond cleavage that costs a large amount of energy and implies very high activation barriers. The least thermodynamically improbable reaction that might be envisaged is a concerted fluorine transfer process from an oxyl radical to a carbon-centered radical:

$$\sim CF_2O + CF_2\sim \rightarrow \sim CFO + CF_3\sim$$

Such a termination reaction by disproportionation, however, should be very unlikely in the studied system, because of the exclusive reaction with oxygen of the carbon radicals. Furthermore, trace amounts of acylfluoride or of fluoroformate end groups have never been detected in the polymer. This fact does also exclude the endothermic fluorine atom transfer from an oxyl radical to oxygen

$$\sim CF_2O + O_2 \rightarrow \sim CFO + FOO$$

whose occurrence has been regarded as possible under substantial oxygen pressure.[9]

4. The Initiation Reaction

In the fluorine-initiated process, the formation of primary radicals is clearly due to the homolytic cleavage of the low energy F−F bond; fluorine atoms are indeed present in the polymer under the form of terminal perfluoroalkyl groups. This initiation process, however, raises several points of interest that are worth discussing, also because of the critical effects that some of its features exert on the whole process.

The reaction of gaseous fluorine with a perfluoroolefin in the condensed phase has been studied for a long time, and it has been described as a free radical process, extremely fast even at the lowest temperatures, with rates comparable to or greater than the rate of diffusion mixing at the gas−liquid interface.[10] The reaction is interpreted as one electron transfer on molecular fluorine by the π-electron system of the fluoroolefin, and its initial step can be simply represented by the following sequence:

$$F_2 + C_2F_4 \rightarrow [\, F_2{\cdot}C_2F_4 \,] \rightarrow F + C_2F_5$$

The fate of these two primary radicals depends on their environment; even if they are formed in close proximity, the likelihood of their mutual recombination to the simple addition product, C_2F_6, is not very great because of the large exothermicity of such a process and because of the tendency of the two reactive species to diffuse apart, where C_2F_5, in the present case, is immediately quenched by oxygen while the fluorine atom, supposedly, adds to another molecule of the fluoroolefin. Under these assumptions, the initiation process would be therefore described by the overall reaction

$$F_2 + 2C_2F_4\,(+O_2) \rightarrow 2C_2F_5O_2$$

in which each "efficient" fluorine molecule forms two chain-initiating peroxyls.

Such a process is expected to be very fast and quantitative with respect to the amount of fluorine introduced into the system; practically, its rate is diffusion-controlled and should not depend either on monomer or on oxygen concentration, as long as a minimum amount of each reagent is present in the reaction zone. Considering that part of the employed fluorine will be lost because of in-cage recombination of primary radicals to C_2F_6, the rate of initiation, R_i, should then be given by the simple relation

$$R_i = 2fF \tag{1}$$

where F is the rate of fluorine introduction in the system and f represents the fraction of fluorine that effectively generates primary radicals.

As to this last point, it is worth noting that in the present experiments the gaseous fluorine inflow was highly diluted with oxygen and rapidly dispersed in the liquid phase containing the fluoroolefin. Under these conditions, as reported in Table 2, rather high values of f, around 0.70 ± 0.1, were generally measured through end group analysis of the polymers; moreover, these values were not influenced in a significant way by the actual monomer and oxygen concentrations in the liquid phase.

Assuming the above-described initiation step, on the basis of the elementary reactions 1−6, one would however derive a set of kinetic equations according to which the overall behavior of the system should be totally independent from the oxygen pressure. Since this is in strong contrast with the experimental results, it is clear that the initiation rate cannot be expressed by eq 1 and that some sort of oxygen intervention has to be considered during the initiation step.

Looking at the data reported in Table 2, it is easily recognized that the overall effect exerted on the polymer chain structure by an oxygen pressure increase is very similar to what would have been obtained by means of an increase of the fluorine flux. In other words, the experimental results show that, at a fixed fluorine flux, the rate of initiation increases (even more than four times) by increasing the oxygen pressure from about 0.5 up to 9 bar. This effect cannot be ascribed to an increase of fluorine efficiency: the experimental f values are not in fact affected by the pressure of oxygen, and even their hypothetical increase to the maximum value would not suffice to explain the overall effect. A further important observation is that the polymerization degree of the polymer remains strictly related to the amount of introduced fluorine, being not at all affected (i.e., diminished) by the increase of the number of initiating radicals produced by the oxygen pressure.

All these observations lead to conclude that (a) the oxygen pressure effect is to increase the number of primary radicals generated by each effective fluorine molecule and (b) the "extra" radicals produced by oxygen intervention do not transform into end groups and therefore they should be of bifunctional nature.

Both the above effects can be explained considering that during the reaction between fluorine and the fluoroolefin, one of the primary radicals formed is a fluorine atom; this species not only can add to a molecule of C_2F_4, but also can reversibly react with molecular oxygen, to yield FO_2.

$$\mathrm{F} + \mathrm{O_2} \leftrightarrow \mathrm{FO_2}$$

Such a reaction is known to be fast even at the lowest temperatures, and to be an equilibrium reaction, shifted to the right by an increase of the oxygen concentration.[11] The F−O bond energy is very low (about 15 kcal $\mathrm{mol^{-1}}$), but the FO_2 molecule cannot be simply considered as a temporary reservoir for F atoms: it is known, indeed, to behave like a very reactive free-radical species and to exhibit a varied chemistry (addition and abstraction reactions).[12] Even if there is no direct information about its ability to add to a fluoroolefin, it is well conceivable that, once formed, FO_2 might readily react with C_2F_4, to give a new radical $FOOCF_2CF_2$, able to initiate the growth of a new chain. The $FOOCF_2\sim$ end group, however, is still to be regarded as a reactive function since it can (a) homolytically cleave the low-energy F−O bond, yielding a peroxyl and releasing again the fluorine atom, or (b) cleave the O−O bond, leaving an oxyl at the end of the growing chain and yielding a very reactive OF radical that will add to another molecule of C_2F_4,[13] to initiate a new chain with a reactive hypofluorite end group. This last function, in its turn, is well-known to behave as a very efficient initiator for the same oxypolymerization process.[5] It cannot even be excluded that the FO_2 radical cross-react with another peroxyl present in the reaction system, to be reduced to FO radical before adding to the fluoroolefin. In conclusion, even if the chemical reaction path of the FO_2 species cannot be well established, it is most probable that their formation will result in the production of a great number of active radicals from each original fluorine atom. The net expected final result is that, in the presence of enough dissolved oxygen, each “effective” fluorine molecule in its reaction with C_2F_4 will generate a number, N, of primary radicals that can be well higher than 2. Among these N radicals, two will be monofunctional $C_2F_5O_2$, while $(N - 2)$ will be, potentially at least, of “bifunctional” nature, belonging to $(N - 2)/2$ molecules formally represented as $\mathrm{(O)OCF_2CF_2O(O)}$.

It has to be noted that the assumption that a “bifunctional” radical can initiate a chain growing at both ends, is not necessarily in contrast with the general belief that such a process is very unlikely in the traditional polymerization chemistry, because of the tendency toward premature chain termination through intramolecular coupling. In the present case, the “bifunctional” chain is not necessarily expected to grow at both ends at the same time, since the reactive functions FOO, or FO, at the end of the growing chains, might well become active only in a second time period, when the primary growth is already terminated. Moreover, even in the case of synchronous growth, the mutual reaction of the two peroxyls at the ends of the same chain will have only a minor probability of leading to chain termination.

According to the above hypothesis, the rate of initiation should then be written as

$$R_i = NfF \tag{2}$$

where N, the number of primary radicals generated by a fluorine molecule, is a number ≥2, dependent on the oxygen pressure.

Since in the present system the initiation reaction is a significant factor also insofar as the monomer consumption and the nature of the formed peroxyl radicals are concerned, its chemistry needs to be further considered. The stoichiometry of the initiation is expressed by

$$\mathrm{F_2} + (1 + {}^{1}\!/_{2}N)\mathrm{C_2F_4}\ (+\mathrm{O_2}) \rightarrow N\mathrm{RO_2}$$

and, among the thus produced radicals, two are monofunctional MO_2, i.e., $C_2F_5O_2$, while those $(N - 2)$ of bifunctional nature should be formally regarded as being half of the MO_2 and half of the CO_2 type.

These facts have been taken into account in doing the balance analysis for each of the various reactive species that is needed for the derivation of the kinetic relationships.

5. Kinetic Relationships

On the basis of the initiation rate expressed by eq 2, and of the elementary reactions 1−6 reported in Scheme 1, the behavior of the reacting system can be easily described by a number of theoretical relationships; as an example, a set of kinetic equations is reported in Scheme 2.

Scheme 2. Some Kinetic Equations Derived from the Reaction Model

$$R_p = \frac{1}{(1 + X_1)}\left(\frac{K_2}{K_6^{1/2}}\sqrt{\frac{1}{2}NfF}[\mathrm{C_2F_4}] + \left(1 + \frac{K_4}{K_6}\right)NfF\right) \tag{3}$$

$$\mathrm{DP_n} = \frac{1}{(1 + X_1)}\left(\frac{K_2}{K_6^{1/2}}\sqrt{\frac{N}{2fF}}[\mathrm{C_2F_4}] + \left(1 + \frac{K_4}{K_6}\right)N\right) \tag{4}$$

$$X_1 = \frac{2}{\left[\frac{K_2K_6^{1/2}}{K_4}\frac{[\mathrm{C_2F_4}]}{\sqrt{\frac{1}{2}NfF}} + 2\left(1 + \frac{K_6}{K_4}\right)\right]\left(\frac{K_3}{K_5}[\mathrm{C_2F_4}] + 1\right)} \tag{5}$$

$$X_p = (1 + X_1)\frac{\frac{K_2}{K_6^{1/2}}\frac{[\mathrm{C_2F_4}]}{\sqrt{\frac{1}{2}NfF}} + 1}{\frac{K_2}{K_6^{1/2}}\frac{[\mathrm{C_2F_4}]}{\sqrt{\frac{1}{2}NfF}} + 2\left(1 + \frac{K_4}{K_6}\right) - (1 + X_1)\frac{2}{N}} \tag{6}$$

$$X_{1\mathrm{E}} = \frac{X_1}{1 - X_1\left(\frac{K_2K_6^{1/2}}{K_4}\frac{[\mathrm{C_2F_4}]}{\sqrt{2NfF}} + \frac{K_6}{K_4}\right) + (1 + X_1)\frac{K_6}{K_4}\left(\frac{N - 2}{2N}\right)} \tag{7}$$

$$X_{1\mathrm{E}} = \frac{1}{1 + \frac{1}{X_1}\frac{[\mathrm{C_2F_4}]}{\left([\mathrm{C_2F_4}] + \frac{K_5}{K_3}\right)}} \tag{8}$$

$$X_{1\mathrm{P}} = \frac{X_1}{1 + X_1} \tag{9}$$

These equations have been derived, with the following assumptions being made.

1. The reaction system is homogeneous, and in particular gas–liquid diffusion control does not affect kinetics.

2. The stationary state is established for each radical species.

3. The rate constants K_{2-6} are not influenced by the nature of the R group of the radical.[14]

Furthermore, to simplify the equations, making their use more practical, the ratio of the stationary concentrations of the two types of peroxyls, $[CO_2]/[MO_2]$, has been considered to be equal to X_1; in reality, such identity holds perfectly true only when $N = 2$, while for higher values of N the presence of biradical species produces a little deviation (generally less than 2%) from the above identity.[15]

Kinetic equations such as those reported correlate the operating variables with the polymer structure (and microstructure) indexes; here all the effects caused by variations of the oxygen pressure are ascribed only to the specific value assumed by the N parameter. (The relationship between N and the oxygen pressure will be discussed in the next paragraph.)

It is also important to underline that, due to the adopted experiments setup, (a) the polymerization rate, R_p, is not a result, but is an almost constant datum (being actually equal to $9.5 \times 10^{-3} \times \eta$ mol L^{-1} min^{-1}), and (b) the monomer concentration, $[C_2F_4]$, is not an operating variable that can be changed at will, but is a result of the experimental conditions.

The experimental data (R_p, F, f, $[C_2F_4]$, DP_n, X_1, X_p) of each run listed in Table 2 have been processed with said equations by iterative fitting using a numerical optimization program. The resulting values of the typical kinetic constant ratios as well as the specific N^* values for each run are reported in Table 3.

The fairly constant values obtained for the kinetic parameters, over the entire range of the explored variables, are good evidence in support of the self-consistency of the assumed reaction model. The averaged values of the kinetic parameters are as follows:

$$\frac{K_2}{K_6^{1/2}} = 1.3 \pm 0.2\ (L^{1/2}\ \mathrm{mol}^{-1/2}\ \mathrm{min}^{-1/2})$$

$$\frac{K_4}{K_6} = 15.3 \pm 0.7 \qquad \frac{K_3}{K_5} = 63.1 \pm 4.8\ (\mathrm{L\ mol}^{-1})$$

On the basis of these averaged values, new N values have been reassessed for each single experiment. These "normalized" data, reported in the last column of Table 3, are only marginally different from the previous N^* values, and will be used in the following quantitative check of the model, with the purpose of a better internal consistency.

By adopting the mean values of the three rate constant ratios, as well as the normalized N values, a good accord is obtained in the whole range of the experimented conditions, between the experimental values of DP_n, X_1, and X_p, and the corresponding values calculated by using eqs 4, 5, and 6.

A fair correlation is also found between the experimental X_{1E} data and those calculated either through eq 7, or through eq 8, as shown in Figure 4; the fact that the two equations provide practically equivalent results is very significant, indeed, because they are based on different experimental inputs and on different kinetic parameters. On the contrary, use of eq 9 to predict the distribution of peroxide bonded units (X_{1p}), does not afford a good accord with the experimental results. As regards the polymer microstructure, however, it is important to note that one could not really expect to find a very good correspondence between experimental values obtained by NMR spectroscopy and values predicted by the kinetic model. Kinetic and spectroscopic data, actually, are not wholly equivalent; kinetic predic-

Table 3. KineticParameters

run	$K_2/K_6^{1/2}$	K_4/K_6	K_3/K_5	N^*	N
1	1.7	14.1	70.6	2.1	1.9
2	1.8	15.2	63.5	2.0	2.0
3	1.6	14.5	68.4	2.1	2.0
4	1.1	14.9	66.8	2.7	2.7
5	1.5	15.1	64.1	2.5	2.5
6	1.6	16.2	56.0	2.1	2.3
7	1.3	13.7	74.0	2.8	2.5
8	1.1	15.0	65.7	4.1	4.0
9	1.0	14.9	66.6	3.5	3.5
10	1.4	15.4	62.4	3.0	3.1
11	0.8	15.3	64.4	4.7	4.7
12	1.1	15.2	64.2	4.1	4.1
13	1.3	15.4	62.6	3.7	3.7
14	1.2	14.0	71.6	5.5	5.2
15	1.0	15.3	64.4	4.4	4.4
16	1.3	15.2	63.7	3.9	3.9
17	1.6	14.8	66.6	3.7	3.7
18	1.1	16.2	58.0	4.6	4.8
19	1.3	15.3	62.8	4.0	4.0
20	1.2	17.0	52.1	4.7	5.1
21	1.3	15.1	64.6	4.1	4.1
22	1.5	15.8	59.8	3.7	3.9
23	0.8	15.4	64.1	5.8	5.8
24	1.3	15.7	60.7	4.5	4.6
25	1.4	15.5	61.4	3.9	4.0
26	1.1	15.8	60.7	5.2	5.3
27	1.2	15.9	59.2	4.9	5.0
28	1.5	15.6	60.9	4.4	4.5
29	1.3	15.4	62.4	4.9	5.0
30	0.9	16.9	52.8	6.3	6.7
31	1.5	15.0	65.1	4.8	4.8
32	1.0	16.6	54.8	6.5	6.9
33	1.2	15.9	59.3	6.5	6.7
34	1.3	14.8	66.8	6.4	6.2
35	1.5	14.7	67.3	5.2	5.1
avgd values	1.3 ± 0.2	15.3 ± 0.7	63.1 ± 4.8		

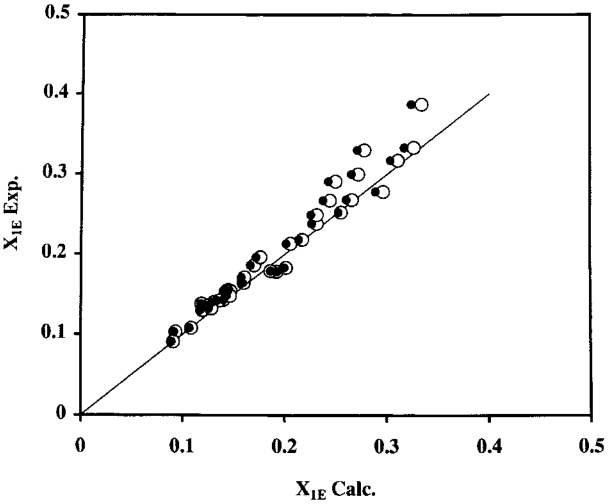

Figure 4. Correlation between the experimental X_{1E} values and those calculated by eq 7 (open circles) and by eq 8 (black circles).

tion refers to the probability of formation of certain sequences of bonds during the growth of the chain along a definite direction, while the NMR analysis of the bulk polymer necessarily does not distinguish any growth direction. For example, a growing structure $\sim OCF_2CF_2$-$OOCF_2O$ kinetically would be regarded as one $-CF_2$-CF_2OO- unit, while the same structural unit of the polymer would be assigned by NMR 50% to a CF_2CF_2-OO unit, and 50% to a CF_2OO unit. This effect becomes particularly critical when the data concern rather small compositional values, such as X_{1p}. Obviously, another possible cause of discrepancy for the kinetic description of the polymer fine structure might be the existence of even small differences among the propagation rate constants of the radicals, related to the nature of their R group.

6. Oxygen Effect on the Initiation Rate

The N values determined for each experimental run can be used to obtain some useful information on the way oxygen pressure exerts its effect on the initiation rate. As assumed, during the initiating process a competition is established between monomer and oxygen for the first generated fluorine atom:[16]

$$F + C_2F_4\ (+O_2) \rightarrow C_2F_5O_2\ (k_1)$$

$$F + O_2 \rightarrow FO_2\ (k_2)$$

Assuming the same molecularity for the two competitive reactions, the monoradical species, $C_2F_5O_2$, and the difunctional ones, from FO_2, will be produced in a ratio dependent upon the ratio $k_1[C_2F_4]/k_2[O_2]$. In particular, the probability p that a fluorine atom will react with oxygen, can be expressed as

$$p = \frac{\dfrac{k_2\varphi P_o}{k_1[C_2F_4]}}{1 + \dfrac{k_2\varphi P_o}{k_1[C_2F_4]}} \qquad (10)$$

where P_o is the oxygen pressure and φ is a constant (0.0791 mol L^{-1} bar^{-1}) corresponding to the molar concentration of dissolved oxygen in the reaction medium at $P_o = 1$ bar.(See Figure 1).

In the absence of any oxygen effect, the N value should be 2, and toward this value should tend N when the probability p, and therefore the ratio $(P_o/[C_2F_4])$, tends to zero. As shown in Figure 5, the calculated N values satisfactorily obey to such a requirement.

To interpret the dependence of N on p, the following two extreme hypotheses can be formulated.

1. Subsequent to the addition of FO_2 to C_2F_4, there occurs the cleavage of the F−O bond, with formation of the biradical species $OOCF_2CF_2OO$ while the fluorine atom is set free to react again, with probability p to form another FO_2 species and probability $1 - p$ to yield a radical $C_2F_5O_2$. Altogether, through such an iterative process, a molecule of fluorine could then generate a number of primary radicals expressed by

$$N = 2(1 + p + p^2 + p^3 + ... + p^n) = \frac{2}{1 - p}$$

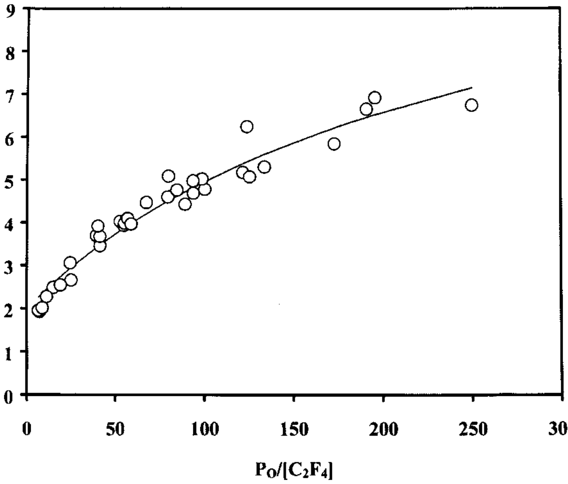

Figure 5. Plot of N vs the ratio between oxygen pressure and the equilibrium concentration of the monomer.

According to this hypothesis, when p approaches unity, N should tend to infinity, and the linear relationship

$$\frac{N}{2} = 1 + \frac{k_2\varphi P_o}{k_1[C_2F_4]}$$

should be verified. In a plot of $(N/2)$ vs $(P_0/[C_2F_4])$, the slope of the straight line, knowing the value of φ, could then furnish the value of k_2/k_1.

Experimentally, however, as has been shown in the similar plot of Figure 5, this correlation is not a linear one and, by increasing the oxygen pressure, the value of N does not tend to be infinite, but tends to reach an asymptotic finite value. The experimental evidence, therefore, does not support this simple hypothesis.

2. As a final consequence of the addition of a fluorine atom to oxygen, there are formed n biradical species; the number n, however, according to this hypothesis does not depend any longer on the ratio $(P_o/[C_2F_4])$, but is a constant, being only determined by the specific chemical path of the intermediate FO_2 species. It will then give the result

$$\frac{N - 2}{2} = np$$

and a plot of $(N - 2)/2$ vs p should give a straight line, whose slope is n.

The experimental N values have been processed into this linear relation and, with a numerical optimization procedure, the best fitting has been obtained, as shown in Figure 6, with $n = 5.1$ and $k_2/k_1 = 0.052$. By using said values, one can further derive a relationship that should quantitatively correlate N with the ratio $P_o/[C_2F_4]$; the result is the solid curve that has been reported in the plot of Figure 5, which, in fact, appears to very well interpret the experimental results in the entire range explored.

To conclude, the above results tend to indicate that the behavior of the initiating system is far better described according to the second hypothesis than by the first one. In other words, the probability for a fluorine atom to react with oxygen would remain rather small, even under substantial oxygen pressures, compared to the probability of its reaction with the monomer, as indicated by the small value of the ratio k_2/k_1.

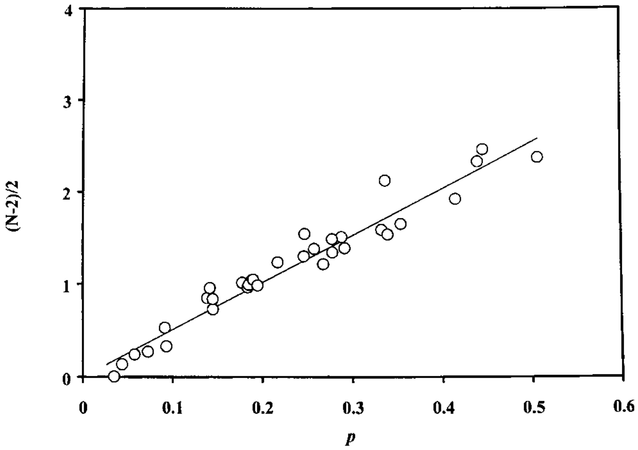

Figure 6. Plot of the number of biradical species, $(N - 2)/2$, vs the probability, p, of a fluorine atom to react with oxygen.

However, once formed, the FO_2 species appears to be able to generate a great number of “extra” primary radicals, i.e., about five biradical species, regardless of the oxygen pressure. Such a behavior of the intermediate reactive species could hardly be explained on the basis of well-defined chemical reaction paths; the overall process might be somehow equated to an ill-defined “fluorine sensitized oxidation” process.

7. Kinetic Chain Length, Molecular Weight, and Its Distribution

As already pointed out, the number-average polymerization degree of the polymer is simply given by the ratio between the polymerization rate, R_p, and the fluorine flux fF (eq 4).

The kinetic chain length of the process, ν, being the ratio between the polymerization rate and the initiation rate, should be related to DP_n by the identity

$$DP_n = \nu N \qquad (11)$$

that shows how, for each fixed DP_n, ν is inversely related to the number of initiating radicals.

The question whether the above relationship linking DP_n, ν, and N holds even in the presence of biradical species can be answered by developing in a different way the correlation between the operating variables and DP_n. As usual, considering the probability P for a growing radical of further propagating instead of terminating the chain, it can be shown that

$$1 - P = \frac{1 + X_1}{1 + \dfrac{K_2\ [C_2F_4]}{K_6^{\ 1/2}\sqrt{2NfF}} + \dfrac{K_4}{K_6} + (1 + X_1)\left(\dfrac{N-2}{2N}\right)} \qquad (12)$$

Taking into account the two terminal units and the presence of $(^1/_2N - 1)$ biradical species incorporated into the chains, one further obtains the relationship linking DP_n, P, and N:

$$DP_n = \frac{N}{1 - P} + \frac{2 - N}{2} \qquad (13)$$

Combining eqs 12 and 13, one actually obtains again eq 4, thus proving the correctness of eq 11. From the above equations, one also derives the identity

$$\nu = \frac{1}{1 - P} + \frac{2 - N}{2N}$$

that, only in the case of $N = 2$, becomes the classical correlation $\nu = (1/(1 - P))$ linking kinetic chain length and the probability of growth.

Knowledge of the molecular weight distribution of the polymers is important because it may provide a very significant index about the closeness of the process to the ideal model. It should be noted, however, that in the present case, even knowing the probability index P, it is not possible to directly obtain the ideal distribution curves through the classical equations that furnish the number-average and weight-average distribution functions. These well-known equations are only valid, in fact, in the absence of biradical species and cannot be used here when $N > 2$. The development, from the probability factor P, of proper equations that describe the ideal molecular weight distribution of the present polymers, even obtained in the presence of a variable amount of bifunctional growing species, is a subject that is going to be dealt with in a separate paper.[17] Here, it is just interesting to remark that, on increasing the ratio biradicals/monoradicals, one should expect a small continuous increase of the polydispersity index, from the ideal value of 1.5 up to a maximum value of 2, for polymers of infinite molecular weight.

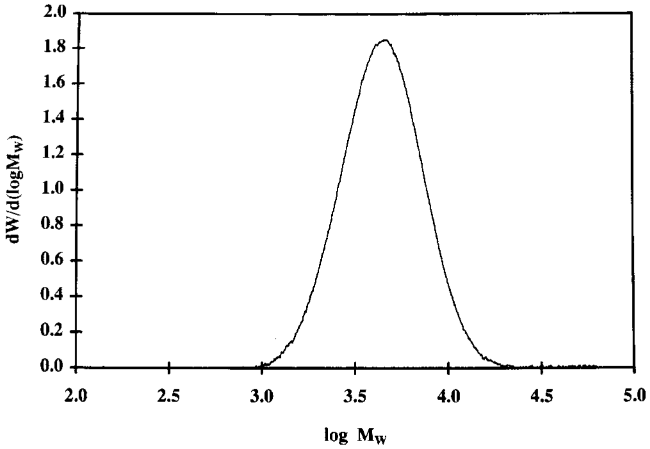

Figure 7. Size exclusion chromatogram of polymer no. 3 (perfluorohexane, 30 °C).

The size exclusion chromatogram reported as an example in Figure 7, has been determined on a polymer (run no. 3, $DP_n = 33.4$) prepared under reduced pressure of oxygen (the N value was practically 2). The molecular weight distribution results to be unimodal and rather narrow, M_w/M_n being ≈ 1.31. It is remarkable the fact that this polydispersity index is even lower than the ideal one (1.47) given by the relationship $(DP_w/DP_n) = 1 + P/2$, valid in a polymerization process like the present one where there is not chain transfer and termination only occurs by coupling of monoradicals, and where the experimental P value (given by $1 - (2/DP_n)$) is 0.94.

8. Discussion and Conclusions

Some general aspects of the overall process, as well as some specific points of the described reaction mechanism, deserve to be further discussed, also with respect to the traditional concepts of free radical polymerization.

1. An important question that might be raised is whether it is correct to adopt a kinetic approach to interpret a process that proceeds, at least during its critical moment of initiation, in the etherogeneous gas–liquid phase. It is well conceivable, indeed, that mass transportation factors across the gas–liquid interface could deeply influence the rate of initiation as well as the nature and local concentration of the primary radicals. In this respect, however, it has to be noted that various preliminary experiments proved that, once the stirring system was able to disperse the fluorine-containing oxygen into very small bubbles, the results, particularly in term of fluorine efficiency, were not at all influenced by even some important variations of the mode of gas introduction into the system and of the intensity of mechanical mixing. It is also considered that, once formed, any primary radical should be immediately transformed into a peroxyl which, as will be discussed later on, is a relatively stable, slowly reacting, and rather long living species that should have enough time to be homogeneously dispersed throughout the medium before reacting. Furthermore, the very narrow molecular weight distribution always measured on the polymer samples is strongly in favor of the homogeneous nature of the reaction system. While all these facts tend to exclude the existence of really important effects due to diffusion problems, it cannot be totally excluded that some kinetic anomalies could locally derive because of an uneven distribution of the reactive species. For instance, in the very proximity of the gas–liquid interface, diffusion mixing barriers could increase the concentration of RO_2 radicals while decreasing that of C_2F_4, with the result that at the beginning of its growth the polymer chain might contain a less than average number of peroxy bonds.

Another aspect that could impair the kinetic reliability of the obtained data is the fact that, due to the batch nature of the experiments, the progress of the reaction involves a steady viscosity increase of the reaction medium that might affect some kinetic parameters. In the present case, however, the maximum polymer concentration reached in each experiment was around 10 wt % and, due to the particularly low molecular mass of the polymers, the viscosity of the medium was not greatly increased during the progress of the reaction. Moreover, structure analysis (composition, molecular weight distribution) made on samples of polymers taken at different reaction times, always yielded fairly coinciding results, thus proving that—under the adopted conditions—the increase of viscosity did not play a significant role.

2. The self-reaction of two growing RO_2 radicals is the most distinctive elementary step of the process leading to polyether formation. The interaction between polymeric radicals is generally known as one of the most complicated questions in the kinetics of radical polymerization; such a step is customarily regarded as a diffusion-controlled process, and its rate, besides being inversely proportional to the viscosity of the medium, is expected to decrease with the growing macroradical length. In the studied system, the effect of progressive diffusion hindrances preventing the macroradicals from approaching and reacting each other would be the broadening of the molecular weight distribution of the polymer and the increase of the probability of simple propagation of the RO_2 radicals, with consequent uneven distribution of peroxide and ether bonds within the same growing macromolecule. One would consequently expect a maximum concentration of adjacent CF_2CF_2-OO units near the center of the final macromolecule, where, statistically, the two growing radicals should have recombined. Diffusion effects on the coupling reaction, however, either related to the growing chain length of the radicals or related to the steady increase of viscosity with the progress of the reaction, did not appear to be observable in the present case. Actually, the molecular weight distribution of the polymers always was observed to be very narrow, regardless of the specific synthesis conditions. Furthermore, various experiments in which polymer samples have been subjected to reductive chemical cleavage of their peroxide bonds yielded results (i.e., molecular weight distribution of the various severed segments and oxalic acid content) in fair accord with those expected on the basis of a random distribution of peroxides within each polymer molecule.

3. There is another aspect to be considered about the self-reaction of peroxyls. This reaction has been assumed to proceed through two different channels, one leading to their reduction to oxyl radicals (rate constant K_4) and the other to terminative coupling (K_6). A different picture is also possible, however, according to which the mutual reaction of the two radicals always follows the same channel:

$$2RO_2 \rightarrow [ROO\cdots OOR] \rightarrow O_2 + [2RO]$$

The pair of oxyl radicals thus formed may be oscillating in a “cage” of surrounding molecules, from where they can diffuse apart:

$$[2RO] \rightarrow 2RO \qquad (K_4)$$

or where, during the interval of their existence as immediate neighbors, they can recombine to terminate the chain:

$$[2RO] \rightarrow ROOR \qquad (K_6)$$

In this case, the characteristic ratio K_4/K_6 would lose its true kinetic significance and would have to be regarded as a measure of the diffusion rate of the RO radicals. This, of course, would not affect the validity of the overall kinetic model, but would suggest that the K_4/K_6 ratio could be also influenced by the average chain length of the radicals (decreasing with increasing their molecular mass) and by the nature of the medium (viscosity, polymer/solvent interactions). While, as said before, no experimental indication has been obtained about any significant deviation from the expected distribution of bonds along the polymer chains, some preliminary experiments did indeed indicate that there is a notable effect of the nature and bulk viscosity of the solvent on the value of the K_4/K_6 kinetic parameter.

4. The kinetic expression of the reaction rate (eq 3) is made by two terms; the first term refers to the rate of formation of peroxide units and is first order in monomer concentration and 0.5 order in rate of initiation. This, indeed, is the traditional kinetic relationship that one would expect in the ideal case of TFE/O_2 alternate copolymerization with bimolecular termination. The second term refers to the rate of formation of ether units: it is independent of the monomer concentration and first order in initiation rate, accordingly to what was previously observed in the case of the photochemical

oxidation[2]. (The overall rate is divided by $(1 + X_1)$ because, for each one-carbon unit introduced into the chain, the whole set of propagation reactions has, obviously, to be doubled). Of course, the breakup of the rate equation is only formal, but still it clearly describes and predicts the behavior of the system under extreme conditions; when the monomer concentration is rather high, while the rate of free radical generation is reduced to a minimum, the system reacts very slowly, yielding a polymer approaching the structure of a true polyperoxide.[18] Conversely, if the monomer concentration is rather low, and the rate of initiation is progressively increased, the fast reaction tends to produce a pure polyether, as experienced working in the gas phase.

5. To produce a polymer containing only a minor proportion of peroxy bonds, in the described experiments the monomer concentration has been kept below 0.12 mol L^{-1}, while the rate of effective free radical generation has been varied within the range $(4-9) \times 10^{-4}$ mol L^{-1} min^{-1}. It is noteworthy that such initiation rate is very high, even more than 100 times higher than that usually employed in a traditional polymerization process. The comparison is even more striking considering that, in the studied TFE/O_2 copolymerization, due to the very low monomer concentration, the number of active radicals for each monomer molecule present in the reacting system was several orders of magnitude higher than what is traditional in the polymerization processes. The picture of the studied reaction, hence, is that of a system where there is an extremely high population of radicals (RO_2) and a great frequency of their coupling reactions. Clearly, another immediate consequence of the high rate of initiation is the extremely short kinetic chain length and the very reduced polymerization degree of the polymer whenever its peroxide content is kept at a low level; a very useful effect, in this respect, is exerted by the presence of biradical species, formed under oxygen pressure, because they do not affect the length of the chains, while providing high initiation rates.

6. According to the kinetic model, in a polymer containing only minor amounts of peroxides, its composition in enchained CF_2O and CF_2CF_2O units substantially depends on the monomer concentration through the relationship

$$X_1 \cong X_{1E} = \frac{1}{1 + \frac{K_3}{K_5}[C_2F_4]}$$

Since the kinetic parameter K_3/K_5 has been estimated to be around 63 L mol^{-1}, to obtain polymers containing more than 50% of CF_2CF_2O units, it is necessary to adopt a concentration of C_2F_4 higher than ~0.017 mol L^{-1}. (The minimum concentration adopted in the described experiments was always higher than this value.) The above relationship, however, does also indicate that polymers containing up to 90% of CF_2CF_2O units could only be obtained in the presence of a steady monomer concentration higher than 0.12, i.e., above the limit imposed by too high a peroxide content. This shows the practical limitation of the present process as regards the obtainable range of polymer compositions.

7. Some comments might be devoted to the absolute value of the kinetic parameters of the process. As shown, on the basis of the rather simplified kinetic model, the values of some typical reaction constant ratios have been estimated; while these data are certainly meaningful for the description of the overall process, they cannot provide direct information as to the absolute reactivities of the different species involved in the various elementary reactions. In the scientific literature, there is now plenty of data concerning the same elementary reactions of the same, or similar, fluorinated radicals, with listed values of their absolute rate constants. These data, however, have been gathered only by studying gas-phase reactions, in connection with the interest of evaluating the fate of various fluorochemicals in the atmosphere. From the said literature, one certainly may draw a lot of valuable indications about the scale of reactivity of the various species but cannot derive quantitative data to be used in the condensed state. The only very pertinent data in this regard are those previously estimated by Faucitano et al. during a kinetic and simulation study of the liquid-phase photooxidation of tetrafluoroethylene[3d] and of hexafluoropropylene,[3e] where the self-reaction of perfluoroperoxyl radicals has been also studied with ESR measurements. From the above studies, the following indicative values of the reaction constant for each elementary step have been estimated at −45 °C in CF_2Cl_2 (units: L mol^{-1} min^{-1}):

$$K_1 \approx 10^{9-10} \quad K_2 \approx 5 \times 10^2 \quad K_3 \approx 1.2 \times 10^5$$
$$K_4 \approx 1.2 \times 10^6 \qquad K_5 \approx 3 \times 10^3\ (\mathrm{min}^{-1})$$

Considering these values, there is a fair correspondence as far as the ratio K_3/K_5 is concerned: 40 L mol^{-1} vs the experimental value of 63, which, however, has been measured at −83 °C, where the value of the rate constant K_5 is surely smaller, because of the rather high activation energy of unimolecular fragmentation. Moreover, taking into account the experimental value $K_4/K_6 = 15.3$, from the above data one derives an estimated ratio $K_2/K_6^{1/2}$ around 1.8 ($L^{1/2}$ $mol^{-1/2}$ $min^{-1/2}$), that well compares to the experimental value of 1.3 (same units).

In addition to the good concordance between all these kinetic parameters of the process, it is interesting to remark the very small value that emerges for the propagation constant of the peroxyl radical, K_2, which appears to be at least 2 orders of magnitude lower than the corresponding rate constant of the oxyl radical. As anticipated, RO_2 has to be regarded as a rather stable free radical, sluggish in its reaction with the monomer and far more inclined to bimolecular coupling. Taking into account the high initiation rates employed in the experiments, and assuming the steady-state concentration of the free radicals, from the identity $NfF = 2K_6[RO_2]^2$ one can estimate a very high equilibrium concentration of the RO_2 radicals in the reacting system, around $10^{-4}-10^{-5}$ mol L^{-1}, to be compared with the 10^{-8} concentration of radicals that usually prevails during a traditional polymerization process. From the above data, it is also possible to conclude that RO_2 species should enjoy a very long half-life, even on the order of a second, enough to ensure their homogeneous distribution throughout the well-agitated reaction system.

In summary, it can be concluded that the overall mechanism proposed for the low-temperature, liquid-phase, fluorine-initiated reaction between tetrafluoroethylene and oxygen is rather consistent and able to account for the various experimental findings. The obtained results implicate the reaction of fluorine atoms with O_2, occurring even under very moderate oxygen pressure, as responsible for the surprisingly large formation of chain initiating radical species; they also support the notion that a significant number of these chain-carrier radicals have bifunctional nature. Obviously, the ability of the proposed model to describe the behavior of the reaction system can only be asserted within the rather restricted limits of the explored variables. However, the values measured for the typical kinetic parameters of the process, even if to be considered of only qualitative merit because of the number of assumptions involved in their derivation, appear to fit well into a self-consistent general picture of the low-temperature reactivity characteristics of the perfluorinated oxyl and peroxyl radical species.

Supporting Information Available: Text giving derivations of kinetic equations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) On statistical grounds, for both bimolecular reactions 4 and 6, the values of the rate constants K_4 and K_6 for the cross-reaction, i.e. $CO_2 + MO_2$, have been considered to be double those of the corresponding self-reactions, i.e. $CO_2 + CO_2$.

(15) It can be shown that $[CO_2]/[MO_2] \cong X_1[\,1 + (^1/_2N - 1)/DP_n]$.

(16) A good support to this assumption is the fact that no significant effect of the oxygen pressure was ever observed when the same fluorine-initiated reaction was carried out using liquid hexafluoropropylene, instead of CF_2Cl_2, as a reaction medium (Marchionni, G.; Guarda, P. A.; Paganin, M. U.S. Patent 5,488,181, 1996). In this case, indeed, the very high concentration of the fluoroolefin makes improbable the competitive capture by oxygen of the fluorine atom.

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