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Novelties and prospects in the synthesis of perfluoropolyethers by oxidative polymerization of fluoroolefins

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Abstract

The direct photoactivated combination of perfluoroolefins with oxygen is the basic process studied and developed by AUSIMONT for the synthesis of a series of perfluorinated polyethers. Recent research is now further widening the scope of this core technology, offering new synthetic opportunities. Here some of the newest advancements in this field are highlighted: the chemically activated process, which affords substantial technological simplifications; an innovative chain-transfer methodology, which enables to directly synthesize perfluoropolyether telomers bearing one functional end group; the successful application of the process to different fluoromonomers, providing a variety of new polyether structures.

All the new achievements confirm and greatly extend the synthetic value of this unique technology in fluorine chemistry.

Keywords: Perfluoroalkylpolyethers; Oxidative polymerization; Telomerization; Perfluorinated functional telomers

1. Introduction

It is several years since the great synthetic potentialities of the oxidation reactions of fluoroolefins have been recognized, not just for the synthesis of some micromolecular oxidation products but, and chiefly, for the obtainment of polymeric substances having polyether structures. In particular, the photochemical oxidation of the simplest perfluoroolefins, such as tetrafluoroethylene and hexafluoropropylene, is the basic process discovered, studied, and developed by AUSIMONT for the commercial production of a series of perfluorinated polyethers [1]. This very special sort of oxidative polymerization is a chain reaction where different free radical species partake in several elementary steps; its reaction mechanism is quite complex, indeed, and there is a strong influence of the reaction conditions on the nature and structure of the polymeric products. Many years of study is dedicated to this process, however, enabled to clarify all the various reaction features and to direct the synthesis to the desired products. The subsequent development work allowed AUSIMONT to select and to implement proper technologies, often very innovative in their nature, to carry out this synthesis at the industrial scale. Today, very efficient commercial plants are exploiting the photooxidation technology to produce various families of perfluoropolyether fluids (Fomblin^{TM}, Galden^{TM}) and of their derivatives. It is worth mentioning here that, in the rather restricted field of photochemical synthesis which has achieved industrial outcome, this process represents a true novelty, being the only industrial photosynthesis operated by high energy UV radiations (below 300 nm) at very reduced temperatures (even below $-80°C$).

Within this area of chemistry, in AUSIMONT's laboratories a great deal of research has been carried out, and is still under way, addressed to the conversion of the raw photosynthesis products into a variety of useful derivatives. In addition to inert fluids endowed with the highest degree of chemical and thermal stability, main targets have been, for example, inert perfluoropolyether fluids containing hydrogen atoms in a proper position of their chains so as to be fully degradable in the troposphere (H Galden^{TM} [2–4]), as well as perfluoropolyethers bearing chemically reactive groups at the end of their molecular chains: actually, such products are very useful intermediates for surface active agents, for specialty auxiliaries, for coating resins (Fluorobase Z), for high performance elastomers, etc. [5–8]. All these final products are designed to exploit, in many application sectors, the excellent and very unique set of properties of the perfluorinated polyether structures.

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Some other aims and achievements of AUSIMONT's research in the area of perfluoropolyethers, however, have still been related to the actual synthetic process, i.e. the oxidative polymerization of fluoroolefins which is the core of all these technologies; important advances have been made here in the past few years. While more detailed papers are going to be published on each specific topic, this paper wants to highlight and briefly discuss some of the newest achievements in this direction; its purpose is to show how this unique technology is highly versatile, has many capabilities and continues to offer new synthetic opportunities.

2. Chemically initiated synthesis

The feasibility of using some chemical initiator instead of UV light to activate the oxidative polymerization of fluoroolefins has been always considered attractive, mainly because of the overall technological simplification that this substitution might have offered to the reactor design and to the running of the process. Rather positive premises for this possibility were some results obtained years ago in these same laboratories during a study of the reaction between tetrafluoroethylene, oxygen, and ozone [9]. It was shown, at that time, that ozone activates the combination of this fluoroolefin with molecular oxygen and that, under proper conditions, the reaction produces, besides prevailing micromolecular oxidation compounds, also macromolecular substances containing oxygen. Basically these polymers were polyperoxides, $(CF_2CF_2OO)_n$, dangerously unstable; however, minor proportions were also present of a different polymer, a quite stable $(CF_2O)_n$ polyether displaying interesting properties. It was clear, therefore, that ozone can initiate the chain combination of oxygen with tetrafluoroethylene leading to polymeric polyethers. However, due to major drawbacks like the very poor yield of useful product, the inherent danger of the system, and the fact that the same process could not be applied to other fluoroolefins, it was preferred, at that time, to study and develop the photochemical methodology which, even at its early stage, was proving to be more efficient and reliable.

More recently, the research of viable chemical initiators has been resumed, focusing on the very few classes of chemicals which could satisfy all the following prerequisites:

1. to be able to generate free radicals even at the lowest temperatures which are needed if the oxidative polymerization is to produce useful perfluoropolyethers;
2. to generate free radicals either capable of direct addition to the fluorinated double bond or to do so after their reaction with oxygen;
3. to be soluble in, or at least compatible with, the reaction medium;
4. to be easily handled at room temperature

This research has been successful; several compounds that can be suitably employed as initiators for the reaction have been identified. Furthermore, the chemical initiation proved to be, under many respects, a very viable and interesting alternative to the photochemical methodology for the synthesis of polyethers through oxidative polymerization of fluoroolefins [10].

In particular, among the various potential initiators major interest centred on elemental fluorine and on the class of perfluoroalkylhypofluorites, particularly CF_3OF. In both cases, the free radicals generating capacity has to be ascribed to the homolytic fission of a rather weak bond ($F–F=37\ \mathrm{kcal\ mol^{-1}}$ and $CF_3O–F=$ is about $40\ \mathrm{kcal\ mol^{-1}}$) producing F atoms or CF_3O radicals, both very reactive species in the addition to a double bond. Elemental fluorine, especially, turned out a very active and efficient initiator.

Few comments seem here appropriate on the initiating mechanism, and particularly on the reaction of fluorine with perfluoroolefins in the condensed phase. Since a long time this reaction is known to be very fast and practically quantitative even at the lowest temperatures; most probably the reaction is initiated by one-electron transfer from a molecule of fluorine to the π electrons system of the fluoroolefin, with formation of free radicals [11,12]. Thus, in the case of tetrafluoroethylene, the first reaction step can be represented as

$$F_2 + C_2F_4 \leftrightarrow [F_2 \cdot C_2F_4] \rightarrow C_2F_5 + F$$

The ultimate fate of this pair of radicals depends upon the reaction conditions: their tendency to mutual combination, to form the simple addition product C_2F_6, could be offset by the out-of-cage diffusion of the two reactive species; the fluorine atom can thus react with another molecule of fluoroolefin, followed by mutual coupling of the primary C_2F_5 radicals to C_4F_{10}, or by their addition to other fluoroolefin molecules, thus producing higher molecular weight compounds.

Similarly, the reaction of perfluoroalkylhypofluorites with a fluoroolefin, in a low polarity medium, proceeds via free radicals produced by homolytic scission of their O–F bond [13,14]. In both cases, however, when the ratio "initiator" to monomer is rather high, the distribution of the reaction products feels the effect of the great tendency of the intermediate fluorocarbon radical to give chain transfer reaction with the initiator:

$$C_2F_5 + F_2(CF_3OF) \rightarrow C_2F_6 + F(CF_3O)$$

favouring the formation of the simple addition products.

In the presence of oxygen, the course of these reactions is profoundly modified due to the extreme reactivity of fluorocarbon radicals with oxygen. While the fluoroolefin-activated decomposition of the initiator proceeds regularly, the primary carbon radicals (i.e. C_2F_5) thus produced react immediately and exclusively with oxygen giving perfluoroalkylperoxy radicals RfO_2 which cannot further interact with the initiator but can only add to another molecule of fluoroolefin or interact with themselves, thus giving rise to the oxidative polymerization chain.

Accordingly, the initiation step, for example in the case of fluorine, can be described by the overall reaction

$$F_2 + 2C_2F_4 + O_2 \rightarrow 2C_2F_5O_2$$

which is extremely fast and quantitative with respect to the amount of initiator that is present in the reaction system; its rate practically does not depend either on C_2F_4 or on O_2 concentration (as long as a minimum amount of each of the two reagents is present in the medium). Quenching by oxygen of the primary carbon radicals is immediate, indeed, and the overall efficiency of this initiation step in bringing about the chain mechanism leading to perfluoropolyethers is fairly good; only a minor part of the initiating reagent is lost under the form of its simple addition compound to the olefin.

2.1. Reaction mechanism and kinetics

It is well known [1] that the low temperature oxidative polymerization of tetrafluoroethylene in the condensed phase yields oligomers, and even polymers of relatively high molecular weight, made by randomly distributed $-CF_2CF_2O-$ and $-CF_2O-$ units, generally also containing varying amount of peroxide bonds.

Scheme 1 shows the elementary steps considered of foremost importance when this synthesis is initiated by fluorine.

Fig. 1 collects some kinetic relationship (for reaction rate and polymer composition) that can be deduced from such a rather simplified reaction mechanism on the basis of the stationary state hypothesis and assuming that the reactivity of each kind of radical (R, RO, RO_2) does not depend on the very nature of its R group ($\sim OCF_2$, $\sim OCF_2CF_2$, C_2F_5). As said before, the initiation rate is considered independent from fluoroolefin concentration and equal, but for an efficiency factor *f*, to the rate of fluorine feeding.

$$\begin{array}{llcl}
\textit{Initiation} & C_2F_4 + F_2 & \xrightarrow{R_i} & 2C_2F_5 \quad (2R) \\
\textit{Propagation} & R + O_2 & \xrightarrow{K_1} & RO_2 \\
 & RO_2 + C_2F_4 & \xrightarrow{K_2} & R \\
 & RO + C_2F_4 & \xrightarrow{K_3} & R \\
\textit{Radical reactions} & 2RO_2 & \xrightarrow{K_4} & 2RO + O_2 \\
 & -CF_2CF_2O & \xrightarrow{K_5} & R + CF_2O \\
\textit{Termination} & 2RO_2 & \xrightarrow{K_6} & ROOR + O_2
\end{array}$$

R_i = *rate of initiation* $= 2fV_F$

f = *efficiency factor* V_F = *rate of* F_2 *feeding*

R = *perfluorocarbon radical* C_2F_5, $-OCF_2CF_2$, $-OCF_2$

Scheme 1. Main elementary reactions in the oxidative polymerization of C_2F_4 initiated by fluorine.

$$R_p = \frac{1}{(1+x_1)}\left[K_2\frac{(fV_F)^{\frac{1}{2}}}{K_6^{\frac{1}{2}}}[C_2F_4] + 2\frac{(K_4+K_6)}{K_6}fV_F\right]$$

$$x_1 = \frac{2K_5}{\left[\frac{K_2}{K_4}\left(\frac{K_6}{fV_F}\right)^{\frac{1}{2}}[C_2F_4] + 2\frac{(K_4+K_6)}{K_4}\right](K_3[C_2F_4]+K_5)}$$

$$x_p = \frac{2K_2\left(\frac{fV_F}{K_6}\right)^{\frac{1}{2}}[C_2F_4] + fV_F}{R_p - fV_F}$$

where

R_p = ***rate of polymer formation***

x_1 = ***molar fraction of*** CF_2 ***units*** $= \dfrac{-CF_2-}{-CF_2- + -CF_2CF_2-}$

x_p = ***molar fraction of peroxides*** $= \dfrac{-OO-}{-OO- + -O-}$

Fig. 1. Kinetic relationships in the oxidative polymerization of C_2F_4 initiated by fluorine.

In this chain process, the kinetic chain length $\surd$ corresponds to the ratio between the rate of monomer incorporation into the polymer, R_p, and the initiation rate, R_i. Since chain termination only occurs by combination of two macroradicals, and in the absence of chain transfer reactions, the resulting polymerization degree DP is equal to $2\surd$.

The reported kinetic equations, as well as other relationships that can be deduced from the same mechanism to describe various structural features of the product (such as the kind of distribution of the different units and bonds along the chain), proved to be fairly in accord with the experimental results obtained in a kinetic study of the reaction. In particular, working at −80°C in a CF_2Cl_2 medium, under one atmosphere of oxygen, the experimental value 0.7±0.1 was found for the efficiency factor *f*, and the following values were approximated for the main constant ratios:

$$\frac{K_2}{K_6^{1/2}} = 0.7 \pm 0.2\left(l^{1/2}\,\text{mol}^{-1/2}\,\text{min}^{1/2}\right),$$

$$\frac{K_4}{K_6} = 20 \pm 2, \quad \frac{K_3}{K_5} = 70 \pm 8\left(\text{l}\,\text{mol}^{-1}\right).$$

A very important exception, however, is the unexpected kinetic effect of oxygen: it was found, indeed, that increasing the oxygen partial pressure over one atmosphere, otherwise than predicted from the mechanism, the reaction rate regularly increased. The kinetic study proved that this effect can be directly correlated to the increase of the initiation rate which, as shown in Fig. 2, even doubles going from one to a few atmospheres of oxygen partial pressure. This effect is of

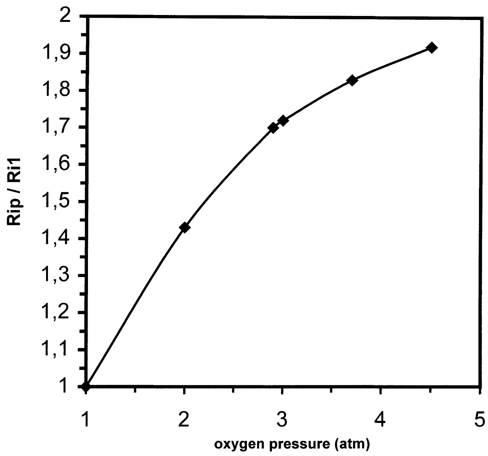


Fig. 2. Ratio of the initiation rate under oxygen overpressure (R_{ip}) to the initiation rate at one oxygen atmoshpere (R_{i1}), in the oxidative polymerization of C_2F_4 initiated by fluorine (temperature −82°C; solvent CF_2Cl_2).

speculative interest; among the reasonable explanations of oxygen intervention, it is gaining ground on the assumption that oxygen can compete with tetrafluoroethylene in the reaction with fluorine atoms:

$$F + O_2 \leftrightarrow FOO$$

This fast reaction, whose equilibrium is shifted to the right by an increase in oxygen pressure [15,16], originates a different kind of primary radical (FOO), able to add (eventually after its conversion to FO through reductive coupling with a peroxy radical) to a molecule of monomer, thus starting a chain. The new growing radical, however, bears an end group containing a weak O–F bond which, interacting with a molecule of fluoroolefin, can produce a new pair of radicals:

$$\sim CF_2O(O)F + C_2F_4 \rightarrow \sim CF_2O(O) + C_2F_5$$

Thus, the net result of oxygen intervention in the initiation step would be the creation from each molecule of fluorine of more than two primary radicals, up to four or even more. This situation might in fact be also regarded as a sort of oxygen activation, brought about by fluorine atoms, to directly react with tetrafluoroethylene (fluorine sensitized oxidation); it is interesting to note that, under this condition, some polymeric chain would grow from both ends, behaving – formally at least – like bi-radicals.

From a practical standpoint, this activating effect of a moderate oxygen overpressure in the system $C_2F_4/O_2/F_2$ is very useful because it allows to obtain a significant productivity increase with reduced fluorine consumption and, consequently, the formation of higher molecular weight polymers [17].

2.2. *Practical exploitation*

The synthesis of perfluoropolyethers through chemically activated oxidation of C_2F_4 is an efficient and productive process; its basic economics and simple technology make such process an attractive candidate for large scale production of polyethers whose structure can be varied within rather wide limits by adopting suitable reaction conditions. Their actual structure can be settled so as to fit the expected utilization; for example, when the raw polymer is to be converted into inert fluid (Fomblin Z^{TM}), the peroxide bonds – which are to be removed from the molecule by thermal treatment – are kept at the lowest level. On the contrary, if the raw polymer is to be used as starting material for lower molecular weight polyethers, even having reactive groups at both ends (perfluoropolyether macromers), the peroxides, which are to be chemically cleaved, are kept at a higher level, chosen so as to provide molecular segments having the desired chain length.

A very similar process is also effective for the synthesis of polyethers from other fluoroolefins, particularly from hexafluoropropylene, and from their mixtures. Productivity, versatility, technological simplicity, chemical efficiency, easy control over product structure, are all factors that characterize this new process which looks very promising for future large scale developments.

3. Functional perfluoropolyethers

The availability of perfluoropolyether molecules having chemically reactive groups at one or both chain ends is certainly very important because of the attractive prospects of their utilization in various sectors (for example, as surface active agents, auxiliaries for surface treatments, macromers for the synthesis of high performance polymers, etc.) where the unique properties of these molecules are highly appreciated.

Recently AUSIMONT studied and developed its own technology for the production of bifunctional perfluoropolyethers through reductive fission of enchained peroxy bonds. Within AUSIMONT's technologies, however, it was much more difficult to obtain polyethers of low to moderate molecular weight and bearing a chemically reactive group at just one chain end (monofunctionals). From the photochemical synthesis, employing hexafluoropropylene as starting olefin, actually one obtains a minor fraction of monofunctional polyethers $CF_3O\text{–}(C_3F_6O)_n\text{–}CF_2CFO$ which can be isolated in the pure state (n from 1 to about 5), rather laboriously indeed, from the raw product. The strong interest aroused by these molecules in several application fields prompted then a research program aiming to the selective production of similar molecules directly in the synthesis.

The principle was to seek for a proper reactant able to act as a transfer agent during the oxidative polymerization leaving a functional group at one end of the polyether chain. The problem, however, was that the carbon radical of the growing chain, which is the active species in the traditional transfer processes, here cannot be effective in a reaction with a transfer reagent because of its exclusive reactivity with oxygen.

3.1. Addition–fragmentation transfer

Since the use of traditional chain-transfer agents was prevented, a different methodology was taken into consideration to achieve the same result. It was based on an elementary reaction which is a characteristic feature of perfluoroalkoxy radicals, i.e. the easy spontaneous breaking of a bond in β position to the oxygen atom bearing the lone electron:

$$\sim O-CF_2CFXO \rightarrow \sim O-CF_2CFO+X$$

This kind of radical fragmentation of perfluoroalkoxy radicals is quite frequent, indeed, particularly at relatively high temperatures, but generally affects the inner C–C bond, leading to the formation of acetalic units in the polyether chain; in the case of hexafluoropropylene ($X{=}CF_3$), however, also the breaking of the $C–CF_3$ side bond can sometimes occur and this indeed is a true chain-transfer process which leaves a –CFO terminated polyether while producing a chain initiating CF_3 radical.

The research has been practically directed to the finding of suitable "comonomers" $CF_2{=}CFX$ which have to be capable of participation to the main elementary steps of the oxidative mechanism, forming intermediate alkoxy radicals $\sim O–CF_2CFXO$ which should have the highest tendency to fragment, breaking their C–X bond rather than their C–C bond. Moreover, these alkoxy radicals ought to fragment in a quantitative way, in order to avoid the "comonomer" being incorporated into the growing chain.

This methodology is conceptually similar to that of "addition–fragmentation transfer" recently described and regarded as potentially useful for the production of functional telomers [18]. Actually it is more involved because in the present case it is not the carbon radical formed in the addition of the modifying comonomer that has to fragment, breaking a relatively weak β bond, but it is the corresponding alkoxy radical which ought to be formed by several preceding elementary steps. Furthermore, the new radical species X formed by fragmentation has to be very reactive, even in the presence of oxygen, in initiating a new chain.

The search of "comonomers" suitable for such chain transfer process has been successful, and various potential candidates have been found [19]. During this study it was also ascertained that, as predictable, the propensity for spontaneous fragmentation of the radical $–CF_2CFXO$ is strictly related to the strength of the C–X bond [20].

The most interesting monomer for addition–fragmentation transfer was chlorotrifluoroethylene (CTFE) which, in effect, showed an excellent set of properties, such as:

- it is very reactive, being able to react even when extremely diluted in the system;
- by addition to the growing chain, followed by quenching with O_2, forms a peroxy radical $–CF_2CFClO_2$ whose only reaction is the reductive coupling with another peroxy radical;
- its alkoxy radical $–CF_2CFClO$ undergoes quantitative fragmentation, leaving a terminal acylfluoride group $–CF_2CFO$ and releasing a chlorine atom;
- the chlorine atom adds very efficiently to a molecule of fluoroolefin, forming a fluorocarbon radical which starts a new chain.

Practically, under the usual conditions of oxidative polymerization, CTFE proved to be a very good transfer agent, showing neither the tendency to be incorporated into the polyether chain, nor the tendency to break its C–C bond with formation of $–CF_2O–$ grouping. The presence of CTFE did not affect any of the kinetic parameters of the reaction, either photochemical or chemically activated, and, due to its reactivity, its transfer action was easily controlled by just adapting its inflow into the reacting system.

Even for this kind of transfer process, the resulting telomerization degree n should be expressed by the classical Mayo equation

$$\frac{1}{n}=\frac{1}{n_0}+C_{\mathrm{tr}}\frac{[\mathrm{CTFE}]}{[\mathrm{M}]}$$

where n_0 is the polymerization degree in the absence of the chain-transfer agent. In the present case, by adopting the typical notation for binary copolymerization, the transfer constant C_{tr} can be also regarded as the reciprocal of the reactivity ratio r_1 in the oxidative copolymerization of C_2F_3Cl (monomer 1) with the fluorolefin M (monomer 2).

Working in a condensed phase of hexafluoropropylene, since the monomer concentration is practically constant the Mayo equation can be simplified to

$$\frac{1}{n}=\frac{1}{n_0}+K\cdot F_{\mathrm{CTFE}}$$

where F_{CTFE} is the flow of chlorotrifluoroethylene supplied to the liquid monomer and immediately converted.

The diagram in Fig. 3 reports the result of a series of photooxidative polymerizations of hexafluoropropylene in which varying amounts of chlorotrifluoroethylene have been continuously supplied to the reaction medium; it is clearly shown that how the reduction in the molecular weight of the product performed by CTFE is very regular and in fair accordance with the above equation.

3.2. Functional polyether telomers

When applied to hexafluoropropylene, the addition–fragmentation transfer technology allows the synthesis of a series of polyether telomers whose ideal structure is expressed by the general formula $Cl–(C_3F_6O)_n–CF_2CFO$ where the mean n value corresponds to a few units. Obviously, the reaction yields a mixture of different molecular weight species; single telomers, however, can be easily

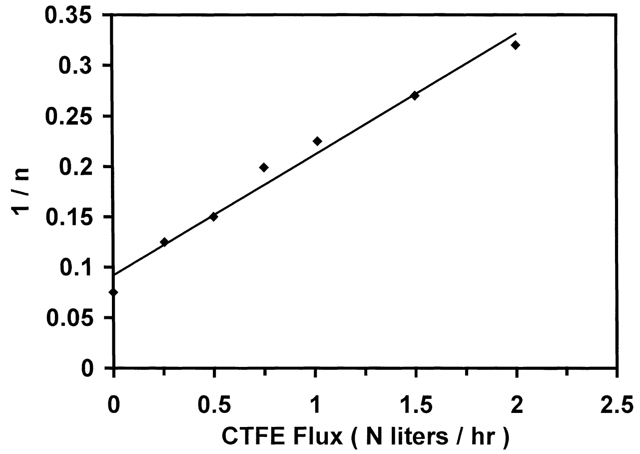


Fig. 3. Reciprocal of the mean telomerization degree (n) vs chlorotrifluoroethylene (CTFE) flux in the photooxidative polymerization of pure C_3F_6 (temperature −60°C; C_3F_6 6 g moles).

isolated through fractional distillation. The structure of these products very closely approaches the ideal one when the synthesis is carried out at the lowest temperatures, under conditions that provide for maximum kinetic chain lengths and for a large transfer effect operated by CTFE. On the other hand, while working at higher reaction temperatures and in the presence of a reduced transfer action, the structure of the telomers feels the effect of the competition between the imposed transfer with CTFE and the typical elementary reactions which normally affect the chain structure, the molecular weight and the nature of end groups of the obtainable oligomers [1]. Obviously, it is also important to operate the synthesis in such a way so as to substantially prevent the formation of enchained peroxy bonds which could pose some problem during the subsequent working up of the product.

The R&D work carried out on this process has now allowed AUSIMONT to establish on the commercial scale the production of these telomer mixtures: from the raw reaction product, more than 85% by weight can be generally recovered under the form of pure perfluoropolyether carboxy acids $Cl\text{–}(C_3F_6O)_n\text{–}CF_2COOH$ with n from 1 to 5. Such compounds, as well as a number of their derivatives, have been proved to be of real interest because of their intrinsic surface activity characteristics, and are now being evaluated and introduced in several application sectors.

The addition–fragmentation transfer technology is not limited to the system C_3F_6/CTFE: other fluoromonomers, such as, for example, C_2F_4, are equally well responsive to the same technology and several different fluorinated comonomers can be employed as transfer agents, leading to the synthesis of a variety of telomers bearing reactive groups. In summary, the addition–fragmentation transfer methodology coupled with the oxidative polymerization, represents a new and very versatile technology which opens new opportunities for the synthesis of a number of useful reactive fluorochemicals.

4. New polyether structures

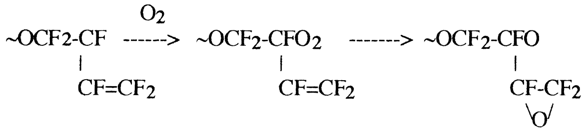
So far the oxidative polymerization has been studied and developed substantially for the two simplest fluoroolefins, tetrafluoroethylene and hexafluoropropylene, and for their mixtures. The corresponding perfluoropolyethers thus contain the basic perfluoroalkylenic units CF_2CF_2 and $CF_2CF(CF_3)$, perhaps along with those (CF_2 and $CF(CF_3)$) deriving from fragmentation of their C–C bond. Nevertheless, a proper combination of these units enables to obtain a large gamma of physical and chemical properties. Potentiality of the synthesis, however, is not confined to the simplest fluoroolefins: the oxidative polymerization technology, in fact, can also be applied to other fluoromonomers for the synthesis of polyethers having different structures and properties. Here only a couple of examples of these wide potentials are briefly described.

4.1. Perfluoroalkylvinylethers

As described in a dedicated paper on this same journal, lower perfluoroalkylvinylethers, $R_FOCF{=}CF_2$, under suitable conditions react with oxygen to produce polymeric perfluoropolyethers. These products are of particular interest since their R_FO– side groups contribute to the increase of the overall ratio of C–O bonds to C–C bonds in the molecules, thus causing significant variations of certain physical and thermodynamical properties which are appreciated in some application fields. According to the group contribution analysis made on perfluoropolyether molecules [21], an increase in the O/C ratio causes, for example, a remarkable lowering of viscosity, of the viscosity variation with temperature, of the glass transition temperature, of the molecular cohesive density, etc. By employing in the synthesis proper mixtures of a fluoroolefin and a fluoroalkylvinylether, it is thus possible to produce perfluorocopolyethers whose properties can be fine tuned to specific application needs.

4.2. Perfluorobutadiene

This diolefin, in a condensed state under UV activation, easily reacts with oxygen, yielding macromolecular products having polyether structure. The composition of the polymer is rather complex, but a recent study of this reaction [22] has now clarified that the diene is prevailingly enchained with 1,2 configuration and that the vinyl side group takes part itself in the chain oxidation process, being transformed into oxirane ring. Since, even when the conversion of perfluorobutadiene is maintained at a very low level the polymer does not contain any perfluorovinyl grouping, it is suggested that the oxidation mechanism of the vinyl group is intramolecular in its nature, occurring during the growth of the chain, for example, according to the scheme



$$\sim OCF_2\text{-}\underset{CF=CF_2}{\underset{|}{CF}} \xrightarrow{O_2} \sim OCF_2\text{-}\underset{CF=CF_2}{\underset{|}{CFO_2}} \longrightarrow \sim OCF_2\text{-}\underset{\underset{\backslash O/}{CF\text{-}CF_2}}{\underset{|}{CFO}}$$

Such intramolecular oxidation reaction is somewhat reminding of the well-known capability of dioxirane, CF_2O_2, in the epoxidation of perfluorinated double bonds [23].

Other minor structures detected in the oxidative polymerization product of C_4F_6, are the units typically formed by fission of a C-C bond of the oxyradicals, such as $-OCF_2O-$ and $-O\underset{\underset{\backslash O/}{CF\text{-}CF_2}}{\underset{|}{CF}}O-$, the latter proving the occurrence of some attack in the 2 position of the diene.

Some few units $-OCF_2\text{-}\underset{\backslash O/}{CF\text{--}CF}\text{-}CF_2O-$ have been also detected in the polymer, which derive from 1,4 enchainment of the diene followed by epoxidation of the internal double bond.

In summary, however, the main structure of this polymer is that of a perfluorinated polyether with oxirane pendent groups which are very reactive functions, that can be further used for a number of chemical transformations. For example, by simple heating they produce acylfluoride side groups; the product is thus converted into an ionomeric perfluoropolyether, a new kind of polymeric polyelectrolyte.

Side functionalized perfluoropolyethers represent a new class of compounds which can be used in the preparation of many useful derivatives and materials. Knowing the insuperable difficulties that would be encountered in the attempt of post-synthesis functionalization of perfluoropolyether chains, the possibility of direct synthesis of polyether macromolecules where pendent chemically reactive groups are present, by oxidative polymerization, or else copolymerization, of a perfluorinated diene looks very attractive and deserving further consideration.

5. Conclusions

The synthesis of perfluoroalkylpolyethers by direct reaction of fluorinated monomers with molecular oxygen has been further proved to be a very versatile technology which offers a number of new opportunities for the synthesis of a large gamma of products.

The possibility of activating this complex mechanism not only by UV radiation but also by employing some simple chemical initiator brings further evidence in support of the general value of the procedure and offers new prospects for production development.

It is also important that, by means of a well-aimed intervention on some elementary step of the process, it has been possible to adopt a new chain-transfer criterion which allows the direct production of polyethers having controlled molecular mass and bearing a chemically reactive group at the end of the chain. Clearly, the availability of this new class of fluorinated compounds and intermediates opens many interesting opportunities of exploiting the unique properties of perfluoropolyether segments in a number of utilizations.

Finally, the proven feasibility of applying the same oxidative polymerization to different monomer structures, shows that the singular oxidation mechanism which leads to macromolecular compounds is quite a common characteristic for fluoromonomers, even others than lower α fluorolefins. This offers additional chances to a technology that already forms the basis of the commercial production of classes of chemicals which are among the most advanced and successful products in fluorine chemistry.

References

[1] D. Sianesi, G. Marchionni, R.J. De Pasquale, in: R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry, Principles and Commercial Applications, Plenum Press, New York, 1994, pp. 431–461.

[2] M. Visca, R. Silvani, G. Marchionni, CHEMTECH 27 (1997) 33.

[3] G. Marchionni, G. Fontana, G. Pezzin, Chemistry, Technology and Application of Fluorocompounds, St. Petersburg 1997, Abstract 44-P1–14 .

[4] S. Radice, M. Causà, G. Marchionni, J. Fluorine Chem. 88 (1998) 127.

[5] J. Scheirs, S. Burks, A. Locaspi, Trends in Polym. Sci. 3 (1995) 74.

[6] S. Turri, M. Scicchitano, C. Tonelli, J. Polym. Sci., Part A 34 (1996) 3263.

[7] G. Simeone, S. Turri, M. Scicchitano, C. Tonelli, Angew. Makromol. Chemie 236 (1996) 111.

[8] C. Tonelli, T. Trombetta, M. Scicchitano, G. Simeone, G. Ajroldi, J. Appl. Polym. Sci. 59 (1996) 311.

[9] F. Gozzo, G. Camaggi, Tetrahedron 22 (1966) 1765, 2181.

[10] D. Sianesi, A. Marracini, G. Marchionni, US Patent 5 149 842 (1992), 5 258 110 (1993).

[11] W.T. Miller Jr., A.L. Dittman, J. Am. Chem. Soc. 78 (1956) 2793.

[12] W.T. Miller Jr., S.D. Koch Jr., F.W. McLafferty, J. Am. Chem. Soc. 78 (1956) 4992.

[13] W. Navarrini, A. Russo, V. Tortelli, J. Org. Chem. 60 (1995) 6441.

[14] F. Conti, C. Corvaja, F. Cremonese, W. Navarrini, V. Tortelli, J. Chem. Soc., Faraday Trans. 91(21) (1995) 3813.

[15] P. Pagsberg, E. Ratajczac, A. Sillesen, J.T. Jodkowski, Chem. Phys. Lett. 141 (1987) 88.

[16] A.S. Hasson, C.M. Moore, I.W. Smith, J. Chem. Soc., Faraday Trans. 93(16) (1997) 2693.

[17] G. Marchionni, P.A. Guarda, M. Paganin, US Patent 5 488 181 (1996).

[18] D. Colombani, P. Chaumont, Addition–fragmentation processes in free-radical polymerization, Prog. Polym. Sci. 21(3) (1996) 439–503.

[19] G. Marchionni, A. Staccione, US Patent 5 143 589 (1992).

[20] G. Marchionni, P.A. Guarda, U. De Patto, Proceedings of the 11th European Symposium on Fluorine Chemistry, Bled, 1995, Abstract, p. 103.

[21] G. Marchionni, G. Ajroldi, G. Pezzin, Structure–Property Relationships in Perfluoropolyethers: A Family of polymeric Oils, Compr. Polym. Sci., 2nd Suppl., 1996, pp. 347–388.

[22] P.A. Guarda, G. Spataro, U. De Patto, G. Marchionni, Proceedings of the 15th International Symposium on Fluorine Chemistry, Vancouver, 1997, Abstract O(1) C-6.

[23] A. Russo, D.D. DesMarteau, Angew. Chem. Int. Ed. Engl. 32(6) (1993) 905.