Synthesis and characterization of poly(tetrafluoroethyleneperoxides)

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ABSTRACT

Tetrafluoroethylene (TFE) and oxygen react at low temperature in radical conditions to give perfluoropolyether–polyperoxide polymers. This oxypolymerization reaction has been applied on industrial scale for the manufacture of perfluoropolyethers, presently used in many application fields.

It is known that highly unstable polymers containing large amounts of peroxidic units $-CF_2CF_2OO-$ can be formed in particular conditions and may represent a potential hazard in the TFE oxypolymerization process. However little has been reported in the literature on the reaction conditions and the characterization of these polymers.

In the present paper we describe the synthesis of perfluoropolyether–polyperoxide polymers with high peroxide content up to the nearly pure poly(perfluoroethyleneperoxide). The investigation is particularly focused to elucidate the relationship between reaction conditions, kinetics and polymer structure. The experimental results indicate that the physical chemical properties of these materials are strongly affected by the peroxide content, this latter depending on the reaction conditions, mainly TFE concentration and initiation rate.

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1. Introduction

Several papers have been published in the second half of the 20th century on the oxidation of perfluorinated olefins, particularly tetrafluoroethylene (TFE), under thermal activation or in the presence of sensitizers, UV radiation and ionizing radiation [1,2]. These studies, generally aimed to find out new methods for the preparation of the epoxide, unexpectedly led to the discovery of the radical route for the synthesis of perfluoropolyethers (PFPEs) [3]. In fact molecular oxygen reacts with the perfluoroolefin at low temperature and in radical conditions giving peroxidic perfluoropolyethers in very good yield [4]. The reaction is substantially an oxypolymerization, which can be conveniently initiated by UV light since the product contains peroxidic units which act as photoinitiator for the polymerization.

Years later the UV initiated low temperature oxypolymerization of tetrafluoroethylene and hexafluoropropene was developed on industrial scale for the manufacture of peroxidic perfluoropolyethers, which are now valuable intermediates for the preparation of perfluoropolyether fluids [5] (Fomblin®Z, Fomblin®Y, Galden®), α,ω-hydrofluoropolyethers [6] (H-Galden®) and functionalized derivatives [7] (Fluorolink® family, Solvera®, Fomblin®HC), presently used in many industrial applications.

All these fluorinated products are obtained by thermal treatment or by chemical reduction of the peroxide bonds present in the peroxidic perfluoropolyether intermediate. Recently, the use of a chemical initiator such as elemental fluorine instead of UV light has been also studied [8].

Due to the peroxidic nature of the polymer, the oxypolymerization process needs to be very well controlled. This is particularly true for the peroxidic perfluoropolyether from TFE, having the following general structure:

$$-(CF_2CF_2OO)_p(CF_2CF_2O)_q(CF_2OO)_r(CF_2O)_s- \quad \textbf{(I)}$$
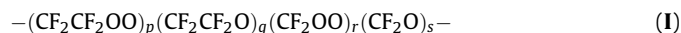
In this case the peroxide content is greatly dependent on the reaction conditions, which are generally selected so as to have a molar fraction of the peroxidic units (p and r units in formula (**I**)) below 0.3.

On the other hand it is known from the literature that under particular conditions the combination of TFE with oxygen can produce highly unstable macromolecular compounds mainly consisting of tetrafluoroethylene peroxy units (p units in formula (**I**)), which are extremely shock-sensitive [9,10]. However, little has been reported on the characterization of these polymers and on the reaction conditions favoring their formation.

In the present paper we describe the synthesis of TFE polyperoxides with variable amount of peroxidic units up to the nearly pure poly(perfluoroethyleneperoxide) $-(CF_2CF_2OO)_n-$.

The discussion will be particularly focused on the correlation between reaction conditions and polymer structure. Moreover,

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Table 1
Synthesis of the polyether–polyperoxide samples (all trials were performed at −78 °C and 4 absolute bars).

Run	Reaction volume ($\times 10^{-3}$ L)	TFE concentration (mol L^{-1})	Reaction time (min)	Fluorine feeding ($\times 10^{-5}$ mmol min^{-1})	Sample amount ($\times 10^{-3}$ g)	PO (^{19}F NMR) (g/100 g)
1	4.9	0.3	20	382	120	5.8
2	7.3	0.2	10	271	40	7.9
3	4.9	0.3	20	190	104	8.0
4	7.3	0.2	30	44	72	9.0
5	4.9	0.3	60	44	120	9.4
6	2.7	1.9	120	29	161	10.4
7	2.7	7.5	270	6.4	64	10.8
8	2.7	7.5	300	2.1	27	10.6
9	4.3	7.5	390	0.6	143	11.0
10	4.3	7.5	1560	0.1	107	11.5

some physical chemical properties of the poly(perfluoroethylene-peroxide) will be presented.

2. Results and discussion

2.1. Synthesis and structural analysis

Table 1 summarizes the reaction conditions used for the preparation of polyether–polyperoxide samples with variable peroxide content. As explained in more detail in the experimental part, the syntheses were performed in a micro-scale semi-batch apparatus in order to have limited amounts (tens or hundreds of milligrams at most) of product for safety reasons. Therefore small amounts of monomer (TFE) were charged in the reactor and diluted with dichlorodifluoromethane (CF_2Cl_2) as solvent in order to have a reasonable volume. The solution was saturated with oxygen at 4 absolute bars to guarantee a good concentration and the reaction was initiated adding very low and controlled amounts of a chemical initiator, namely elemental fluorine diluted in oxygen at concentrations ranging from few ppm (v/v) to thousands of ppm (v/v). The initiator mixture was fed with a constant flow rate during all the trial, calibrating the reaction time so as to avoid the complete conversion of TFE.

We checked that no reaction takes place without the initiator (auto initiation) also at the highest TFE concentration and for a long time period (8 h).

Before describing the polymers obtained, it may be useful to remind that the peroxidic polyether from TFE oxypolymerization (see formula (I)) is substantially a copolymer of oxygen units (ether and peroxide) and carbon units ($-CF_2CF_2-$ and $-CF_2-$), which form four different dyads as reported in the formula. As a consequence of the reaction mechanism the $-CF_2-$ units (C_1), which derive from radical β-fragmentation reactions, are abundant in polymers with low peroxide content, whereas they become less and less abundant as the peroxide content increases [11].

Our previous knowledge however referred to polymers with limited peroxide contents (molar fraction of peroxidic units [OO] of 0.34 at most) since both the synthesis and the handling of polymers with high peroxide content is too dangerous using normal lab techniques. The peroxide content can be expressed as molar fraction of peroxidic units [OO] (or X_P), which is related to the relative abundances of the dyads according to the following equation:

$$[OO] = X_P = \frac{p+r}{p+q+r+s}$$

In alternative, a common expression of the peroxide content is the oxidizing power (PO), directly obtained by the iodometric titration, or calculated from the NMR analysis. The PO is defined as the amount, in grams, of active oxygen (MW = 16) per 100 g of

polymer. Therefore the limit structure corresponding to the polyperoxide $-(CF_2CF_2OO)_n-$ has $X_P = 1$ and PO = 12.1.

The conditions we used in the first experiments derived from our previous experience on the fluorine initiated oxypolymerization of TFE to yield peroxidic perfluoropolyethers at low peroxide content [8]. In those experiments we measured the equilibrium concentration of the monomer during the reaction, which was found to be well correlated to the peroxide content in the product. In particular, trials with a TFE concentration of about 0.1 mol/L produced polymers having a peroxide fraction X_P of about 0.3.

Therefore in the actual micro-scale semi-batch reactor the first trials were performed using TFE concentrations of this order of magnitude, but feeding lower amounts of fluorine initiator.

In particular, trials 1–5 (see Table 1) were done with TFE concentrations ([TFE]) ranging between 0.1 and 0.3 mol/L and changing the amount of the fluorine feeding within one order of magnitude. The polymers obtained in these conditions showed a peroxide fraction X_P between 0.4 and 0.75, corresponding to PO values from 5.9 to 9.4.

Additional trials were made in the attempt to increase the peroxide content, both raising the [TFE] and further reducing the amount of the initiator. The [TFE] was increased to 1.9 and then to 7.5 mol/L (corresponding to 50% of TFE in weight in the CF_2Cl_2 solution) and the fluorine feeding was further reduced of about three orders of magnitude. Using these extreme conditions we observed a gradual increase of the peroxide content, but it proved very difficult to obtain the pure polyperoxide. The best result was the product of trial 10, with PO = 11.5 ($X_P = 0.95$) which reasonably approaches the polyperoxide structure, but is not yet the pure polyperoxide $-(CF_2CF_2OO)_n-$.

The observation of the cold reactor at the end of each trial (through the shellproof glass window) allowed us to estimate the solubility of the polymers in the reaction mixture at −78 °C: the products with PO ≤ 9 gave clear solutions while those with PO ≥ 9.4 were insoluble white solids with a fluffy appearance.

Since it was necessary to reduce progressively the amount of the initiator, i.e. reduce the initiation rate, in order to increase the peroxide content, consequently the productivity (amount of polymer per time unit) decreased with the increase of the PO. It was in fact necessary to prolong the reaction time to many hours in order to obtain reasonable amounts of polymers with a high peroxide content, whereas the same amount of polymer with PO ≅ 6 was synthesized in about 20 min. These data are plotted in Fig. 1, where a roughly linear correlation between productivity and peroxide content can be observed. The reaction that yields the polyperoxide is therefore a very slow reaction.

The composition of the polymers obtained in runs 1–10 was determined by ^{19}F NMR analyses of diluted solutions in hexafluorobenzene (1–3% by weight). Thanks to the enhancement of the polymer's signals obtained by suppression of the C_6F_6
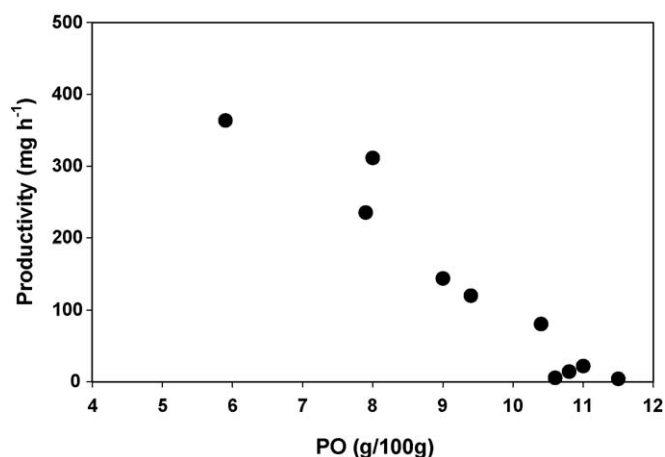
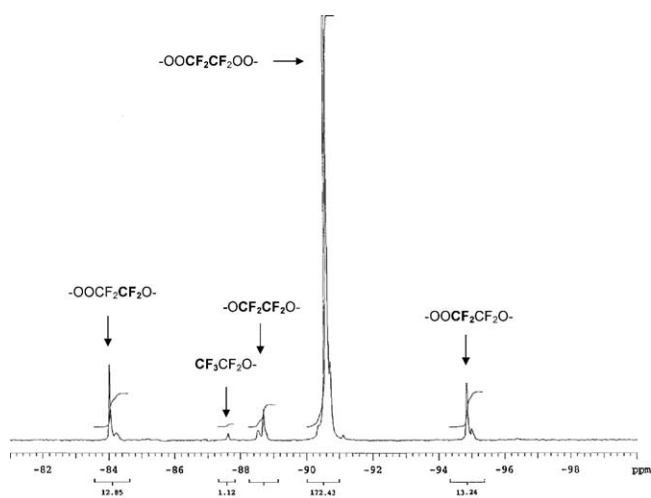Fig. 1. Productivity (mg of polyether polyperoxide sample per hour) as a function of the peroxidic content (PO).

Fig. 3. Comparison between experimental and calculated values for the triads –OOC$_2$OO– ((●) exp.; (- - -) calc.), –OOC$_2$O– ((□) exp.; (—) calc.) and –OC$_n$O– (n = 1 and 2) ((■) exp.; (- -) calc.) as a function of the peroxide fraction X_P.

Fig. 2. Typical ^{19}F NMR signals of a polyether polyperoxide sample (run 8).

resonance, it was also possible to quantify the chain ends at least for samples 1–8 and therefore measure the average molecular weight.

Fig. 2 shows the typical pattern of the main ^{19}F NMR signals and the corresponding attributions (the signals of the –OCF$_2$O– units and of the CF$_3$O– chain ends are outside the expansion reported in the figure). The chain ends observed were mainly CF$_3$CF$_2$O–.

Composition and molecular weight data are reported in Table 2; the dyads and triads were calculated as previously reported [11]. It is possible to see that the C$_1$ units are substantially absent for X_P
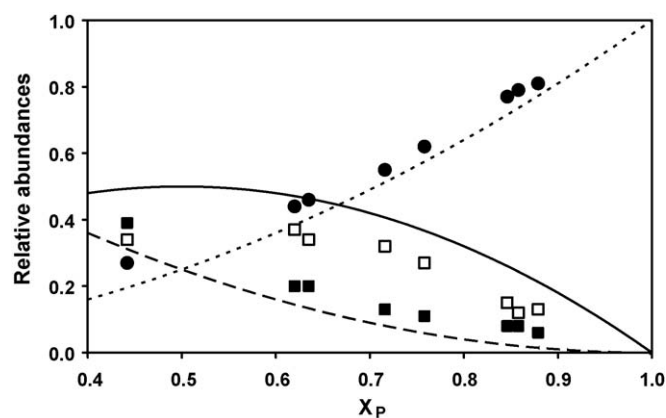
above 0.6 (PO ≈ 8) and these polymers can be well described by the formula:

$$-(CF_2CF_2OO)_p(CF_2CF_2O)_q- \qquad (\textbf{II})$$

The micro-structural analysis of the triads (–OO–C$_2$–OO–, –OO–C$_2$–O–, –O–C$_2$–O–), allows to compare the composition of copolymers (**II**) with the theoretical random distribution of the peroxide and ether units. The experimental data reported in Fig. 3 show a small but systematic deviation from the random calculated values, indicating a slight tendency toward the block copolymer.

The comparison with the random copolymer can be done also in terms of length of the polyperoxidic sequences –(CF$_2$CF$_2$OO)$_n$– (block length B_L). The experimental B_L values were obtained from the ^{19}F NMR components N_N (–OOCF$_2$**CF$_2$**OO**CF$_2$**CF$_2$OO–) and N_F (–OOCF$_2$**CF$_2$**OOCF$_2$CF$_2$OCF$_2$–) according to the equation $B_L = (N_N/N_F) + 2$, as previously reported [11]. The obtained values are plotted in Fig. 4 in comparison with the calculated curve expected for the random copolymer: the experimental points follow the theoretical curve, but are systematically shifted upward. This difference confirms the small compositional drift toward the block copolymer observed by the triads' analysis.

The deviation from the random copolymer is however very small, and therefore the copolymer can be considered in first approximation a random copolymer.

2.2. Properties of the TFE polyperoxides

The neat products, obtained by gentle evaporation of the C$_6$F$_6$ solutions with a nitrogen stream at room temperature, are crystalline-like solids at high peroxide content (X_P > 0.62 or

Table 2
Structural data of the polyether–polyperoxide samples (for symbols and definitions see text).

| Run	Mn (amu)	Dyads			Triads			N$_N$/N$_F$
		[C$_2$OO]	[C$_2$O]	[C$_1$O]	[OOC$_2$OO]	[OOC$_2$O]	[OC$_n$O] (n = 1 and 2)	
1	7980	0.44	0.48	0.08	0.27	0.34	0.39	2.0
2	13960	0.62	0.35	0.03	0.44	0.37	0.20	2.3
3	12340	0.64	0.34	0.03	0.46	0.34	0.20	2.9
4	20600	0.72	0.27	0.02	0.55	0.32	0.13	3.7
5	23230	0.76	0.23	0.01	0.62	0.27	0.11	4.3
6	23600	0.85	0.13	0.02	0.77	0.15	0.08	7.4
7	40180	0.88	0.11	0.01	0.81	0.13	0.06	9.0
8	47120	0.86	0.12	0.02	0.79	0.12	0.08	8.3
9	n.d.	0.90	0.09	0.01	n.d.	n.d.	n.d.	n.d.
10	n.d.	0.95	0.05	0.01	n.d.	n.d.	n.d.	n.d.
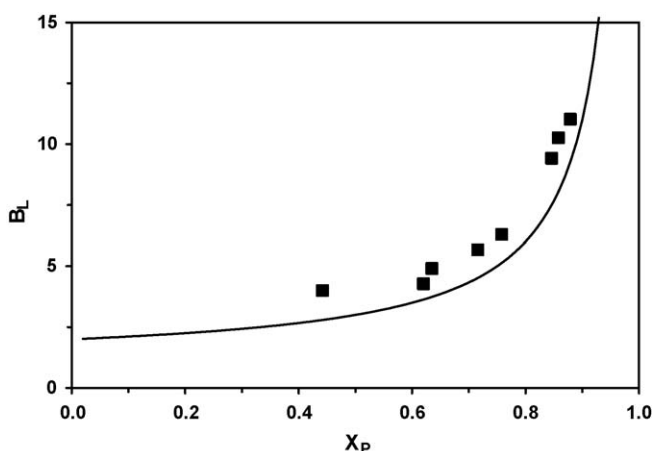
Fig. 4. Experimental values of the polyperoxidic blocks length (B_L) as a function of the peroxide fraction X_P, in comparison with the calculated values (continuous line).

PO > 7.9), whereas for X_P below 0.44 (PO < 5.9) they are substantially viscous liquids.

The polymer with the highest peroxide content ($X_P = 0.95$), namely the nearly pure polyperoxide, is soluble in $CF_2ClCFCl_2$ (CFC 113) and C_6F_6, but surprisingly it is completely insoluble in the typical solvents of the peroxidic perfluoropolyethers with low peroxide content (e.g. perfluorocarbons, perfluoroethers and hydrofluoroethers).
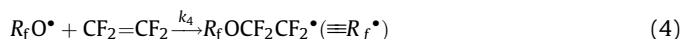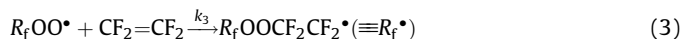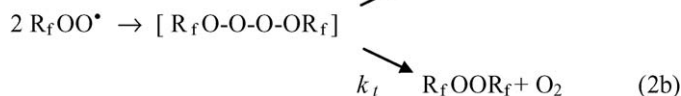
When dissolved in C_6F_6 or CFC 113, the polyperoxide (in the concentration range 1–3% by weight) is stable: the solutions can be safely handled and also heated up to 120 °C without appreciable degradation of the polymer. Instead, the neat solid polyperoxide (with PO > 9) is extremely shock sensitive and detonates under the slightest mechanical stress or by uncontrolled heating.

2.3. Mechanistic and kinetic considerations

The impact of the various process parameters on the composition of the peroxidic polymers obtained by the fluorine initiated oxypolymerization of TFE has been discussed in previous papers [8]. The reaction conditions used in those experiments were chosen on purpose to obtain peroxidic perfluoropolyethers with low peroxide content ($X_P < 0.4$), which are useful intermediates for the manufacture of PFPEs and PFPE derivatives. Instead polymers with high peroxide content are dangerous materials which cannot be handled with the usual lab techniques. However, since these polymers represent a potential hazard in the TFE oxypolymerization process, it is important to better understand the conditions which favor their formation and study their properties.

The work previously done in controlled conditions for the synthesis of polymers with low peroxide content demonstrated that the kinetics and the polymer composition are very sensitive to small variations in the initiation rate. In the continuous flow process, especially at high oxygen pressure, changes of about 10–20% in the fluorine feeding caused significant variations in the monomer stationary concentration and, as a consequence, in the polymer composition and peroxide content. The modeling of the reaction is quite difficult, due to the large number of reaction steps which play a role in the oxypolymerization of TFE. However, this mechanism can be simplified for the high peroxide content polymers of formula (II) (with $X_P > 0.6$), where the β-fragmentation reactions of radicals $-OCF_2CF_2O^•$ (which afford the C_1 units) are absent. In this case the chain propagation steps of the

mechanism can be simplified as follows:

$$R_f{}^• + O_2 \xrightarrow{k_1} R_f OO^• \qquad (1)$$

$$2\,R_fOO^• \rightarrow [\,R_fO\text{-}O\text{-}O\text{-}OR_f\,] \begin{cases} \xrightarrow{k_c} 2\,R_fO^• + O_2 & (2a) \\[2mm] \xrightarrow{k_t} R_fOOR_f + O_2 & (2b) \end{cases}$$

$$R_fOO^• + CF_2{=}CF_2 \xrightarrow{k_3} R_fOOCF_2CF_2{}^• (\equiv R_f{}^•) \qquad (3)$$

$$R_fO^• + CF_2{=}CF_2 \xrightarrow{k_4} R_fOCF_2CF_2{}^• (\equiv R_f{}^•) \qquad (4)$$

Reaction (1) is extremely fast (close to the diffusion limit) and therefore the chain propagation involves exclusively the peroxy- and alkoxy-radicals. The self-coupling of peroxyradicals (reaction (2)) is a key reaction: it has been reported previously that the perfluorinated structure renders this reaction very fast (much faster than the hydrogenated analogues) and selective [12]. In media with a low cage effect reaction (2) produces free alkyloxy-radicals with a high selectivity (>90%) (reaction (2a)), being the complementary reaction (2b) the in-cage radical coupling, which represents the main chain termination of the oxypolymerization process [8]. Once formed the alkyloxyradicals react with TFE faster than the parent peroxyradicals, since the rate constant k_4 is much higher than k_3.

This mechanism predicts that reaction (2) has to be inhibited in order to maximize the relative rate of reaction (3), making it possible the formation of polymers with very high peroxide content. Since the rate of reaction (2) depends on the square of the peroxyradicals concentration, whereas the rate of reaction (3) depends on its first power, the relative rate of reaction (3) should increase as the concentration of the peroxyradicals decreases, i.e. as the initiation rate decreases. In addition the rate of reaction (3) should be sensitive to the concentration of the olefin.

Qualitatively, the experimental results confirm that the peroxide content of the polymers obtained in runs 1–10 depends both on monomer concentration and on initiation rate: if the PO values are plotted against the fluorine feeding rate per unit of volume QF_2 (in logarithmic scale) the points are extremely scattered, but when the PO values are plotted vs. $Log(QF_2/[TFE])$ the points re-compact on a single curve (see Fig. 5).
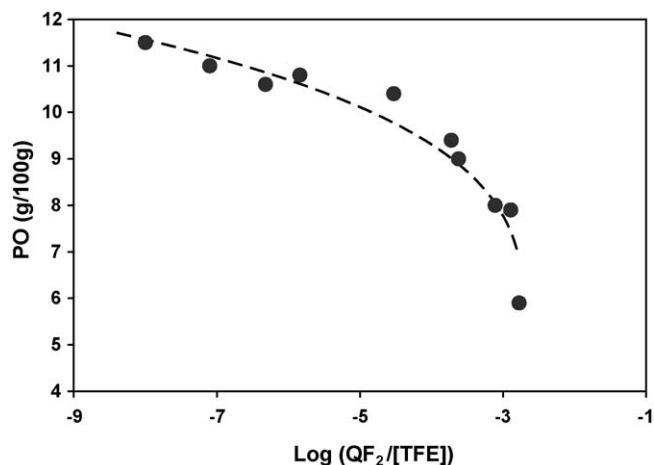

Fig. 5. Peroxidic content (PO) as a function of the reaction parameters: TFE concentration ([TFE]) and fluorine feeding (QF_2).

Under a more quantitative point of view, the kinetic model based on the above reactions allows to obtain a relationship between the peroxide fraction in the polymer and the process parameters initiation rate and TFE concentration. The relationship is the following (see Section 4 for details):

$$X_P = \frac{[\text{TFE}]}{C \times I^{1/2} + [\text{TFE}]} \tag{5}$$

where C is the ratio between the rate constants $k_c/(k_3 \times k_t^{1/2})$ and I is the initiation rate, defined as

$$I = 2\varphi\, Q F_2$$

being φ the fraction of fluorine which effectively gives initiating radicals.

The initiation rate was calculated for runs 1–8 from the amount of polymer and its molecular weight. The selectivity of fluorine into effective initiating radicals, φ, resulted in the range 10–20% for all trials. Such low values may be justified by the low concentration of fluorine in the oxygen stream and by the low residence time of the oxygen bubbles in the non-stirred reaction medium. Both these conditions may limit the gas–liquid mass transfer of fluorine and therefore the observed selectivity. Moreover some fluorine may be lost by gas phase reactions (within the bubble) with TFE (and oxygen) to yield C_2F_6 or other gaseous by-products such as CF_3OOCF_3.

Being I and [TFE] known for each trial, the experimental X_P values were best fitted according to Eq. (5). The best fit gave $C = 13\ \text{L}^{-1/2}\,\text{mol}^{1/2}\,\text{min}^{1/2}$, in good agreement with the value of about 10 estimated from previously reported rate constants substantially obtained at the same temperature ($-83\ ^\circ$C vs. actual $-78\ ^\circ$C) [8]. However, the correlation between calculated and experimental X_P is satisfactory in the range 0.6–0.8, but very poor for the higher X_P values (see Fig. 6). When the model predicts the formation of the substantially pure polyperoxide, the experimental runs instead indicate that further relevant reductions of the initiation rate are needed in order to increase the purity of the product. The limit polyperoxide structure however was not reached even at the lower initiation rate ($X_P = 0.95$ as maximum value obtained).

The discrepancy between the model and the experimental results of the highest peroxide contents may be related to the segregation of these polymers in the reaction medium (observed for $X_P \geq 0.75$). In these conditions the homogeneous liquid phase model is not applicable. However, we expected an opposite deviation from the model, based on the consideration that when the growing macroradicals are substantially blocked (in case of the segregated product), the coupling reaction (2) should be hindered and the formation of the polyperoxide easier.

Even if it is difficult to obtain the pure polyperoxide, polymers with high PO content (X_P in the range 0.4–0.8) are formed also at relatively low monomer concentration, provided that a sufficiently low initiation rate is applied (this is consistent with the model). For example, in run 5 we obtained a product with PO = 9.4 ($X_P = 0.75$) using [TFE] = 0.3 mol/L, which is a concentration only three times higher than the typical values of the oxypolymerization. This suggests that polyperoxide by-products may be formed also in the oxypolymerization process, in regions where the concentration of radicals is particularly low. Under a practical point of view, the dangerous by-products are the insoluble polyperoxides, since they segregate from the reaction mixture onto the walls of the reactor. The results of the present work indicate that these products are polyperoxides with very high PO content ($X_P \geq 0.75$). Fortunately the formation rate of these products is very low, as confirmed by the productivity values obtained in the present experiments.

3. Conclusions

The present work on the micro scale synthesis of perfluoro polyether–polyperoxides indicates a clear correlation between the reaction conditions and the polymer composition. In particular the experimental results show that the peroxide content (PO) depends both on the initiation rate and on the monomer concentration. The formation of polymers with high PO content is favoured by a high concentration of monomer, but it is also possible to synthesize these products at low TFE concentration, provided that the initiation rate is sufficiently low. The results obtained are compatible with the reaction mechanism generally accepted for the TFE oxypolymerization reaction and the kinetics observed are in agreement with the previously estimated reaction rate constants of the key reaction steps.

The peroxide content has a strong impact on the physical–chemical properties of these materials. Viscous liquid polymers at low peroxide content they become crystalline like solids at peroxide fractions X_P exceeding about 0.6. The solid polymers with $X_P > 0.7$ are very unstable materials which detonate under the slightest mechanical stress, whereas the polyether–polyperoxide polymers having $X_P < 0.3$ are stable materials.

Also the solubility changes dramatically: the common perfluorinated solvents of the low peroxide polymers do not dissolve the polyperoxide, with the exception of very few solvents such as trichlorotrifluoroethane and hexafluorobenzene.

When in solution however the polyperoxide is stable both to shear stress and to heating up to 120 $^\circ$C.

The polymers with $X_P > 0.75$ were found to be insoluble in the reaction conditions typically used in the oxypolymerization process for the synthesis of the low PO polyether–polyperoxide. Since the high PO polymers are potential by-products formed in regions of the reactor where the concentration of radicals is very low, their segregation onto the reactor walls and accumulation during time can represent a significant risk for the oxypolymerization process.

4. Experimental

4.1. Synthesis procedure

Caution! The chemicals employed in this work are hazardous and should only be used by skilled operators with appropriate equipment and procedures. In particular, the TFE/oxygen mixtures are thermodynamically unstable and the perfluoropolyether–polyperoxides at high peroxide content are heat and shock sensitive materials.
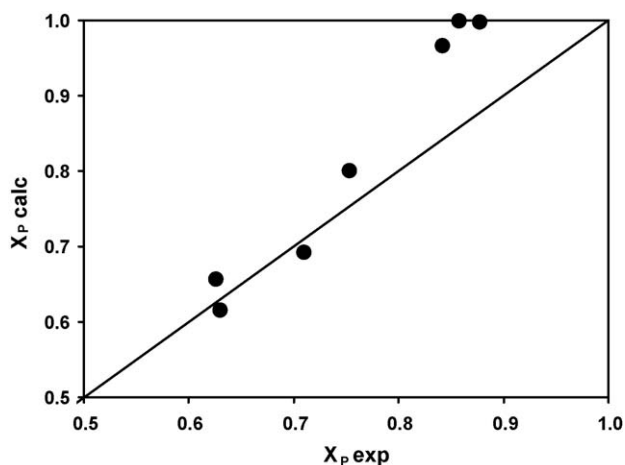

Fig. 6. Experimental values of peroxide fraction X_P in comparison with the calculated ones.

The polyether–polyperoxide samples were synthesized in a pressure proof micro reactor consisting in a glass test-tube (volume = 35 mL; external diameter = 1.5 cm) soldered at the upper edge to the metal inlet and outlet pipes. The reactor was cooled at low temperature ($-78\ ^{\circ}$C) using a double concentric Dewar bath: the internal Dewar vessel contained Galden® and dry ice in contact with the reactor, whereas the interspaces between the two Dewar vessels were filled with liquid nitrogen and dry ice. This simple cooling system guarantees a constant low temperature for many hours without extra operations.

Temperature was measured by a thermo-resistance placed in contact with the external surface of the reactor. The syntheses were carried out under oxygen pressure (4 absolute bars) measured on the off-gas pipe and controlled by an automatic valve.

Reactants and solvent feedings (tetrafluoroethylene, oxygen, fluorine, dichlorodifluoromethane) were measured and controlled by thermal mass flowmeters (Bronkhorst, HI-TEC) calibrated with the corresponding gases.

The radical initiator mixture (fluorine in oxygen, F_2/O_2 mixture) was prepared before the synthesis in a stainless steel cylinder at pressure exceeding 4 absolute bars. The fluorine content was checked by potentiometric titration of the iodine evolved from an aqueous solution of sodium iodide after adsorption of a known amount of F_2/O_2 mixture.

Both the reactor and the cooling bath were shielded by a stainless steel box equipped with a bulletproof safety glass window positioned in order to allow the visual inspection of the reactor (the shield has an arrow slit which makes it possible to raise and lower the bath without removing the shield). The protective shield allowed working under pressure and in the presence of the potentially explosive products in safe conditions, since all the operations (reactants feeding, inspection of the reactor, dissolution of product, etc.) were done from outside the box.

The typical procedure was the following: the reactor was evacuated, cooled at $-78\ ^{\circ}$C, charged with solvent CF_2Cl_2 and with TFE. Then the reactor was pressurized with oxygen up to 4 absolute bars and the reaction initiated by feeding a controlled amount of the F_2/O_2 mixture for the desired time.

The initiator mixture feeding was stopped and the reactor was degassed in order to reduce pressure gradually till the atmospheric value. Then the cooling bath was lowered for a limited time (about 60 s) so as to observe trough the safety glass the aspect of the reaction medium, in particular the presence or not of insoluble material.

The reactor was dipped again in the cooling bath and a weighed amount of hexafluorobenzene C_6F_6 (reagent analytical grade purified by distillation) was injected trough the outlet pipe; the cooling bath was lowered and the reactor let warm up to room temperature in order to eliminate CF_2Cl_2 and excess TFE by distillation.

After a gentle degassing with nitrogen, the polyether polyperoxide solution was discharged, weighed and submitted to ^{19}F NMR analysis (Varian INOVA 400 MHz instrument operating at 376.21 for ^{19}F; chemical shifts were referred to CFCl$_3$ used as external standard). The NMR analysis allowed to calculate the concentration of the polymer in the solution, using the C_6F_6 solvent as internal standard. Moreover it was possible to investigate the fine structure of the polyether polyperoxide by suppression of the C_6F_6 signal with a pre-saturation sequence.

4.2. Calculations and kinetic model

Calculations of the polymer structure were done according to the previously reported algorithms [11].

As far as the synthesis is concerned, the simplified kinetic model which originates relationship (5), is based on Eqs. (1), (2a), (2b), (3), (4) and the additional initiation step:

$$F_2 + CF_2{=}CF_2 \rightarrow 2\,C_2F_5^{\bullet} \tag{6}$$

Reaction (6) is very fast even at low temperature and therefore the initiation rate becomes: $I = 2\varphi\,QF_2$, where QF_2 is the fluorine feeding rate per unit volume and φ is the yield of fluorine into effective initiating radicals.

Also reaction (1) is extremely fast and has no kinetic impact: the carbon radicals (included the $C_2F_5^{\bullet}$) are supposed to evolve immediately to the corresponding peroxy radicals. The only chain termination is considered to be reaction (2b).

The propagation rates to form ether (R_E) and peroxy (R_P) units can be written as follows:

$$R_E = k_4[R_fO^{\bullet}][TFE] \tag{7}$$

$$R_P = k_3[R_fOO^{\bullet}][TFE] \tag{8}$$

The formation of peroxy units by reaction (2b) is neglected in Eq. (8) for simplicity (this is a good approximation if the degree of polymerization is quite high, as in the present case).

The fraction of peroxy units in the polymer, X_P, can be written as

$$X_P = \frac{R_P}{R_P + R_E} = \frac{k_3[R_fOO^{\bullet}]}{k_3[R_fOO^{\bullet}] + k_4[R_fO^{\bullet}]} \tag{9}$$

Applying the stationary state approximation to the concentrations of growing radicals, we have:

$$\frac{d[R_fO^{\bullet}]}{dt} = k_c[R_fOO^{\bullet}]^2 - k_4[R_fO^{\bullet}][TFE] = 0 \tag{10}$$

$$\frac{d[R_fOO^{\bullet}]}{dt} = I - k_t[R_fOO^{\bullet}]^2 = 0 \tag{11}$$

Substituting the radical concentrations of Eqs. (10) and (11) in Eq. (9), we easily obtain Eq. (5).

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