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Erratum

Peroxidic perfluoropolyether from tetrafluoroethylene oxidation: micro structural analysis by NMR spectroscopy and mechanistic considerations

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Dedicated to Prof. R.D. Chambers on the occasion of his 70th birthday.

Abstract

The oxypolymerization reaction of perfluoro olefins is one of the industrial routes for the synthesis of perfluoropolyethers (PFPEs). The distinctive feature of this radically initiated process is that one obtains peroxidic perfluoropolyethers from the oxypolymerization reaction. In the particular case of tetrafluoroethylene (TFE), due to the high reactivity of the olefin, it is possible to obtain peroxidic polymers with variable amounts of peroxide units. It is, therefore of great interest to know in detail the micro structure of this peroxidic polymer with ^{19}F and ^{13}C NMR spectroscopy by far the most suitable techniques for the analysis. A recent investigation on samples with variable peroxide content using a 400 MHz instrument allowed a significant improvement in the analysis of the peroxidic sequences. The results have been discussed in terms of reaction mechanism and kinetics.

Keywords: Perfluoropolyethers; Peroxide; NMR spectroscopy; Micro structural analysis

1. Introduction

It is well known that the oxidation of tetrafluoroethylene (TFE) performed at low temperature (generally in the range −80 to −40 °C) gives peroxidic perfluoropolyether polymers in good yield, together with the low boiling oxidation by-products carbonyl difluoride (COF_2) and tetrafluoroethylene epoxide (C_2F_4O). The peroxidic polymer is the result of a complex free radical oxidation reaction dominated by the chemistry of perfluoro oxy radicals. The high rate of oxygen addition to the carbon radicals, close to the diffusion limit, results in the stationary concentration of the carbon radicals being orders of magnitude lower than that of the oxy radicals. Therefore, the radical propagating species are almost exclusively the perfluoroalkylperoxy ($RfOO^\bullet$) and the perfluoroalkoxy ($RfO^\bullet$) radicals [1,2].

The most important consequence of this reaction mechanism is that the product is an alternated copolymer of oxygen and carbon units, with the complication that the oxygen units can be ether (–O–) or peroxide (–OO–) and the carbon units can be perfluoromethylene ($-CF_2-$) or perfluoroethylene ($-CF_2CF_2-$). The perfluoromethylene units originate from carbon–carbon scission reactions of the growing perfluoroalkoxy radicals $RfOCF_2CF_2O^\bullet$, as reported in previous work [2,3]. Longer carbon units (C3 and C4), arising from TFE addition to the carbon radicals, are present only in trace amount as the reaction is usually performed with oxygen in excess.

Considering the alternated nature of the polymer, a useful representation of the structure is:

$$T(CF_2CF_2O)_m(CF_2O)_n(CF_2CF_2OO)_p(CF_2OO)_qT' \qquad (1)$$

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The average molecular weights generally range between some thousands and tens of thousands, T and T' are perfluorinated or acyl fluoride chain ends; the ether units are generally in higher amount compared with the peroxidic units, i.e. $(m + n) > (p + q)$.

The raw peroxidic polymer is the starting material for the industrial manufacture of perfluoropolyether oils (Fomblin Z^{TM} and Fomblin M^{TM}), α,ω-hydroperfluoropolyethers (H-Galden ZT^{TM}), bifunctionalized perfluoropolyethers (e.g. Fomblin Z-DOL^{TM}, Fomblin Z-DOL-TX^{TM} and Fluorolinks^{TM}) [4–6]. NMR spectroscopy is a well-known technique for the micro structural analysis of the perfluoropolyether compounds above reported [7].

All these products are obtained from the peroxidic polymer either by thermal treatment or by chemical reduction of the peroxide units. The chemical reduction is performed with reducing agents, such as hydrogen iodide or with molecular hydrogen in the presence of a noble metal catalyst. It is, therefore very important to know in detail the micro structure of the peroxidic sequences, which are the reactive sites of the polymer chain. In this connection, NMR spectroscopy proved to be a very useful technique and the recent use of high frequency instruments allowed a significant improvement in the micro structural analysis of the peroxidic sequences.

2. Results and discussion

Several polymers of formula (1) with variable amount of peroxidic units, [OO], have been synthesized according to well-known procedures [2,3]. In particular, some samples have been prepared using the photochemical technique (photosynthesis) and the others using the fluorine initiated oxypolymerization technique, as reported in Table 1 and in Section 4. The peroxidic units [OO] in the samples examined are limited to about 33% of the total units, since higher peroxide contents make the polymer unstable and dangerous when manipulated.

2.1. ^{19}F NMR spectroscopy with 200 MHz instruments

The fluorine chemical shifts of the different $–CF_2–$ groups in the polymer of formula (1) are well known and previously reported [2,8]; they are summarized in Table 2 for comparison with the recent results obtained with higher frequency instruments.

Due to the strong effect of the vicinal oxygen atoms, the $–CF_2–$ units (C1) and the $–CF_2CF_2–$ units (C2) resonate in distinct regions of the ^{19}F NMR spectrum (signals A–E and F–N, respectively, in Table 2). Moreover, the presence of an ether or a peroxide unit influences the chemical shift: for example the $–CF_2–$ group in the $–OCF_2O–$ sequence resonates in the −50 to −56 ppm region, whereas the signals of the $–OCF_2OO–$ sequences are in the region −64 to −66 ppm. Similarly, the $–OCF_2CF_2O–$ sequence resonates between −88 and −90 ppm, whereas the signals of the two $–CF_2–$ groups in the $–OCF_2CF_2OO–$ sequence are in the regions −84 to −86 ppm and −95 ppm, respectively.

The fluorine chemical shifts in some cases are influenced significantly also by longer range effects: the substitution of a $–CF_2–$ group by an oxygen in the γ position along the backbone produces a chemical shift change of about 1–2 ppm. Signals with this chemical shift difference, though intrinsically broadened by the polymeric nature of the sample, are generally resolvable also with 200 MHz instruments. This results in the possibility of differentiating sequences of about six to seven backbone atoms in most cases, as reported in Table 2. However, some sequences cannot be resolved, since they differ from each other for the δ position relative to the resonating $–CF_2–$ group. Using

Table 1
Characteristics and structural data of the examined polymer samples (for symbols and related definitions, see Section 4)

Samples	Synthesis process[a]	PO (iodometry)	Mn (^{19}F NMR)	[OO]	X_{2P}	X_{2E}	r
1	F_2	0.36	8700	0.016	0.323	0.047	0.88
2	F_2	0.53	8000	0.024	0.462	0.148	1.05
3	F_2	0.56	7700	0.026	0.405	0.118	0.94
4	F_2	0.62	8300	0.030	0.571	0.192	1.73
5	F_2	0.65	8600	0.032	0.616	0.257	1.94
6	F_2	0.94	9020	0.052	0.768	0.410	3.45
7	$h\nu$	0.89	14000	0.052	0.752	0.518	2.30
8	$h\nu$	1.09	19800	0.063	0.742	0.508	2.05
9	$h\nu$	1.50	12450	0.089	0.791	0.535	3.10
10	$h\nu$	1.85	29900	0.117	0.851	0.647	3.79
11	F_2	1.93	6150	0.129	0.909	0.759	8.80
12	$h\nu$	2.68	28200	0.177	0.890	0.699	5.04
13	$h\nu$	2.96	39500	0.201	0.916	0.758	7.42
14	F_2	3.20	5250	0.225	0.948	0.839	12.04
15	$h\nu$	3.84	30100	0.272	0.945	0.835	7.60
16	F_2	4.13	6360	0.299	0.974	0.869	19.66
17	F_2	4.64	5850	0.340	0.975	0.889	28.72

[a] Photochemical process ($h\nu$) or process with fluorine (F_2) as chemical initiator.