



Countercurrent fractionation of methylol-terminated perfluoropolyoxyalkylene oligomers by supercritical carbon dioxide

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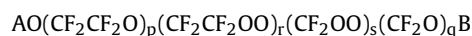
ABSTRACT

A methylol-terminated perfluoropolyether having a broad molecular weight distribution has been countercurrent fractionated with supercritical carbon dioxide using an isothermal increasing pressure profile. Depending on the selected physical conditions, a fractionation as a function of the molecular weight has been observed while the influence of different end-groups, present as admixtures, on the solubility was negligible. As a consequence, the different $-\text{CF}_2\text{H}$, $-\text{CF}_2\text{Cl}$, $-\text{CF}_2\text{CH}_2\text{OH}$ and $-\text{COOH}$ ($\text{X} = \text{CH}_2\text{CH}_3$ or H) end-groups content in the fractions reflected their non-statistical distribution in the starting mixture. This last finding opens the way to a deeper investigation of the reason for this structural diversification. Based on a full evaluation of the multi-step process for the synthesis of the methylol-terminated perfluoropolyether it appears that these end-groups originate from different stability/reactivity of PFPE-reagents and PFPE-intermediates involved in the whole process. These differences are not only function of the specific reaction and experimental conditions considered, but also depend on the PFPE chain length (i.e. molecular weight of the species).

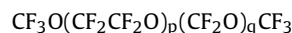
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1. Introduction

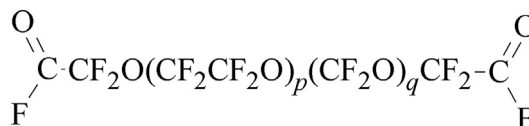
Perfluoropolyethers (PFPEs) are a class of compounds with outstanding chemical and thermal resistance used in a wide range of applications; among them, their use as high-performance lubricants represents one of the most preminent applications. Perfluoropolyether lubricants are proposed for a variety of industrial and specialty applications where ordinary lubricants fail. The scientific literature reports few synthetic routes for the production of these molecules: a) anionic oligomerization of oxirane and oxetane rings [1] and b) photo-copolymerization of oxygen and perfluoroolefins activated by UV light at low temperatures (-40 – -60°C) [2–4]. This latter process offers distinctive advantages in terms of productivity, flexibility, selectivity, and quality control of the final products; it generates, as intermediates, peroxidic structures which are submitted to further chemical reactions in order to target specific products. In particular, the low temperature oxypolymerization of tetrafluoroethylene (TFE) gives linear peroxidic polymers in which perfluoroether repeating units are randomly distributed together with peroxide units:



The terminal groups (A and B) are $-\text{CF}_3$, $-\text{CF}_2\text{Cl}$, fluoroformate $-\text{CF}_2\text{OCOF}$, or acyl fluoride $-\text{CF}_2\text{COF}$. The p/q ratio ranges from 0.5 to 2, while the average molecular weight varies between 10000 and 40000, depending on the reaction temperature. The reaction is carried out in the solvent CF_2Cl_2 . The peroxidic units can be completely eliminated to give stable perfluoropolyether structures through thermal or photochemical treatment involving complex reaction mechanisms, so that the following linear, nonfunctionalized PFPEs are obtained:



Alternatively, these labile groups can be catalytically reduced to give suitable functional end-groups where the first key functional precursor is a diacyl fluoride (DAF), having the following chemical structure:



The availability of PFPE with functional end-groups which can be further converted to other chemical compounds, according to well-established known chemical reactions, has opened up a vast new field to PFPE chemistry and applications. For instance, the alcoholysis of the DAF gives a PFPE alkyl-ester that, through a chemical

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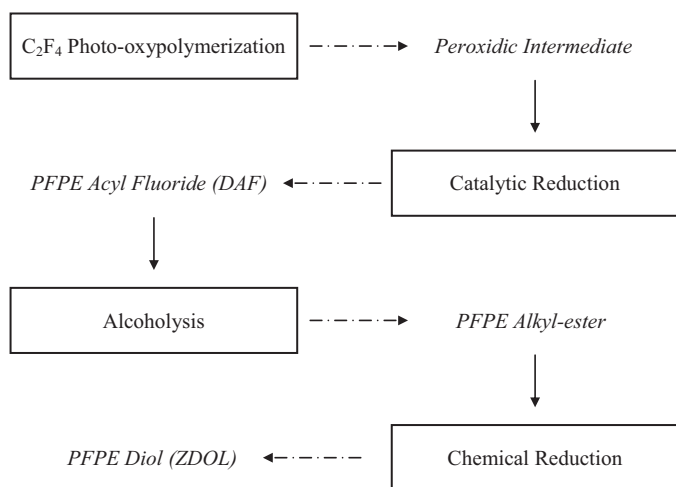
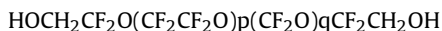


Figure 1. Multi-step process to prepare the PFPE-diol derivative described in the present paper.

reduction, is easily converted to the corresponding alcohol (PFPE-diol):



which finds application in several areas including the boundary lubrication of magnetic recording media or other substrates or as a building block to synthesize quite a large range of PFPE derivatives and related polymers suitable for high-demanding applications. The process step to produce the PFPE-diol is represented in Figure 1. The product obtained through this route is generally a polydisperse mixture, covering a large molecular weight range (from 500 up to 10000). Since many applications require lubricants characterized by high purity and narrow molecular weight distribution [5], a fractionation procedure of the starting polydisperse mixtures is generally applied. Typically, this broad distribution is narrowed by high vacuum thin-layer distillation. However, it must be considered that PFPE derivatives fractionation by distillation, when carried out at high temperature (> 250 °C), must be carefully evaluated, in order to avoid degradation during the process. In fact, even if the PFPE chain is very thermally stable, when the thermal stress combines with metal salts often present in metal equipments (especially having Lewis-acid nature) severe degradation can occur [6,7]. Moreover, metal salts promote high temperature decarboxylation, followed by a complex rearrangement mechanism [8]. Finally, in the presence of oxygen, hydroxyl end-groups can be oxidized. All these evidences suggest that an accurate selection of equipment and set of experimental conditions for the extreme distillation of PFPE derivatives must be done. Apart from these considerations, there is also a physical limit to the distillation when PFPE derivatives having a MW higher than 5500 are considered. In fact, in this case, the product volatility is so low that the efficiency of the process would be extremely limited. For all these reasons the definition of different fractionation methods becomes mandatory [9]. Among the other possible techniques, extraction/precipitation, by the choice of an appropriate solvent-nonsolvent system, gives good results but only for MW higher than 1500; in fact when lower MW are considered the dominant effect of end-units, known in literature as “copolymer end effect” [10], precludes an efficient fractionation. Therefore, vacuum distillation and fractional precipitation can be considered complementary purification techniques to tailor the average molecular weight and molecular weight distribution.

Interestingly, during fractional distillation and solubility fractionation a slight, regular change in the molecular p/q ratio and

hydroxylic functionality was observed [9]. However, these findings were not discussed deeply and only a qualitative relation between hydroxylic functionality and molecular weight was hypothesized without analyzing in detail the nature of functional end-groups. Besides, scientific data in the open literature describing a possible nonhomogeneous structural composition in the starting polydisperse mixture as a function of molecular weight, with a special reference to the nature of the end-capping groups, are not available.

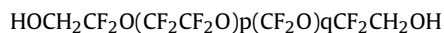
Supercritical carbon dioxide (scCO₂) fractionation represents a very efficient alternative to the use of conventional nonpolar fluorinated solvents in combination with polar precipitating nonsolvents to “cut” a polydisperse PFPE mixture. ScCO₂ is a good solvent for perfluoropolymers [11–13] and specifically PFPEs oils (i.e., non-functionalized species) [14,15] and functionalized PFPEs [16] have shown adequate solubility in scCO₂. In spite of the high investment costs in comparison with conventional equipment, the high-added value of these functional perfluoropolyetheric oligomers, together with its green characteristics, make scCO₂ an attractive solvent for industrial applications, where the usage of large amounts of organic and fluorinated solvents represents a significant problem in terms of process economy, environmental impact, operation hazards, and cost-effectiveness. ScCO₂ is also a nonflammable, recyclable, and widely available solvent, having low critical pressure (7.3 MPa) and temperature (31 °C); these characteristics makes it an ideal solvent for extracting and fractionating thermally labile materials. Furthermore scCO₂ shows a strong, pressure and temperature dependent, dissolving power and therefore it selectively solubilises the compounds according to their molecular weight, by gradually matching the respective solubility parameters. This makes it possible to obtain narrow cuts starting from a polydisperse mixture [16,17]. However, the combined effect of the different nature of the end-groups and PFPE MW on the solubility in scCO₂ is not described in the literature. For all the above reasons scCO₂ has been selected and tested for the fractionation of methylol-terminated PFPEs. Its ability to give narrow fractions is described and discussed in the present work, with special focus on the correlation between the molecular weight of each fraction and its composition in terms of end-groups and internal repeating units.

Results give direct information about the selectivity/conversion of the different multi-step reactions performed from the key PFPE-diacyl precursor to the final PFPE-diol. In such a way evidences about the lability of some terminal groups or, at the contrary, their inertness can be acquired, also as a function of the PFPE chain length.

2. Materials and Methods

2.1. Materials

The hydroxyl-terminated perfluoropoly(oxyethylene-co-oxyethylene) macromer fractionated in this work is obtained by the multi-step process described in Figure 1. It is named Fomblin® ZDOL 2000 PFPE and it is characterized by the following general formula:



where $p/q \sim 1$. It has an average number molecular weight M_n of about 2000, a relatively broad molecular weight distribution (MWD) and about 3% of foreign nonfunctionalized end-groups, meaning end-groups different from $-\text{CH}_2\text{OH}$. Density of Fomblin® ZDOL 2000 PFPE at 20 °C is 1804 kg/m³ and linearly decreases with the temperature (at 100 °C the extrapolated value is ~ 1650 kg/m³ [18]).

The main characteristics of Fomblin® ZDOL 2000 PFPE used as starting material in this work are summarized in Table 1.

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