

Supercritical Carbon Dioxide Fractionation of Perfluoropolyether Diols

Roberto Valsecchi*, Fabrizio Mutta, Ugo De Patto and Claudio Tonelli

Solvay Specialty Polymers, R&D Center, Viale Lombardia 20, 20021 Bollate (MI), Italy

*Corresponding author. Tel.: +39 02 3835 2123; fax: +39 02 93661357

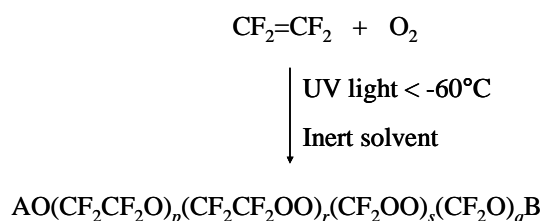
E-mail address: roberto.valsecchi@solvay.com

Perfluoropolyether lubricants are proposed for a variety of industrial and specialty applications where ordinary lubricants fail. Since many applications require lubricants characterized by high purity and narrow molecular weight distribution, a fractionation procedure of the starting polydisperse mixtures is generally applied. Specifically, vacuum distillation or solubility fractionation techniques are very efficient in tailoring the molecular weight; scientific data in the open literature describing a possible fractionation as a function of other macromolecular parameters, for instance the nature of the end-capping groups, are not available. The present contribution refers to the use of supercritical carbon dioxide as solvent for the fractionation of a starting fluorinated polydisperse macromer. This approach offers some intrinsic and distinctive advantages with respect to the use of non polar fluorinated solvent. Among them, the green characteristic of the solvent, joined to its fine tunable solubility parameter represent the major benefits. In this work, a methylol-terminated perfluoropolyether having a broad molecular weight distribution (polydispersity = 1.54), a number average molecular weight of about 2000 and an average functionality $f = 1.954$, has been fractionated through supercritical carbon dioxide using an isothermal increasing pressure profile. According to the selected physical conditions, a fractionation as a function of molecular weight has been achieved. Consistently with the prevalent effect of molecular weight on separation, a monotonic increase of the molecular dimension and a parallel decrease of the polydispersity are observed as a function of the number of iterative step, whereas, the observed different $-CF_2H$, $-CF_2Cl$, $-CF_2CH_2OH$ and $-COOX$ end-groups content in the fractions reflects their non statistic distribution in the starting mixture, rather than an effective fractionation as a function of the different end-groups. This last evidence opens the way to a deeper analysis of the selectivity of each different synthesis step involved in the perfluoropolyether functionalization. This *ex post* rationalization will be, tentatively, discussed.

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. 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-co-polymerization 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 oxypolymerisation of tetrafluoroethylene (TFE) gives linear peroxidic polymers in

which perfluoroether repeating units are randomly distributed along with peroxide units (see Scheme 1).



Scheme 1 – Oxidative photopolymerization of TFE. The terminal groups (A and B) are $-\text{CF}_3$, $-\text{CF}_2\text{Cl}$, fluoroformate $-\text{COF}$ 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

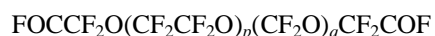
The peroxide units are reactive connecting entities that can be further converted to suitable functional groups; alternatively, they can be completely eliminated to give very stable perfluoropolyether structures through thermal or photochemical treatment involving complex reaction mechanisms, so that the following linear non functionalized PFPEs are obtained:



A further advantage of the photo-oxidation technology is the easy tuning of the PFPE-polyperoxide intermediate structure by modulating the main process parameters. As anticipated above, this process flexibility, joined to the presence peroxidic groups that can be converted to different functional groups, allow to obtain a family of functional PFPE derivatives.

These functionalized PFPEs, which can be further diversified to other chemical compounds, building blocks and polymers, according to well-established known chemical reactions, find use in several high-demanding applications.

The first key functional precursor is a diacyl fluoride (DAF), having the following chemical structure:



The structural flexibility is well represented by the ability of the process in modulating the p and q values; so that macromers characterized by different number average molecular weights can be achieved. The production batches obtained through this route are generally polydisperse mixtures, covering a large molecular weight range (from 500 up to 10000). In order to obtain materials suitable for some high demanding applications, a fractionation of this mixture is generally applied. Typically, a broad distribution is narrowed by high vacuum thin-layer distillation. Unfortunately, PFPEs characterized by very high molecular weight cannot be distilled and the use of a fractionating solvent becomes mandatory.

The use of supercritical carbon dioxide (scCO_2) represents from this perspective a very efficient alternative to the use of conventional solvents.

Indeed, supercritical fluid fractionation is an economically feasible way for processing macromers and polymers. Supercritical CO_2 is a good solvent for perfluoropolymers [5-7]; specifically PFPEs and functionalized PFPEs have shown adequate solubility in scCO_2 [8]. Furthermore scCO_2 shows a strong, pressure and temperature dependent, dissolving power

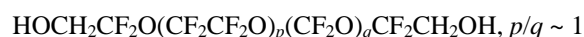
and therefore it selectively solubilises the compounds according to their molecular weight, by gradually matching the respective solubility parameters. This makes it possible to obtain narrow cuts starting from a polydisperse mixture [8,9]. The green nature of scCO₂, which is non flammable and recyclable, is a further reason why this solvent has been widely investigated in many different fields of industrial and applicative chemistry; such as, separation and fractionation processes, particle forming, cleaning, synthesis and modification of polymers and organic reactions.

ScCO₂ is also a low cost, widely available solvent, having low critical pressure (73 bar) and temperature (31°C); these last characteristics make it an ideal solvent for extracting and fractionating thermally labile materials, even if this is not the case of the PFPE derivatives of the present study.

MATERIALS AND METHODS

Materials

The purpose of this study is to fractionate a bifunctional hydroxyl-terminated perfluoropoly(oxymethylene-co-oxyethylene) macromer named Fomblin[®] ZDOL 2000 PFPE characterized by the following general formula:



which is the largest dominating species in the PFPE mixture.

Fomblin[®] ZDOL 2000 PFPE is obtained by a multi-step process involving the following reactions:

1. Photo-oxypolymerisation of C₂F₄ ⇌ Peroxidic intermediate
2. Catalytic reduction of intermediate 1 ⇌ PFPE acyl fluoride
3. Alcoholysis of intermediate 2 ⇌ PFPE alkyl-ester
4. Chemical reduction of intermediate 3 ⇌ PFPE diol (Fomblin[®] ZDOL 2000 PFPE)

The fractionation of Fomblin[®] ZDOL 2000 PFPE, as a function of the processing parameters (pressure, temperature and CO₂/Fomblin[®] ZDOL 2000 PFPE flow ratio), was evaluated, in order to find a possible correlation of between solubility and the structural parameters of the different species present in the mixture, both in terms of molecular weight, end-groups nature and backbone structure.

The main characteristics of Fomblin[®] ZDOL 2000 PFPE used as starting material in this work are summarized in Table 1, where the number average molecular weight (M_n), equivalent weight (EW), polydispersity index M_w/M_n , end-groups content and hydroxyl functionality f are reported.

M_n	EW	M_w/M_n	-CF ₂ Cl (%)	-OCF ₃ (%)	-CF ₂ H (%)	-COOX (%)	-CH ₂ OH (%)	f
1940	992	1.54	0.8	1.0	0.5	0.9	96.8	1.936

Table 1 – Characterization of Fomblin[®] ZDOL 2000 PFPE used as starting material. X = CH₂CH₃

It is evident from these data that Fomblin[®] ZDOL 2000 PFPE has an average number molecular weight M_n of about 2000, a relatively broad molecular weight distribution (MWD) (see also its GPC chromatogram of Figure 2) and about 3 % of non-functionalized end-

groups. Since these hetero-groups are present at low concentration, the number of species having non functional groups at both ends can be considered negligible.

Characterization

Molecular weight, equivalent weight, composition and the hydroxylic functionality f of the starting Fomblin[®] ZDOL 2000 PFPE and related fractions were determined on neat samples by ¹⁹F-NMR spectroscopy by using a Varian Mercury 300 spectrometer working at 282.176 MHz. All chemical shifts were referred to the group $-OCF_2CF_2CF_2CF_2O = -125.8$ ppm. Polydispersity was calculated with Gel Permeation Chromatography (GPC), by dissolving the samples in a 1,3-bis(trifluoromethyl)benzene/isopropanol (80/20 v/v) mixture at a concentration of 0.5 % w/v. Dissolution was performed at 30°C under stirring for about 1 hour. Three-column set of PLgel 10 μ m Individual Pore Size columns: 1000Å + 100Å + 50Å was used, in combination with a Waters 410 Refractive Index Detector. 1,3 bis(trifluoromethyl)benzene/isopropanol (80/20 v/v) mixture was used also as mobile phase at a flow rate of 1 ml/min. Column and detector temperature was set at 35°C.

Experimental apparatus and procedure

A schematic diagram of the supercritical fluid equipment employed in this work is depicted in Figure 1. Liquid CO₂, stored in a reservoir, was pumped and heated to be introduced in supercritical state at the bottom of the extraction column while Fomblin[®] ZDOL 2000 PFPE was pumped at the top. Carbon dioxide rises flows up the column, while the fluorinated compound flows down providing a good counter-current mixing. At a given pressure Fomblin[®] ZDOL 2000 PFPE is partially dissolved in carbon dioxide. The solution flows to the head of the column and then to the separator where CO₂ expands and Fomblin[®] ZDOL 2000 PFPE condenses. In this way the soluble fraction is recovered and collected by opening the bottom valve. Carbon dioxide was then recycled by condensation and stored. Non-soluble molecules were recovered at the bottom of the column as raffinate and were pumped again up for a further fractionation step. At each step, pressure was increased starting from 100 bar and up to 210 bar maintaining the temperature at 100°C and keeping the CO₂/Fomblin[®] ZDOL 2000 PFPE flow ratio constant at about 5.

Mis en forme : Couleur de police : Automatique, Exposant

Mis en forme : Couleur de police : Automatique, Exposant

Mis en forme : Couleur de police : Automatique, Exposant

Mis en forme : Couleur de police : Automatique, Exposant

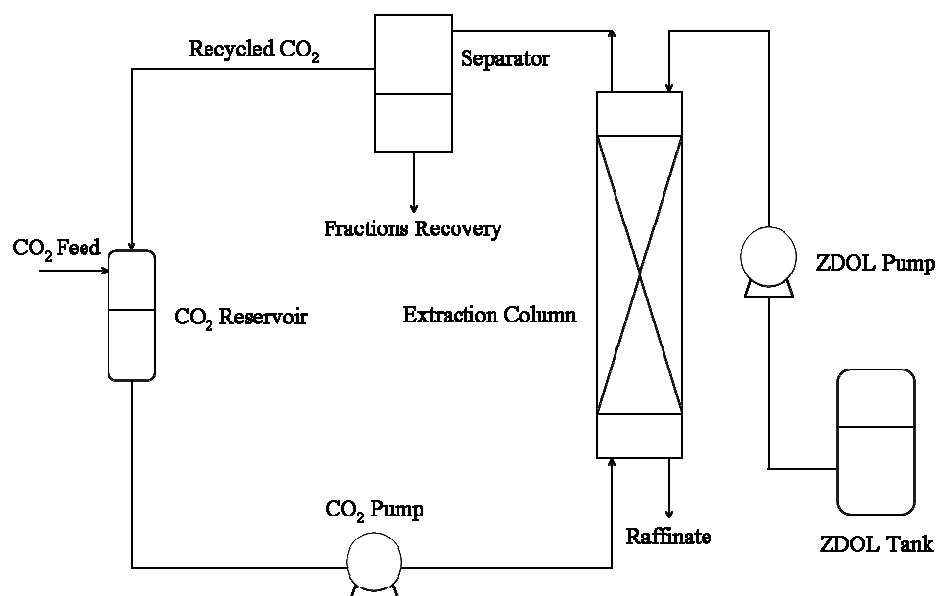


Figure 1 – Schematic representation of the fractionation equipment

RESULTS

Fomblin® ZDOL 2000 PFPE was separated and collected into 23 fractions. Their characterization, in terms of molecular weight (M_n), composition and hydroxylic functionality f is summarized in Table 2, where the M_w/M_n polydispersity index of some fractions is also reported. It can be observed that, according to pressure, scCO₂ selectively dissolves molecules depending on their length. Specifically, lower molecular weight components show higher solubility so that they are the first to be dissolved and recovered. In this way it was possible to cut the starting molecular weight distribution and obtain fractions having an increasing molecular weight.

Fraction	P (bar)	M_n (NMR)	M_w/M_n (GPC)	-CF ₂ Cl (%)	-OCF ₃ (%)	-CF ₂ H (%)	-COOX (%)	-CH ₂ OH (%)	f (NMR)
1	100	797	1.28	0.2	1.5	1.1	0.2	97.0	1.940
2	105	827		0.2	1.4	1.1	0.4	96.9	1.938
3	110	861		0.2	1.4	1.0	0.4	97.0	1.940
4	115	903		0.3	1.3	0.9	0.4	97.1	1.942
5	120	966		0.4	1.2	0.9	0.4	97.1	1.942
6	125	1009	1.23	0.4	1.1	0.8	0.5	97.2	1.944
7	130	1091		0.4	1.1	0.8	0.5	97.2	1.944
8	135	1144		0.5	1.0	0.7	0.6	97.2	1.944
9	140	1217		0.5	1.0	0.6	0.6	97.3	1.946
10	145	1308		0.6	0.9	0.6	0.7	97.2	1.944
11	150	1469	1.24	0.7	0.9	0.5	0.7	97.2	1.944
12	155	1480		0.7	0.9	0.4	0.9	97.1	1.942
13	160	1615		0.7	0.9	0.4	1.0	97.0	1.940
14	165	1774		0.8	0.9	0.4	1.1	96.8	1.936
15	170	1944	1.14	0.9	0.8	0.4	1.3	96.6	1.932
16	175	2142		1.0	0.8	0.4	1.4	96.4	1.928
17	180	2469		1.1	0.8	0.3	1.6	96.2	1.924
18	185	2763		1.1	0.9	0.3	1.7	96.0	1.920
19	190	2996		1.0	0.8	0.2	1.8	96.2	1.924
20	195	3416	1.10	1.2	0.9	0.1	1.8	96.0	1.920
21	200	3832		1.3	0.9	0.2	2.0	95.6	1.912
22	205	4155		1.4	0.9	0.3	1.8	95.6	1.912
23	210	5098	1.11	1.2	1.0	0.2	1.7	95.9	1.918
Final Raffinate	210	7216	1.13	1.5	1.2	0.0	2.6	94.7	1.894

Table 2 – Fractions characteristics in terms of molecular weight (M_n), polydispersity, end-groups content and hydroxylic functionality (f). The final raffinate characterization is also shown. X = CH₂CH₃

Consequently, constitutive fractions from ~ 800 to over 5000 M_n were separated whereas the final raffinate has a M_n of 7216. As expected, all fractions have a lower M_w/M_n index compared with the starting material ($M_w/M_n = 1.54$). Figure 2 clearly shows the effectiveness of the scCO₂ fractionation technique in order to obtain tailored fractions both in terms of M_n and polydispersity. The MWD of the starting Fomblin® ZDOL 2000 PFPE is also reported for

Code de champ modifié

Mis en forme : Anglais (Royaume-Uni)

Code de champ modifié

easy of comparison. It is worth noting that the M_w/M_n index decreases during the fractionation process. This is due to the applied iterative procedure, wherein the fluid fed at the top of the column at each passage has a progressively narrowed MWD. As a consequence the first collected fractions have the highest polydispersity. Theoretically the polydispersity limit is 1, because it depends only on the number of passages through the column when an iterative procedure is adopted. Other operative parameters can help in modulation polydispersity; for instance, by operating at a higher $\text{CO}_2/\text{Fomblin}^\circledR$ ZDOL 2000 PFPE flow ratio (i.e. ~ 20 vs. ~ 5) a faster polydispersity index decrease with the cumulative weight of the collected fractions was observed, as clearly shown in Figure 3. In this way it was therefore possible to reduce the polydispersity of the first recovered fractions. A more detailed analysis of the end-groups, as reported in Table 2, shows some unexpected results that seem to suggest a non-statistical distribution of these functional groups.

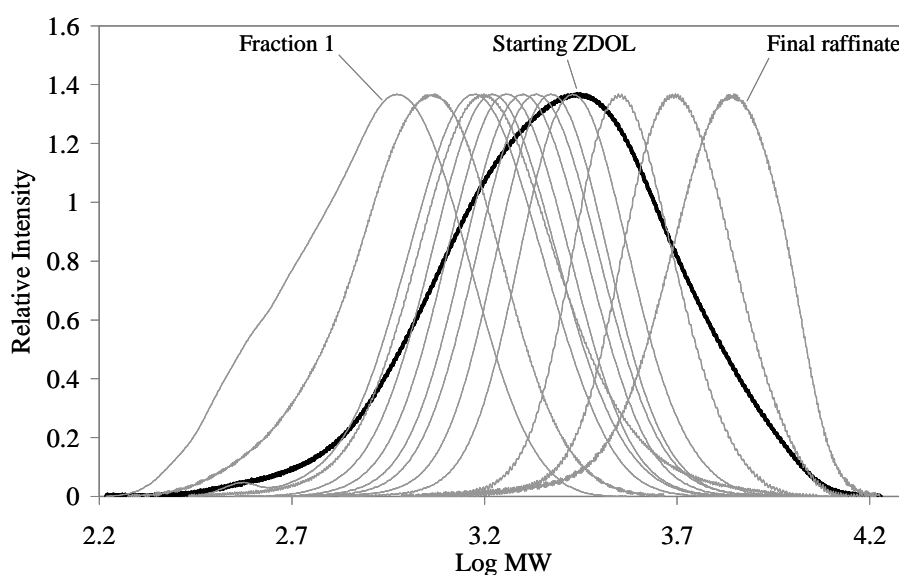


Figure 2 – Overlapped GPC chromatograms of broad Fomblin[®] ZDOL 2000 PFPE precursor, of some fractions and of the final raffinate

Specifically, the $-\text{CF}_2\text{Cl}$ and $-\text{COOX}$ content parallels M_n , while $-\text{CH}_2\text{OH}$ and $-\text{CF}_2\text{H}$ show an opposite trend; finally, $-\text{OCF}_3$ presents a non monotonic trend as a function of the macromer molecular weight. These evidences can not find an explanation on the basis of a simple solubility parameter variation as a function of end-groups nature. In fact, the contribution of these end-units to the overall solubility parameter of the species is very small. Moreover, they are statistically combined with the methylol group as second functional group; this further reduces their effect on the total solubility parameter. Consequently, it appears highly probable that the chain length (i.e. the molecular weight of each species present in the fraction) is the main variable determining the fractionation process.

This hypothesis is substantiated by the evidence that some end-groups variations, as a function of the fractionation step, are mutually correlated, or can find an explanation on the analysis of the selectivity of the entire multi-step process that, starting from the peroxidic PFPE precursor, brings to the final diol species.

For instance, the sum of the $-\text{CF}_2\text{Cl}$ and $-\text{CF}_2\text{H}$ end groups is constant along the entire distribution (1.4 ± 0.2 %), while the concentration of the $-\text{CF}_2\text{H}$ group in the final raffinate is zero. It must be considered that $-\text{CF}_2\text{H}$ group is originated by hydrogenolysis of the

Mis en forme : Anglais (Royaume-Uni)

Code de champ modifié

Mis en forme : Anglais (États Unis)

Code de champ modifié

Mis en forme : Police :(Tipo di carattere testo asiati, Couleur de police : Automatique, Exposant

Mis en forme : Anglais (États Unis)

corresponding $-\text{CF}_2\text{Cl}$ and that this side-reaction has been observed during the catalytic reduction of the PFPE peroxidic precursor; so that the fractionation magnifies the fact that hydrogenolysis essentially affects the shortest and more reactive species present in the peroxidic mixture. This phenomenon is so dependent on the molecular weight that the final raffinate does not contain $-\text{CF}_2\text{H}$ groups at all.

The one order of magnitude variation of the carboxylic end-groups within the collected fractions is due to the fact that the chemical reduction of the PFPE ester precursor, performed in protic solvent in presence of NaBH_4 , is not 100% selective. More precisely, as the chain length increases the ester hydrolysis side-reaction becomes more favourable. This is due to thermodynamic and kinetic reasons; in other words longest species are both less soluble and less reactive in the reaction medium. These carboxylic acids and salts are no more reactive vs. NaBH_4 , so that they remain as admixtures [10].

On the contrary, $-\text{OCF}_3$ end-groups are so stable that they withstand the whole multi-step process, so that their distribution reflects their original content, which is only function of the photopolymerization conditions.

Apart from the above considerations, which are focused on a detailed analysis of the relative content of hetero-groups, it is evident from the experimental data that it is impossible to obtain through the above process an enrichment of the hydroxylic functionality; more precisely the $-\text{OH}$ functionality variation is minimal, being 1.929 ± 0.017 . Instead, this process makes it possible to achieve a very efficient fine tuning of M_n and M_w .

Mis en forme : Anglais (États Unis)

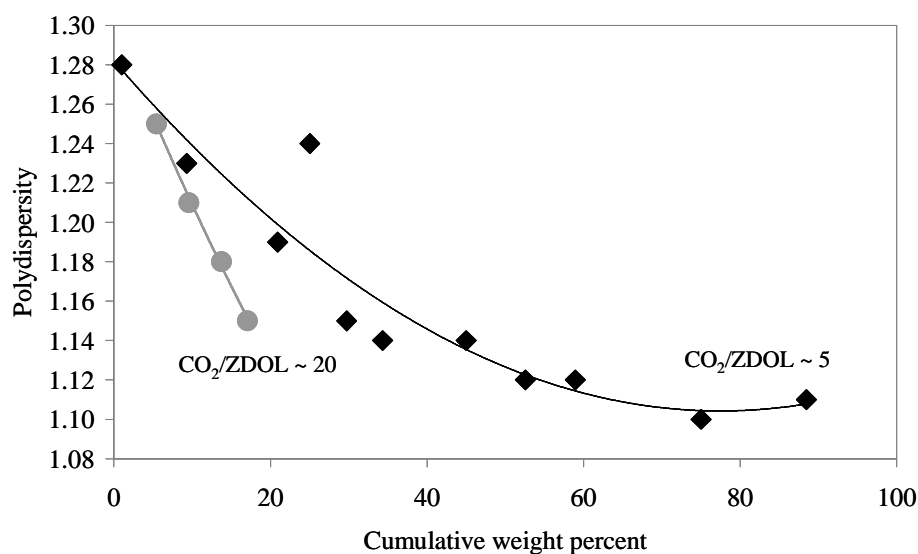


Figure 3 – M_w/M_n as a function of the cumulative weight of collected fractions for two different $\text{CO}_2/\text{Fomblin}^\circledast\text{ZDOL 2000 PFPE}$ flow ratio (~ 5 and ~ 20)

As far as the internal fluorinated structure composition is concerned, a slight, and regular change was also observed in terms of $-\text{CF}_2\text{O}-$ (C1), $-\text{CF}_2\text{CF}_2\text{O}-$ (C2), $-\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$ (C3) and $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$ (C4) units. Table 3 summarizes the chain composition of the different obtained fractions. The p/q ratio (i.e. the ratio between C2 and C1 units) is also shown.

Specifically, the C1, C3 and C4 units content parallels the M_n increase while the C2 unit percentage shows an opposite trend. As a consequence the C2/C1 ratio decreases in opposition to the molecular weight. Namely, this ratio decreases from 0.959 to 0.853 from the

Mis en forme : Anglais (États Unis)

Mis en forme : Anglais (États Unis)

Code de champ modifié

Mis en forme : Anglais (Royaume-Uni)

first fraction ($M_n = 797$) to the last one ($M_n = 5098$). Consistently, the p/q ratio of the final raffinate ($M_n = 7217$) is the lowest of the entire series (i.e. 0.845).

It is evident from these data that there is a non-monotonic trend of the backbone composition as a function of the molecular weight, because, while C2 units decrease, the superior C3 and C4 units increase, so the number of methylene repeating units does not depend in a clear way on the fraction molecular weight. This leads to the conclusion that scCO₂ fractionation is not sensitive to this structural diversification.

Therefore, the observed trend should simply reflect the non-statistical distribution of the same units in the broader molecular weight distribution of the starting Fomblin[®] ZDOL 2000 PFPE, as previously observed for end-groups composition.

Once more, this fractionation technique magnifies and confirms, in a very clear manner, detailed phenomena occurring in each step of the synthesis, thereby providing an important contribution to the comprehension of the physic-chemistry involved.

Fraction	M_n (NMR)	C1 (%)	C2 (%)	C3 (%)	C4 (%)	p/q
1	797	50.71	48.63	0.37	0.29	0.959
2	827	50.76	48.58	0.37	0.29	0.957
3	862	50.76	48.53	0.41	0.30	0.956
4	903	50.83	48.57	0.41	0.19	0.955
5	966	50.83	48.46	0.40	0.31	0.953
6	1009	50.83	48.44	0.41	0.32	0.953
7	1092	50.92	48.33	0.42	0.33	0.949
8	1144	50.95	48.28	0.44	0.33	0.948
9	1218	51.03	48.20	0.42	0.35	0.945
10	1308	51.15	48.07	0.43	0.35	0.940
11	1469	51.40	47.75	0.48	0.37	0.929
12	1480	51.33	47.84	0.46	0.37	0.932
13	1615	51.55	47.60	0.47	0.38	0.923
14	1775	51.75	47.38	0.48	0.39	0.916
15	1944	51.94	47.17	0.49	0.40	0.908
16	2142	52.14	46.94	0.51	0.41	0.900
17	2469	52.40	46.66	0.52	0.42	0.890
18	2763	52.58	46.45	0.53	0.44	0.883
19	2997	52.72	46.30	0.54	0.44	0.878
20	3416	52.94	46.04	0.57	0.45	0.870
21	3833	53.06	45.91	0.57	0.46	0.865
22	4155	53.15	45.79	0.59	0.47	0.862
23	5098	53.36	45.55	0.61	0.48	0.853
Final raffinate	7217	53.59	45.29	0.62	0.50	0.845

Table 3 – Chain composition in terms of –CF₂O– (C1), –CF₂CF₂O– (C2), –CF₂CF₂CF₂O– (C3) and –CF₂CF₂CF₂CF₂O– (C4) units. The p/q ratio is also shown. For the parent Fomblin[®] ZDOL 2000 PFPE C1, C2, C3 and C4 percentage are 52.20, 46.87, 0.52 and 0.42 respectively while the p/q ratio is 0.898

In this specific case, the internal structure diversification, as a function of the molecular weight depends on the kinetic control of the different reactions involved during the photooxidative polymerization.

More precisely, due to the radial geometry of the photochemical reactor, there is a non-homogeneous condition along the reactor radius, both in terms of TFE concentration and radiation intensity. Specifically, at high TFE concentration, C2 units formation is prevalent; while a starvation of the monomer causes an increase in C1 units, which are originated from C2 oxyradicals through a β -scission mechanism [11]. Furthermore, high TFE concentrations generate, inside the reactor, a polyperoxide precursor (see Scheme 1) having a higher content in –OO– peroxide units compared to that obtained from the zones at lower monomer concentration. Therefore, after catalytic reduction, the resulting molecules will have low molecular weights. Conversely, a higher C1 content is expected when the M_n of the molecules is high, these molecules being originated from reactor zones having lower TFE concentration. Unlike the case of C1 and C2 units, the slight increase in C3 and C4 units with M_n is not simply predictable; however, their variation with molecular weight could be related to the non homogeneity in terms of monomer concentration inside the reactor. Therefore, a specific study, evaluating the multi-variables that must be taken into account during the photopolymerization, should be carried out in order to clarify this secondary but intriguing anomaly.

CONCLUSION

Supercritical carbon dioxide processing has been shown to be an effective method for the fractionation of a polydisperse mixture of PFPE oligomers having methylol end-groups. The experimental results of the specific PFPE considered in this work show that $scCO_2$ separates the raw sample substantially in terms of molecular weight. Specifically, through $scCO_2$ fractionation it was possible to obtain fractions having a very narrow MWD in a larger range of molecular weight than that obtained through classical fractionation methods (vacuum distillation and solubility fractionation). Therefore, in this specific case, being prevalent the chain contribution to the total solubility in $scCO_2$, enrichment in hydroxylic functionality was not observed. Consequently, the observed different distribution of –CF₂H, –CF₂Cl, –CF₂CH₂OH and COOX end-groups content in the fractions reflects their real distribution in the starting mixture, rather than their fractionation as a function of the different end-groups solubility in supercritical carbon dioxide. This unexpected evidence underlines the ability of this fractionation technique in magnifying, in a very clear manner, detailed phenomena occurring in each step of the synthesis, thereby providing a very important contribution to the comprehension of the involved physic-chemistry.

REFERENCES

- [1] DING, J.F., PROUDMORE, M., MOBBS, R.H., RASHID KHAN, A., BOOTH, C., PRICE, C., *Makromol. Chem.*, Vol. 193, **1992**, p. 2211
- [2] SIANESI, D., PASETTI, A., FONTANELLI, R., BERNARDI, G.C., CAPORICCIO, G., *Chim. Ind. (Milan)*, Vol. 55, **1973**, p. 208
- [3] SIANESI, D., MARCHIONNI, G., DE PASQUALE, R.J., in: *Organofluorine Chemistry: Principles and Commercial Applications*, R.E. Banks, Ed., Plenum Press, New York, **1994**, p. 431
- [4] MARCHIONNI, G., AJROLDI, G., PEZZIN, G., in: *Comprehensive Polymer Science*, 2nd Supplement, S.L. Aggarwal, S. Russo, Eds., Pergamon Press, Oxford, **1996**, chapter 9, p. 347
- [5] HOEFLING, T., STOFESKY, D., REID, M., BECKMAN, E., ENICK, R. M., *The Journal of Supercritical Fluids*, Vol. 5, **1992**, p. 237
- [6] TUMINELLO, W. H., DEE, G. T., MCHUGH, M.A., *Macromolecules*, Vol. 28 (5), **1995**, p. 1506
- [7] RINDFLEISCH, F., DINOIA, T. P., MCHUGH, M.A., *J. Phys. Chem.*, Vol. 100, **1996**, p. 15581
- [8] SCHONEMANN, H., GALLAGHER-WERMORE, P., KRUKONIS, V., *Proc. 3rd. Int. Symp. On Supercritical Fluids*, Vol. 3, **1994**, p. 375
- [9] YILGÖR, I., MCGRATH, J. E., *Polymer Bulletin*, Vol. 12 (6), **1984**, p. 491
- [10] RUSSO, A., TONELLI, C., *Journal of Fluorine Chemistry*, Vol. 125, **2004**, p. 181
- [11] GUARDA, P.A., BARCHIESI, E., FONTANA, G., PETRICCI, S., PIANCA, M., MARCHIONNI, G., *Journal of Fluorine Chemistry*, Vol. 126, **2005**, p. 685