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Cyclic acetals of fluorinated polyether macrodiols

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Abstract

Telechelic hydroxy terminated perfluoropolyethers were derivatized with dihalomethanes (CH_2Cl_2;CH_2Br_2;CH_2BrCl) in different stoichiometric ratios. The GPC analysis of the raw reaction product showed a general bimodal molecular weight distribution. Separation of the different fractions was carried out by solvent–non-solvent fractionation procedure or by vacuum distillation. It was proved that the lowest molecular weight product (about 50% of the whole polymer) corresponded to a fluorinated, cyclic monoacetal structure, while the higher MW fractions consisted predominantly of linear, polyacetal polymers.

The tendency of fluorinated macrodiols to yield cyclic, instead of linear acetals, is discussed, even in comparison with the behavior of their non-fluorinated analogs. Some physical properties of the new cyclic fluoropolyethers are briefly reported.

Keywords: Cyclic acetals; Macrodiols; Fluoropolyethers

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1. Introduction

Fomblin® ZDOL (Ausimont) is the trade name of a family of perfluoropolyether (PFPE) diols consisting of a random distribution of perfluoroethylenoxy and perfluoromethylenoxy units end-capped with methylol groups according to the following structure:

$$HOCH_2CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2CH_2OH,\quad p/q = 0.5 - 2. \tag{1}$$

Molecular weights of commercially available products range between 1000 and 3000–4000, and depending on it, the oligomers or their ethoxylated derivatives have been used as building blocks for the preparation of both coatings [1,2] and elastomers [3,4], as well as in the modification of conventional polymeric materials [5,6].

Etherification reactions of Fomblin® ZDOL macrodiols have been widely investigated in our laboratories for modulating the nature of the end groups by introducing stable, low-polar linkages between the fluorinated segment and the reactive end functions. In general, the strong electron-withdrawing effects of the perfluorinated chain makes the salification of the $-CF_2CH_2OH$ ends rather easy, leading to the corresponding fluorinated alkoxide $-CF_2CH_2O^-M^+$. This can be obtained both in solution using more basic alcoholates, like potassium *t*-butoxide, or under heterophasic conditions, using aqueous NaOH or KOH. In this latter case, the use of phase transfer catalysts (PTC) is often very effective. In any case, the fluorinated macroalkoxide, under inert atmosphere, is quite stable at temperatures as high as 80°C, thus allowing the synthesis of several polyfunctional fluorinated oligomers through Williamson-type reactions. Some interesting examples [2,7,8] are reported in Table 1.

Etherification reactions of ZDOL in acid media were investigated as well. For instance, poly-perfluoropolyether-acetals (2) with different molecular weights were recently synthesized and characterized [9,10] by reaction of ZDOL with paraformaldehyde catalyzed with sulfuric acid:

$$-[CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2CH_2OCH_2OCH_2]_n- \tag{2}$$

In this work, we investigated a very distinctive reaction like the etherification reaction of ZDOL (MW 1000–2000) with dihalomethanes. In principle, this polyreaction may lead to an alternative method of preparation of acetal-extended fluoropolyether polymers; it resulted, however, that a very significant – and even major – proportion of the reaction product consists of “monomeric” cyclic acetals. It is worth noticing that quite recently some crystalline fluorinated macrocyclic ethers have been described: they have been obtained either by polymerization of trifluorovinyl ether alcohols [11], or by condensation reaction of difunctional silyl ethers with fluorinated olefines [12] and also by controlled elemental fluorination of the corresponding hydrogenated crown-ether [13]. To our best knowledge, no examples are reported in literature concerning the

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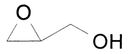
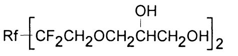
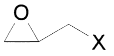
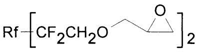
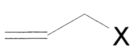
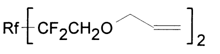
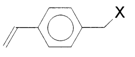
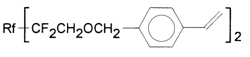
Table 1
Some products of the etherification reactions of ZDOL

Ref.	Electrophilic agent	Syntheses condition	product
2		• t-BuOK/t-BuOH (catalytic)	$Rf\left[CF_2CH_2O(CH_2CH_2O)_nH\right]_2$
2		• t-BuOK/t-BuOH (catalytic)	 $Rf\left[CF_2CH_2OCH_2\overset{OH}{C}HCH_2OH\right]_2$
7		• t-BuOK/t-BuOH (stoichiometric) • PTC process	
7		• t-BuOK/t-BuOH (stoichiometric) • PTC process	
8		• t-BuOK/t-BuOH (stoichiometric) • PTC process	
2	$Br(CH_2)_mBr$	• t-BuOK/t-BuOH (stoichiometric)	$Rf\left[CF_2CH_2O(CH_2)_mBr\right]_2$

X : Br, Cl

synthesis and characterization of amorphous cyclic fluorinated polyethers.

2. Experimental

2.1. Materials

Two grades of ZDOL were used for this work. Their structure characteristics are summarized in Table 2. All the dihalomethanes, *t*-butanol, *n*-heptane and trifluorotoluene were purchased by Aldrich, and were distilled before use. CFC 113 (1,1,2-trichloro-trifluoroethane) and Galden® D80 (perfluoroheptane) were supplied by Ausimont and distilled before use. Potassium *t*-butoxide and KOH (pellets) were purchased by Aldrich and used as received.

2.2. Syntheses

Several synthetic procedures were employed, using different dihalomethanes and various OH/halide stoichiometric ratios. Some general examples follow.

2.3. Reaction of ZDOL 1000 (1) with dibromomethane (DBM)

ZDOL bis-potassium salt was prepared by dissolving 50 g of (1) in 150 ml of anhydrous *t*-butanol containing an excess of *t*-BuOK (15.6 g). This mixture was then added dropwise over 4 h in an inert atmosphere at 82°C to 71 ml of DBM (Br/OH equivalent ratio=10). The reaction mixture was stirred for 1 h, cooled to room temperature and washed several times with water. The organic layer was dissolved in Galden® D80, dried with sodium sulfate, and the solvent and the excess of dibromomethane were distilled off. The product (47 g) was obtained as a dark-yellow oil (conversion by ^{19}F-NMR=100%).

2.4. Reaction of ZDOL 1000 (1) with bromochloromethane (BCM)

ZDOL potassium salt was prepared by dissolving 10 g of (1) in 45 ml of anhydrous *t*-butanol containing excess of *t*-BuOK (2.4 g). The mixture was added dropwise over 3 h in an inert atmosphere at 76°C to 13.15 ml of BCM (X/OH equivalent ratio=5). After 2 h from the addition, the etherification of (1) was quantitative by NMR. The product was recovered as described in the previous synthesis.

2.5. Reaction of ZDOL 1000 (1) with dichloromethane (DCM)

DCM (200 ml), 5.0 g of (1) and finely grounded KOH (3.3 g) were charged in a reaction flask and stirred under nitrogen at 40°C for 16 h. Then, the mixture was filtered and the solid was poured in acid water and Galden® D80. The organic layer was dried with sodium sulfate, filtered and

Table 2
General characteristics of ZDOL base samples

Mn (NMR)	*p*/*q* (NMR)	Functionality	Mw/Mn (GPC)	Density (g/ml) 20°C	T_g (°C)
1000±100	0.8±0.1	>1.98	1.1	1.78	−101/−105
2000±100	1.0±0.1	>1.96	1.6	1.81	−115/−118

evaporated under vacuum. The product (4 g) was obtained as yellow viscous liquid.

2.6. Reaction of ZDOL 2000 (2) with bromochloromethane (BCM)

ZDOL potassium salt was prepared by dissolving 20 g of (2) in 20 ml of anhydrous *t*-butanol containing an excess of *t*-BuOK (2.4 g). The mixture was then added dropwise over 6 h in an inert atmosphere at 73°C to 13 ml of BCM (X/OH equivalent ratio=10) dissolved in 40 ml of trifluorotoluene. After 9 h the pH of the reaction mixture was neutral, but ^{19}F-NMR showed still 10% of ZDOL ends uncreated. A further amount of *t*-BuOK (20% excess) was added. After 6 h from the addition the conversion of (2) was quantitative. The mixture was washed three times with water, the organic layer was dried with sodium sulfate, filtered and evaporated under vacuum. The product was recovered as yellow viscous liquid.

2.7. Characterization

1. *NMR Spectroscopy*: Conversion of ZDOL in all the etherification reactions was determined [7] by ^{19}F-NMR spectroscopy checking the shift of $–CF_2CH_2OH$ signals (-81.3 and -83.3 ppm) to the $–CF_2CH_2OR–$ ones (about -79 and -81 ppm). ^{19}F-NMR was carried out on neat samples using $CFCl_3$ as internal standard with a VARIAN XL 200 instrument. ^{1}H-NMR was carried in CFC113/acetone d6 azeotropic mixture solution using TMS as internal standard with VARIAN Unity 300 instrument. Proton decoupled ^{13}C-NMR spectra were obtained on neat samples after an overnight acquisition with the same instrument. Heteronuclear shift correlation 2D NMR spectroscopy was carried out according to the high sensitivity HMQC method [14].
2. The overall bromine content in the polymer was measured by Ionic Chromatography (Dionex 2000 SP) after burning the sample in a Parr bomb according to an internal procedure.
3. Gel Permeation Chromatography (GPC) was carried out with a Waters Model 5900 instrument equipped with a set of a "Ultrastyragel" columns using *m*-hexafluoroxylene at 50°C as solvent (elution rate 1 ml/min).
4. Solubility fractionation was carried out using CFC 113 as solvent (5% w/v) and using *n*-heptane as non-solvent [15].
5. Vapor Pressure Osmometry (VPO) was carried out by a Knauer Vapor Pressure Osmometer at 25°C using CFC 113 as solvent, and biphenyl as standard for the calibration.
6. Differential Scanning Calorimetry was performed using a PERKIN ELMER DSC 2 instrument indium and *n*-hexane calibrated after runs from 50°C to -160°C at 10°C/min.

3. Results and discussion

The nucleophilic displacement reaction between ZDOL and α-ω dibromoalkanes was recently described [2]. The general structure of the reaction product, obtained using a strong excess of dibromo alkanes, can be schematized as

$$Br-(CH_2)_n–OCH_2R_F-CH_2O(CH_2)_n–Br, \qquad n > 6,$$

where R_F indicates the perfluorinated molecular body, namely $–CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2$.

In the present work, we studied the reaction between ZDOL (Mn=1000–2000) and dihalomethanes, especially CH_2Br_2, under the same experimental conditions. In principle, this polyreaction could produce linear, acetal extended copolymers of the type (2), as well as lower molecular weight oligomers bearing bromide (chloride) reactive end groups, but it could also undergo cyclization as reported for hydrogenated polyethers [16–20]. The effect of the stoichiometric ratio between the reactants was therefore explored using ZDOL samples with Mn about 1000, as shown in Table 3. The conversion of the etherification reaction was controlled by ^{19}F-NMR (see Section 2) and resulted always nearly quantitative. The GPC chromatograms of the raw reaction products are shown in Fig. 1(a). Even if a certain effect of the stoichiometric ratio was observed, a clean bimodal molecular weight distribution (MWD) was always present, even using a very small excess of dihalomethane. The peak retention volume of the lower molecular weight chromatographic band was constant (25.4 min) for the different runs, but significantly lower than that of the ZDOL precursor (27.2 min) under the same elution conditions. A bimodal MWD product was obtained also by reaction of ZDOL 2000 with a large excess of dibromomethane (Fig. 1(b)), using slightly different experimental conditions, as explained in Section 2. However, higher molecular weights (much lower retention times) were obtained in this latter case.

Fractions corresponding to the two GPC chromatographic peaks were separated efficiently by solvent fractionation (see Section 2), and furtherly characterized at GPC, VPO and NMR. Alternatively, the lower molecular weight component could be separated effectively by vacuum distillation.

Table 3
Reactions between ZDOL 1000 and dibromomethane

Run	Br/OH (molar)	ZDOL concentration (%w/w)	Fraction r_t>25 min (GPC)
1	1.1	31.2	48%
2	2	27.9	49%
3	5	16.8	45%
4	7	18.6	50%
5	10	17.8	60%

r_t=Retention time.

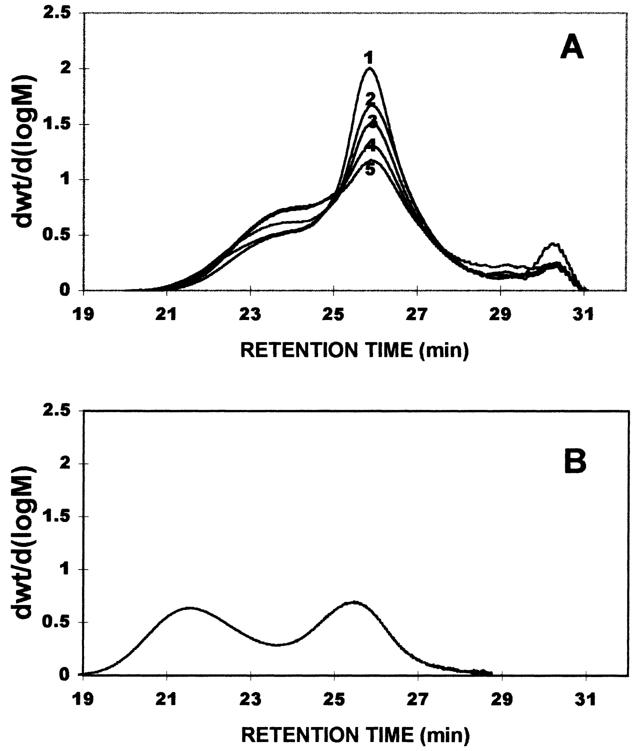


Fig. 1. GPC chromatograms of the reaction products from ZDOL 1000 (a) and ZDOL 2000 (b).

The 2D-(^{1}H–^{13}C-NMR spectrum of the lowest MW fraction having GPC retention time 25.2 min is shown in Fig. 2. It corresponds to the higher retention time band obtained by etherification of a ZDOL sample with Mn=1060. The signals correlated are +97 ppm (^{13}C) with +4.9 ppm (^{1}H), corresponding [9] to the acetalic O–CH_2–O, and +68 ppm (^{13}C) with +3.95 ppm (^{1}H) for the $CF_2\underline{C}H_2O$-groups, indicating a possible formation of acetal structure. In fact, the formation of bromine-terminated oligomers could be ruled out since Br was not detected (see Section 2). The number average molecular weight of this fraction was measured by VPO. The Mn of the distilled fraction was practically the same of the ZDOl precursor (1035 vs 1060), in spite of the very different GPC results. Finally, Fig. 3 shows the comparison between the ^{19}F-NMR spectra of the etherified product in comparison with its ZDOL precursor. The quantitative disappearance of signals related to the $-C\underline{F}_2CH_2OH$ end groups (−81 and −83 ppm) and the presence of a couple of signals at −78.5 and −80.5 ppm ($-C\underline{F}_2CH_2OCH_2O-$ groups) indicate the formation of an "infinite molecular weight" acetal polymer. All these data lead to conclude that the cyclic perfluoropolyether monoacetal is the main product of the reaction between ZDOL and dihalomethane.

On the other hand, the compounds having lower GPC retention times resulted predominantly linear PFPE-acetal polymers of type (2), as recently reported through a different synthetic route [9,10]. In fact, the ^{1}H-NMR spectra of the separated higher molecular weight fractions are characterized by peaks at +3.95 ppm (CH_2CH_2O) and +4.85 ppm (OCH_2X), with a ratio between the corresponding integrated intensities always close to 2. The proton decoupled ^{13}C-NMR spectra show the presence of the diagnostic singlet (therefore, not coupled with fluorine) at +97.2 ppm, therefore, already attributed [9] to the acetal carbon $-CF_2CH_2O\underline{C}H_2OCH_2CF_2-$. The ^{19}F-NMR analysis showed the presence of residual $-C\underline{F}_2CH_2OH$ ends (signals at −81.3 and −83.3 ppm), from which the number average molecular weight Mn of the polyacetal could be estimated [9]. Mn measured by NMR resulted however always somewhat higher than that calculated by GPC (20–30%). This fact could be attributed to the difficult separation of the polyacetal fractions free of the lower molecular weight cyclic monoacetal, even if we cannot exclude the formation of higher molecular weight cyclic oligoacetals.

The reaction pathway can be therefore summarized as reported in Scheme 1, with the formation of cyclic monoacetal and predominantly linear polyacetals.

It is worth noticing that the cyclic monoacetals were obtained in spite of the very concentrated reacting solutions, and that their abundance was poorly dependent on the stoichiometric ratio used. The cyclization tendency of non-fluorinated polyether diols is different. Actually, high yields of cyclic polyethers were reported [20] from polyethyleneglycol and dichloromethane but only working under heterophase conditions at high dilution. Under the same experimental conditions perfluorinated polyethers provide only low conversion to prevailingly linear polyacetalic structures. Also the polyethyleneglycol based cyclic oligomers are characterized by lower retention volumes (higher hydrodynamic volume) than those of the corresponding linear structures having the same molecular weight [19].

The relatively high yield in the cyclization of perfluorinated polyethers with the *t*-butoxide/*t*-butanol low dilution process seems quite independent of the stoichiometric ratio used and in no case a bromine (or chlorine) terminated oligomer was obtained. This may be explained on the grounds of the formation of an α-haloether intermediate $-CF_2CH_2OCH_2X$ (X=halide), which is much more reactive than the XCH_2X monomer. Since the bis-potassium salt of ZDOL is miscible with *t*-butanol, but the bis-alkylated compound precipitates due to its lower polarity, it can be argued also that the formation of the monoether PFPE intermediate changes the solubility characteristics of the oligomer promoting phase separation. This last point, as well as the flexibility of the fluoropolyether chain, may partially explain why cyclization is favored over the chain extension even in very concentrated solutions and why the stoichiometric ratio plays a very minor effect. Finally, Table 4 reports some preliminary characterizations of the novel cyclic perfluoropolyether monoacetals, highlighting the relationship between the glass transition (T_g) and the molecular weight. Although a quantitative interpretation of the data is at the present difficult, due to the limited number

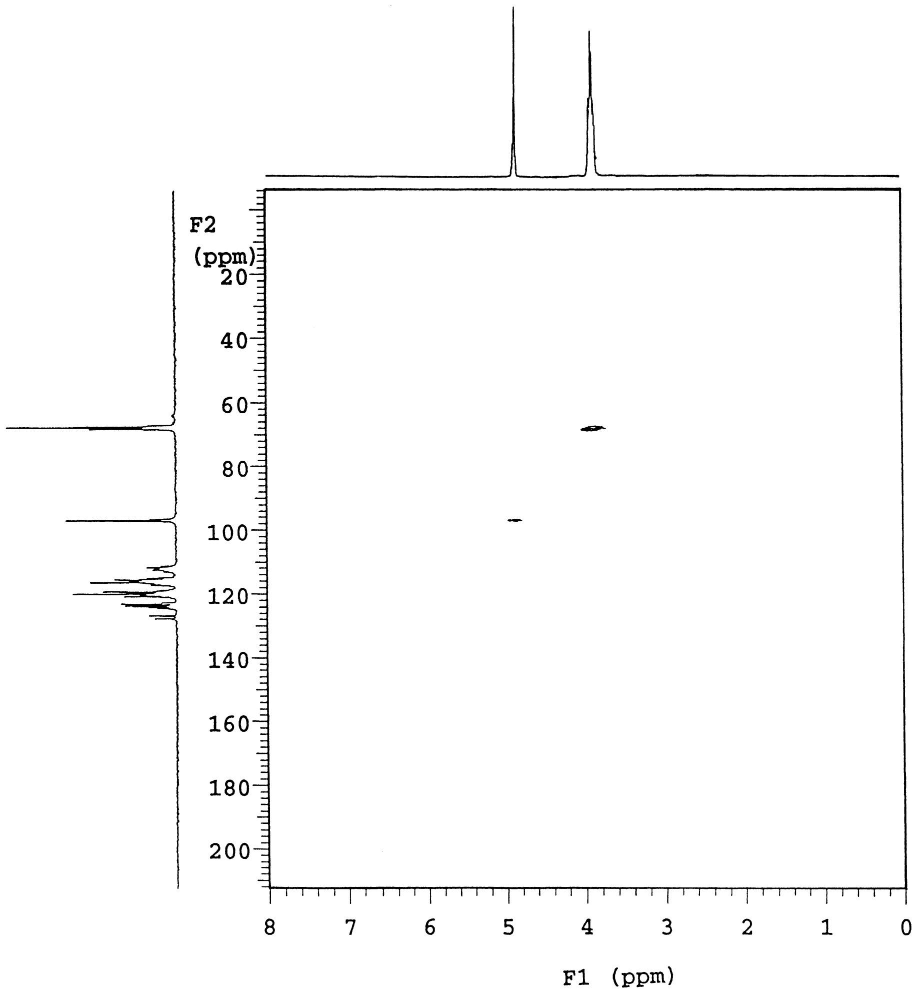
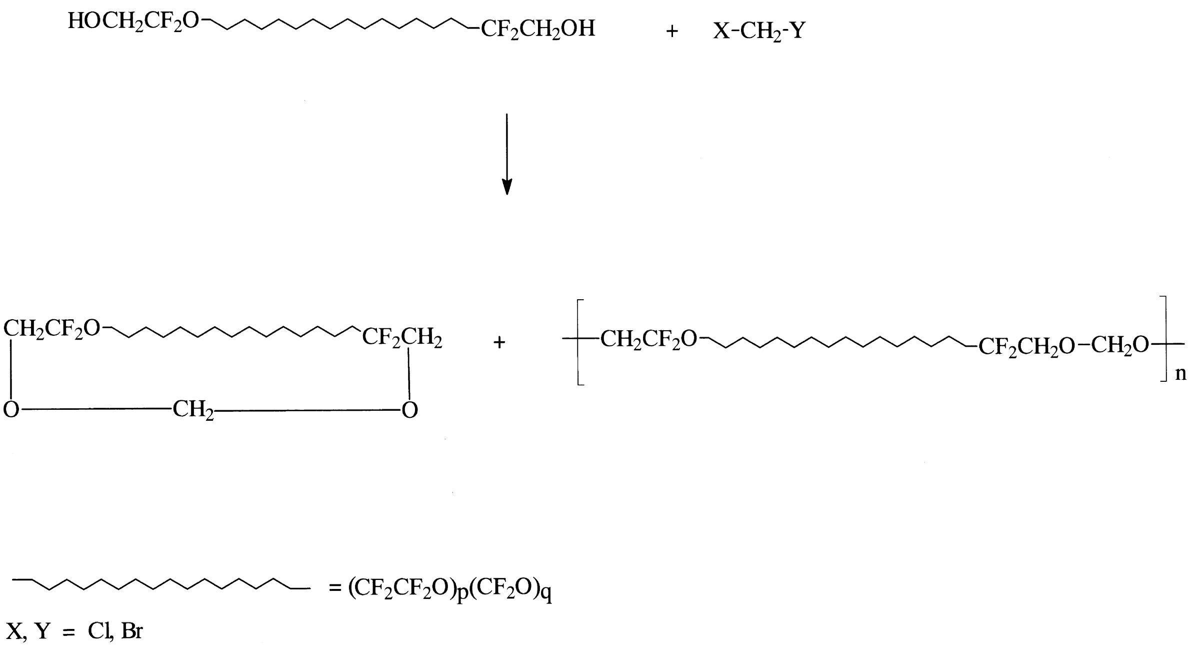


Fig. 2. 2D-(^{1}H–^{13}C)-NMR spectrum of fraction with r_t 25.2 min. (cyclic PFPE-monoacetal).



Scheme 1. Reaction between ZDOL and dihalomethanes.

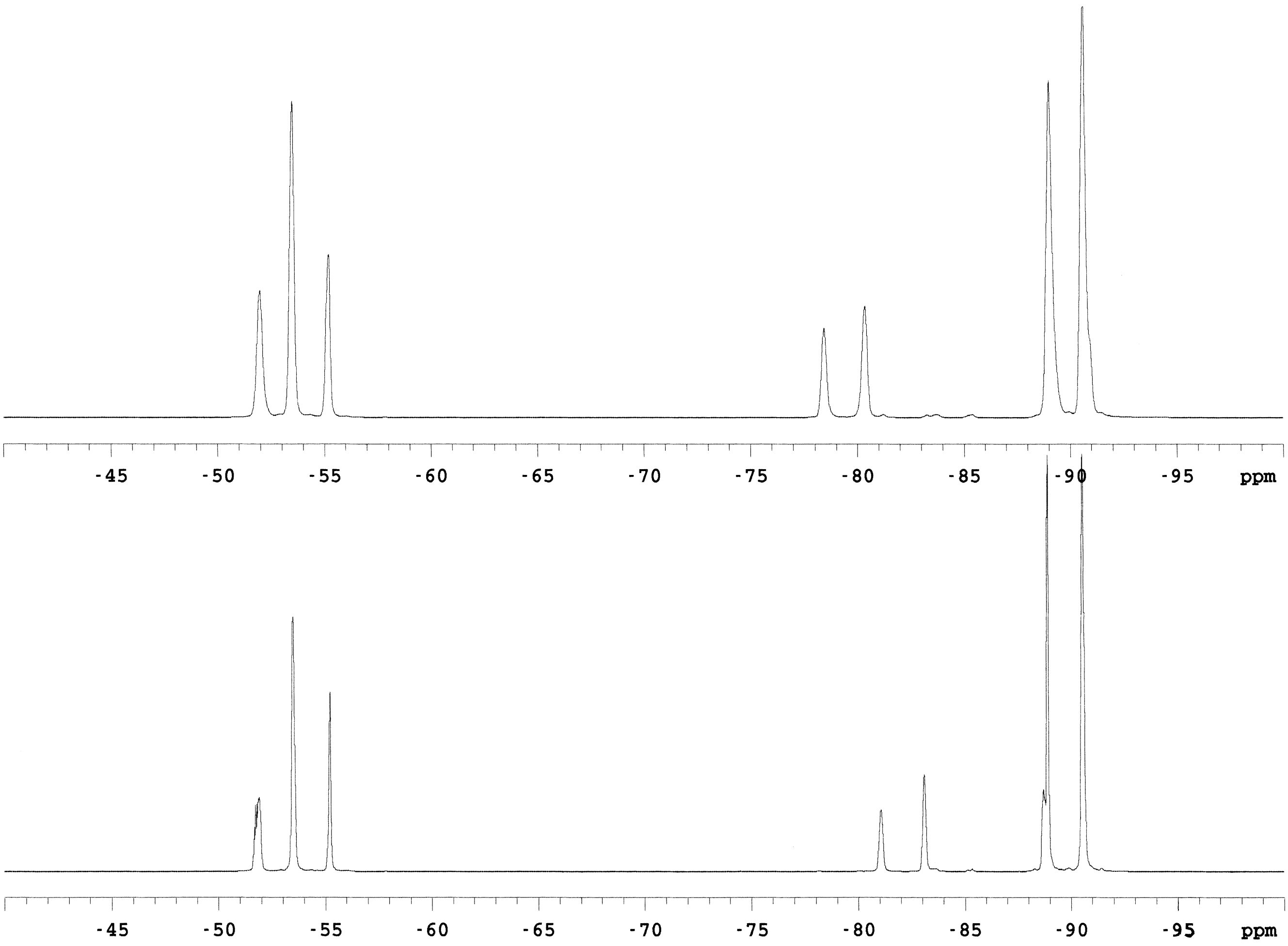


Fig. 3. ^{19}F-NMR spectra of ZDOL 1000 and its etherified product.

Table 4
Some physical properties of ZDOL cyclic oligoacetals

p/q NMR	Mn (VPO)	r_t (GPC) min	T_g (°C)
1	630	25.9	−100
0.8	1035	25.4	−106
1	1060	25.7	−103
1	1650	25.2	−108

r_t=Retention time.

of well separated fractions, it is evident that, in contrast to linear, perfluorinated Fomblin® Z polyethers [21], the T_g slightly decreases by increasing the molecular weight of the oligomer, like in the case of ZDOL. This trend is the same as described [22] for other cyclic oligomers and it can be justified by considering the loss of conformational degrees of freedom when the length of the cyclic chain diminishes.

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