*Macromolecules* **1995,** *28,* 7271–7275

# NMR of Perfluoropolyether Diols and Their Acetal Copolymers

**Stefano Turri* and Emma Barchiesi**

*Ausimont S.p.A., Centro Ricerche e Sviluppo CRS, Viale Lombardia, 20,*
*20021 Bollate, Milano, Italy*

**Marinella Levi**

*Dipartimento Chimica Industriale ed Ingegneria Chimica "G. Natta", Politecnico di Milano,*
*Piazza Leonardo da Vinci, 32, 20133 Milano, Italy*

*Received April 7, 1995; Revised Manuscript Received July 3, 1995*®

ABSTRACT: A $^{19}F$, $^{1}H$, and $^{13}C$ NMR structural study is presented for a selected sample of a perfluoropolyether macrodiol (ZDOL), as well as one of its copolymers with formaldehyde. From their $^{19}F$ spectra the average composition of perfluorooxymethylene and -oxyethylene units along the chain is clearly evaluated; the end group analysis allows the calculation of the number average molecular weight and functionality of samples of the macrodiol and, to a first approximation, those of the copolymer. The $^{1}H$ and $^{13}C$ NMR spectra are studied also in order to clarify the nature of the bridging units in the copolymer between perfluoropolyether segments; in particular the absence of oligo(oxymethylene) sequences $-(OCH_2)_n-$ is verified. A comparison is also made with the spectroscopic data of a corresponding low molecular weight compound, which was prepared by reaction of trifluoroethanol with paraformaldehyde. For that reference compound the heteronuclear shift correlation 2D NMR spectrum is also reported and discussed.

## Introduction

Perfluoropolyethers (PFPE) are interesting linear compounds, of various molecular weights, which are obtainable by photooxidative polymerization of perfluoroolefins. They are commercially known for their advanced applications as stable fluids in aggressive environments.[1] They can also be used as macromonomers when their end groups bear appropriate chemical functions.[2-4]

Their perfluoroether main chains are characterized by a very high flexibility, and therefore very low glass temperatures in corresponding polymers or macromer segmented copolymers.

Diolic fluoroether oligomers named Fomblin ZDOL (AUSIMONT S.p.A.) belong to this class of PFPE. They are substantially characterized by a perfluoropoly(oxyethylene-*co*-oxymethylene) chain end-capped by primary alcoholic end functions:

$$HOCH_2CF_2O(CF_2CF_2O)_p(CF_2O)_9CF_2CH_2OH \quad (I)$$

$$\text{(briefly } HOCH_2{-}Z{-}CH_2OH \text{ or ZDOL)}$$

In recent papers[5-9] several physico-chemical properties of fractions of ZDOL of different molecular weights have been reported, also compared with those of corresponding oligomer series with diversified pairs of end units. Syntheses of new fluorinated/nonfluorinated segmented copolymers using these diolic fluoroether macromonomers were realized; in particular, interesting acetal copolymers were obtained by reaction of ZDOL with formaldehyde.[10]

As a matter of fact, the reaction between diols and formaldehyde appears to be an interesting way to synthesize substantially high molecular weight fluoroether copolymers containing very short and flexible hydrogenated sequences. These copolymers can be seen as an interesting model very suitable for investigating structure–property relationships of perfluoropolyethers in the region of high molecular weights (not easily available by the photosynthesis process). For this, proper synthesis conditions are to be stated in line with the particular reactivity features of the rather acid hydroxyl end groups. The reaction of formaldehyde with negatively substituted alcohols (e.g. fluoroalcohols, as trifluoroethanol) is known to require a strong catalysis (e.g. the use of concentrated sulfuric acid).[11] Similar procedures were followed also in the polyreaction with fluorinated diols (typically 2,2,3,3,4,4-hexafluoropentanediol), leading however to low molecular weight products.[12,13] In the case of ZDOL, high molecular weights can be instead obtained.[10] In the resulting copolymers, the bridging units between the fluorinated Z segments may reasonably be expected to be linear dimethyleneoxymethylene, i.e. monoformal:

$$-Z{-}CH_2OH + CH_2O + HOCH_2{-}Z{-} \xrightarrow{-H_2O} -Z{-}CH_2OCH_2OCH_2{-}Z{-}$$

the reaction being carried out at temperatures above the estimated ceiling temperature of a possible polyautoaddition of the formaldehyde in the specific reaction system.

In the present work, special attention was paid to the refinement of NMR analyses of starting and final fluorinated products of the above reaction. In particular, a checking of the correctness of the expected monoformal structure of the bridging units appears to be of special interest, in that it determines the minimum chemical dissimilarity with the PFPE chain. For a comparison of spectroscopic data with those of the copolymer, the following low molecular weight reference compound (1,1,1,7,7,7-hexafluoro-3,5-dioxaheptane) was also prepared and used:

$$CF_3CH_2OCH_2OCH_2CF_3 \quad (II)$$

## Experimental Part

**Materials.** The fluoropolyether macromonomer was a selected Fomblin ZDOL sample (AUSIMONT), which, on the basis of this work, resulted as having $p/q = 1.05$, $M_n = 2060$,

---

® Abstract published in *Advance ACS Abstracts,* August 15, 1995.

0024-9297/95/2228-7271$09.00/0

and a hydroxyl functionality of 1.94. Trifluoroethanol and paraformaldehyde (both Aldrich) were used as received; Delifrene LS (1,1,2 trichlorotrifluoroethane, AUSIMONT) and diethyl ether were distilled before use.

The sample of perfluoropolyether–formaldehyde copolymer was prepared by a typical synthesis procedure[10] as follows. Paraformaldehyde (1 mol of $CH_2O$) was dissolved in 96% sulfuric acid (3 mol) at room temperature and ZDOL (1 mol) rapidly added under magnetic stirring. The viscosity of the mixture immediately rises, leading in a few minutes to the stopping of the magnetic bar. After 1 h the mixture was diluted with Delifrene (10 g of polymer/100 mL of solvent) and saturated with gaseous $NH_3$; the salt formed was filtered off. The resulting solution was washed with $H_2O_2$ 30% (10% v/v with respect to the organic phase) and two times with water (50% v/v) and then dried over $Na_2SO_4$. The solvent was finally removed under vacuum (initially 20 mmHg, then down to $10^{-2}$ mmHg) at 50 °C for 2 h, and the polymer separated as a viscous oil. About 9 g of acetal copolymer was recovered starting with 10 g of ZDOL.

A sample of 1,1,1,7,7,7-hexafluoro-3,5-dioxaheptane $CF_3CH_2OCH_2OCH_2CF_3$ (II), was also prepared by the reaction between trifluoroethanol and paraformaldehyde, carried out as described in the literature,[11] using 96% sulfuric acid. After 1 h, the crude reaction product (upper phase) was separated out, diluted with diethyl ether (50% v/v), and washed with an equivolumetric aqueous $NaHCO_3$ 5% solution (two times) and then with water up to neutral pH. The organic phase was dried over anhydrous $Na_2SO_4$ and the solvent carefully evaporated. The crude reaction product (yield 75%) was analyzed without further purification.

**FT-NMR.** Both ZDOL (I) and its acetal copolymer are relatively low viscosity liquids down to very low temperatures ($T_g$ below −100 °C).[6,10]

Solvents suitable for PFPE are practically some fluorinated or chlorofluorinated hydrocarbons. For partially hydrogenated PFPE copolymers, like the polyacetal here described, it is even more difficult to find a solvent or solvent mixture able to give a truly homogeneous solution. For these reasons it was preferred to record all the spectra on neat isotropic samples (at 30 °C for ZDOL and 50 °C for the higher viscosity copolymer). Accordingly, the reference compound (II) spectra were also registered without solvents.

A Varian XL 200 instrument was used for $^{19}F$ analysis and a Varian Unity 300 was used for $^1H$ and $^{13}C$ NMR. $^{19}F$ chemical shift values (ppm) were referred to those of $CFCl_3$ (trichlorofluoromethane), determined in separate experiments. Tetramethylsilane (TMS) was used as the internal standard (0.5% w/w) for the $^1H$ and $^{13}C$ chemical shifts. $^{19}F$ spectra were registered at 188.22 MHz (spectral width 25 kHz) with about 1000 scans, acquisition time 0.5 s, flip angle 12°, and pulse delay of 3 s. $^1H$ NMR spectra were registered after 500 scans at 300 MHz (spectral width 4 kHz) with acquisition time 4 s, flip angle 12°, and pulse delay 8 s. The proton-decoupled qualitative $^{13}C$ NMR spectra were obtained after a generally overnight acquisition at 75.5 MHz (spectral width 16 kHz) with acquisition time 1 s and pulse delay 2 s. The spectrometer was previously locked on acetone-$d_6$.

In addition to one-dimensional spectra heteronuclear shift correlation 2D NMR spectroscopy was also used in order to obtain information on correlation among $^1H$ and $^{13}C$ signals of the reference compound (II). The experiment was carried out according to the higher sensitivity Heteronuclear Multiple Quantum Coherence method (HMQC), based on the detection of the satellite peaks of protons coupled to $^{13}C$ nuclei.[14]

## NMR Results

The structure of ZDOL may conveniently be schematized as follows:

$$\alpha\text{-}(OCF_2CF_2)_p(OCF_2)_p\text{-}\omega \qquad \text{(III)}$$

The $p$ tetrafluorooxyethylene ($C_2$) sequences (or units) and the $q$ difluorooxymethylene ($C_1$) sequences are randomly distributed along the chain. In practice, very small amounts of hexafluorooxytrimethylene ($C_3$) and octafluorooxytetramethylene ($C_4$) units are also present. The end units are $\alpha = -CF_2CH_2OH$ and $\omega = -OCF_2CH_2OH$ or, in a minor amount, $-OCF_3$ (taking into account the particular synthesis process, macromolecules with both $-OCF_3$ end groups can be considered absent).

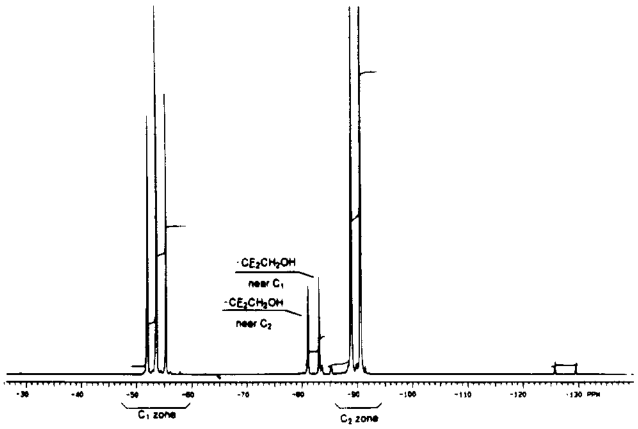

**Figure 1.** $^{19}F$ NMR spectrum of the ZDOL sample.

**Table 1. Assignments (ppm) and Relative Normalized[a] Areas of $^{19}F$ Signals of ZDOL and Its Acetal Copolymer**

| assgnt | chemical shift | area (ZDOL) | area (copolymer) |
|---|---|---|---|
| $-OCF_2CF_2OCF_2OCF_2CF_2O-$ | −52.0/−52.1 | 95.4 | 95.4 |
| $-OCF_2CF_2OC\overline{F}_2OCF_2O-$ | −53.6/−53.7 | | |
| $-OCF_2OC\underline{F}_2O\overline{C}F_2O-$ | −55.3/−55.4 | | |
| $-OCF_2CF_2OC\underline{F}_2CF_2OCF_2-$ | −89.0/−89.1 | 100 | 100 |
| $-OCF_2OC\underline{F}_2C\overline{F}_2OCF_2-$ | −90.6/−90.7 | | |
| $-OCF_2CF_2\overline{O}CF_2CF_2CF_2-$ | −83.8 | | |
| $-OCF_2O\overline{C}F_2CF_2CF_2-$ | −85.4 | | |
| $-OCF_2CF_2\overline{C}F_2CF_2O-$ | −126.0 | 0.5 | 0.5 |
| $-OCF_2C\overline{F}_2C\overline{F}_2O-$ | −129.7 | 0.7 | 0.7 |
| $-OCF_2C\overline{F}_2OCF_2CH_2OH$ | −81.3 | 18.8 | 0.8 |
| $-OCF_2OC\underline{F}_2C\overline{H}_2OH$ | −83.3 | | |
| $-OCF_2CF_2OC\underline{F}_2CH_2OR$ | −78.5 | 0 | 18.0 |
| $-OCF_2OC\underline{F}_2C\overline{H}_2OR$ | −80.5 | | |
| $-OCF_2CF_2OC\underline{F}_3$ | −56.3 | 0.5 | 0.5 |
| $-OCF_2OC\underline{F}_3$ | −58.0 | | |

[a] Normalization involves the registered integrals to be divided by the number of magnetically equivalent F atoms; i.e the $C_1$ integral is quoted $^1/_2$, the $C_2$ $^1/_4$, the $-OCF_3$ $^1/_3$, and so on. To the most intense signal (the $C_2$ in the specific instance) is attributed the relative value 100.

The $^1H$ NMR spectrum is characterized by a multiplet at +3.92 ppm, which can be assigned to the $-CH_2-$ group (two overlapped triplets from the statistical presence of $C_2$ and $C_1$ units in $\beta$ position with respect to methylene). The hydroxyl proton resonates at +4.99 ppm as a relatively sharp singlet.

Previous studies[15] on $^{19}F$ spectroscopy of low molecular weight perfluoroether model compounds give with high precision the effect of oxygen atoms linked with an ether type bond to $-CF_2-$ and $-CF_2CF_2-$ groups. This effect consists of a systematic decrease of the $^{19}F$ NMR chemical shift with respect to the pure perfluoroalkylene structure. On this basis, an exhaustive analysis of the Z perfluoropolyether chain was previously reported.[16] Similarly, the spectrum of ZDOL shown in Figure 1 is dominated by three main chemical shift zones: from −51 to −56 ppm (the $C_1$ zone), from −81 to −84 ppm (the functional end groups zone), and from −88 to −92 ppm (the $C_2$ zone). Table 1 summarizes the $^{19}F$ NMR assignments of signals for ZDOL. For the purpose of this work, it is particularly significant to stress the presence of two signals at −81.3 and −83.3

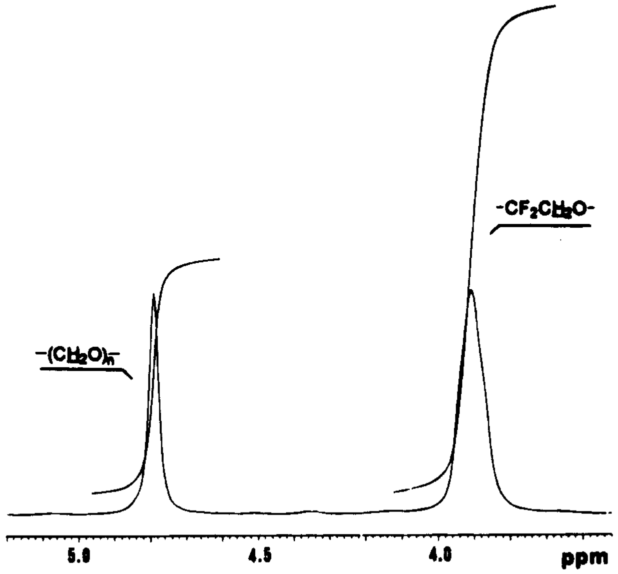

**Figure 2.** $^1$H NMR spectrum of the ZDOL–formaldehyde copolymer.

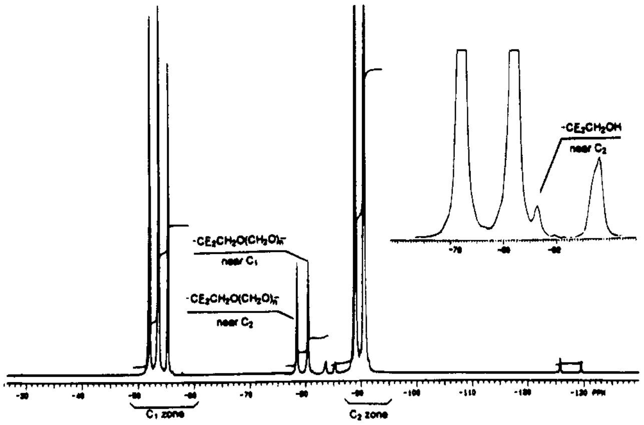

**Figure 3.** $^{19}$F NMR spectrum of the ZDOL–formaldehyde copolymer.

ppm, corresponding to the $-CF_2CH_2OH$ ends bound to a $C_2$ and a $C_1$ unit, respectively.

The $^{13}$C NMR proton-decoupled spectrum of the ZDOL sample is characterized by a triplet at +64.1 ppm ($J_{CF}$ = 33 Hz), which can be assigned to the $-CH_2OH$ chain ends, while the signals of $-CF_2-$ belonging to the internal units and the $-CF_3$ chain ends are located between +110 and +130 ppm.

Figures 2–4 show the spectra of the ZDOL–formaldehyde copolymer. The $^1$H-NMR spectrum shown in Figure 2 consists of a broad signal at +3.90 ppm and of a singlet at +4.79 ppm. The former signal may be attributed to the $-CF_2CH_2-$ methylene; the broadening due to the relatively high viscosity (low spin–spin relaxation times) of the polymer masks the fine coupling between fluorine and hydrogen. The singlet at +4.79 ppm may be assigned to the oxymethylene sequences $(-CH_2O-)_n$.

The $^{19}$F NMR spectrum reported in Figure 3 is very similar to that of the ZDOL precursor, except for two new signals appearing at −78.5 ppm ($-CF_2CH_2OR$ near to a $C_2$ unit, where R = $(CH_2O-)_n$) and at −80.5 ppm ($-CF_2CH_2OR$ near to a $C_1$ unit), respectively. One of the signals of unreacted $-CF_2CH_2OH$ end groups, at −81.3 ppm, can also be recognized and integrated (see expansion); the other signal, at −83.3 ppm (quite overlapped by the $C_3$ signal at −83.8 ppm), can be estimated from the former by knowing the *p*/*q* ratio. Table 1 reports all the $^{19}$F assignments of ZDOL and the copolymer.

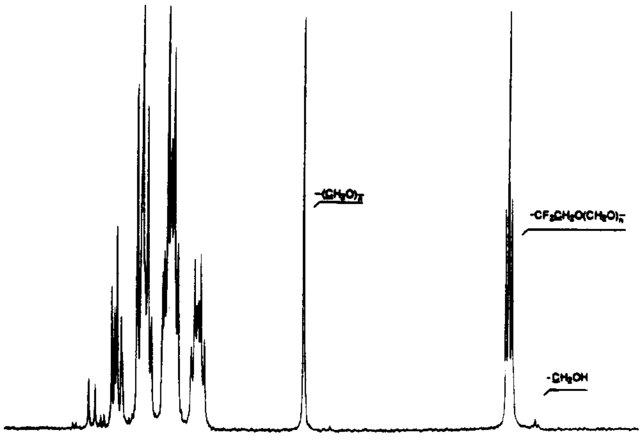

**Figure 4.** $^{13}$C NMR spectrum of the ZDOL–formaldehyde copolymer.

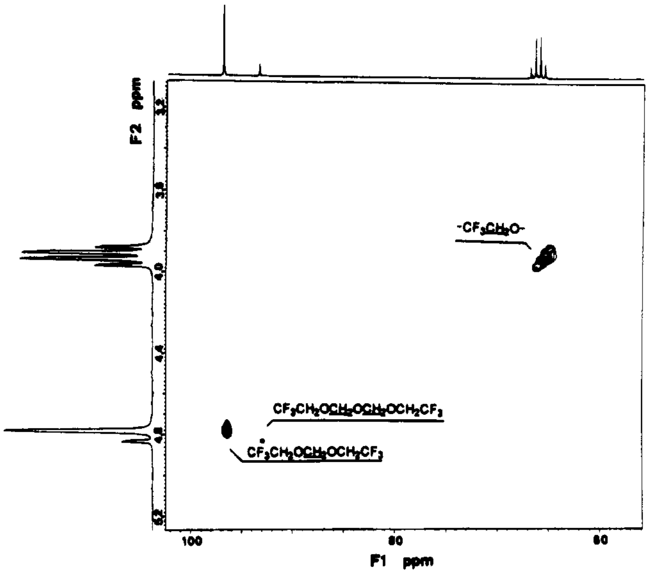

**Figure 5.** 2D $^{13}$C–$^1$H NMR spectrum of the reference compound.

Figure 4 shows the $^{13}$C NMR proton-decoupled spectrum of the copolymer, which is characterized by the rather complex patterns from +110 to +130 ppm, corresponding to the carbon atoms with fluorine couplings. The triplet at +64.3 ppm (the $-CF_2CH_2OH$ chain ends) has a very weak intensity and is accompanied by another triplet ($J_{CF}$ = 33 Hz) at +68.0 ppm, which may be attributed to the etherified $-CF_2CH_2OR-$ methylene groups. Accordingly, the main signal at +97.2 ppm, devoid of fluorine coupling, may be assigned to the oxymethylene species $(-CH_2O-)_n$.

Figure 5 finally reports the 2D $^{13}$C–$^1$H spectrum of the sample of the reference compound (II), having the $^1$H spectrum as the ordinate and the $^{13}$C one as the abscissa.

The former shows a quartet at +3.92 ppm (intensity = 120, $J_{FH}$ = 8.6 Hz), assigned to the $CF_3CH_2O-$ group, and two sharp singlets at +4.78 (intensity = 55) and +4.83 ppm (intensity = 9) in the range of the $(-CH_2O-)_n$ species.

The $^{13}C$ NMR proton-decoupled spectrum is characterized by two main singlets at +96.9 and +93.3 ppm (the oxymethylene range) and by a quartet centered at +66.1 ppm ($J_{CF}$ = 37 Hz, $-CH_2-$ bound to the $-CF_3$). The main $^1H$ oxymethylene singlet at +4.78 ppm is overlapped to the $^{13}C$ signal +96.9 ppm, whereas the lower intensity $^1H$ signal at +4.83 ppm appears closely correlated to the other $^{13}C$ signal located at +93.3 ppm.

The $CF_3-$ group would appear as a quartet centered at +125.5 ppm with $J_{CF}$ = 280 Hz (not indicated in the figure).

## Discussion

The above described NMR results and the corresponding signal assignments can be now properly discussed for an exhaustive structural analysis of the ZDOL−formaldehyde copolymer. Then, once the structure is defined, the spectral data are going to be used in order to obtain the macromolecular parameters (composition, functionality, molecular weight) of both ZDOL and its acetal copolymer.

For the ZDOL−formaldehyde copolymer, in order to take into account the mentioned possible presence of oligoacetal bridging groups in its main chain, reference can be made to the following general expression of its constitution ($Rf = (OCF_2CF_2)_p(OCF_2)_q$)

$$\alpha\text{-}Rf-[OCF_2CH_2O(CH_2O)_nCH_2CF_2-Rf-]_m-\omega \quad \text{(IV)}$$

where α and ω have the meanings given in formula III. Reasonably, the presence of possible poorly stable residual hemiacetal ends $-CF_2CH_2OCH_2OH$ (which are formed in the first step of the base reaction of ZDOL with formaldehyde) in the considered sample should in fact have been eliminated, with the chosen synthesis procedure, by the oxidizing treatment of the product with $H_2O_2$.

Of course, the determination of *n* in IV, that is the average number of oxymethylene units in the hydrogenated bridging groups, can properly be done by means of $^1H$ and $^{13}C$ NMR spectroscopy of the copolymer.

The $^1H$ NMR spectrum (Figure 2) shows the $-CF_2CH_2O-$ methylene signal with intensity 120 and the oxymethylene one with intensity 58. The corresponding integrated areas ratio is very close to the theoretical ratio 2, which would represent the structure with only the monoformal group. The $^{13}C$ NMR spectrum (Figure 4) shows the presence of the proton-decoupled singlet at +97.2 ppm, i.e. the $-OCH_2O-$ carbon resonance.

A finer structural analysis may also be made by comparison with spectra of the reference acetal of trifluoroethanol, as well as by taking into account data on other polyacetal compounds reported in the literature.

The expected product of the reaction between trifluoroethanol and formaldehyde, formally 1,1,1,7,7,7-hexafluoro-3,5-dioxaheptane, as expressed by formula II, may be seen as representing a simple case of fluorinated alcohol acetal having low molecular weight and viscosity, able to provide information about chemical shifts of corresponding oxymethylene sequences devoid of the signal broadening typical of NMR spectra of high molecular weight compounds.

The correlations between the $^1H$ and $^{13}C$ signals are shown in Figure 5. The comparison with the chemical shifts of different oxymethylene sequences (as monoformal, diformal, or triformal ether links) in fully hydrogenated acetal copolymers like 1,3,5-trioxane/1,3-dioxolane copolymers[16,17] allows us to conclude that the crude product of reaction of the trifluoroethanol with formaldehyde mainly consists of monoformal ether and diformal ether in relative abundance of about 12 to 1. The assignments are summarized in Table 2.

**Table 2. Assignments (ppm) of $^{13}C$ and $^1H$ Acetal Signals Derived from the 2D Heterocorrelated Spectrum of the Reference Compound**

| assngt | $^{13}C$ | $^1H$ |
|---|---|---|
| $CF_3CH_2O\underline{CH}_2OCH_2CF_3$ | +96.9 | +4.78 |
| $CF_3CH_2O\underline{CH}_2O\underline{CH}_2OCH_2CF_3$ | +93.3 | +4.83 |

Similar indications may be found from other literature data on $^{13}C$ NMR spectroscopy of different polyacetal copolymers. In the case of polysulfide prepolymers,[19] in which the first synthesis step consisted of the reaction of chloroethanol and paraformaldehyde with acid catalysis, the $^{13}C$ analysis of the product showed the presence of diformal ethers as main byproducts; the assignments were +95.5 (monoformal) and +92.0 ppm (diformal). Also $^{13}C$ NMR studies on 1,3,5-trioxane/1,3-dioxolane copolymers[20] report a difference in chemical shift of about 3.5 ppm between $-O\underline{C}H_2O-$ and $-O\underline{C}H_2O\underline{C}H_2O-$ sequences and of about 3.0 ppm between $-O\underline{C}H_2O-$ and $-O\underline{C}H_2OCH_2O\underline{C}H_2O-$. These shifts are in quite satisfactory agreement with that found for the sample of our reference compound.

On the basis of all the above considerations, a definite interpretation of the spectrum of the ZDOL−formaldehyde copolymer is now easier. In particular, the $^{13}C$ NMR signal of the copolymer at +97.2 ppm is not far from the chemical shift value of the monoformal ether of the reference compound, and there is no other detectable singlet at significantly higher fields. Thus, the structure of the copolymer can be considered effectively alternated; that is the value of n in (IV) is 1.

The second level of this discussion concerns the application of NMR spectroscopic data in the determination of the numerical average quantities of macromolecular interest, such as composition, functionality and molecular weight. In the specific instance, $^{19}F$ NMR appears to be particularly helpful because it shows a good resolution of signals related to internal and end units that are easy to integrate correctly: as known, $^{19}F$ spectroscopy combines a high sensitivity to the resonance, common to $^1H$ NMR, with a wider chemical shift range (about 25 kHz) which allows a finer analysis of the polymer structure. Moreover, quantitative integration of $^{19}F$ signals is easier than in the case of $^{13}C$ spectroscopy. On this basis, it is possible to calculate composition, hydroxyl functionality *F*, and number average molecular weight Mn.

In the case of ZDOL, with $U_1$, $U_2$, $U_3$, and $U_4$ defined as the normalized integrated areas of signals corresponding to $C_1$, $C_2$, $C_3$, and $C_4$ internal units and $E_r$ and $E_i$ as those of "reactive" ($-CF_2CH_2OH$ and $-OCF_2CH_2OH$) and "inert" ($-OCF_3$) end units, the main compositive parameter may be easily calculated as

$$p/q = U_2/U_1 \quad (1)$$

The hydroxyl functionality *F*, that is the number of functional (reactive) ends per molecule, may be expressed as

$$F = 2E_r/(E_r + E_i) = 2f_b + (1 - f_b) \quad (2)$$

where $f_b = (E_r - E_i)/(E_r + E_i)$ is the fraction of bifunctional molecules and $(1 - f_b)$ the fraction of monofunctional ones.

The number average degree of polymerization $x_n$ is given by

$$x_n = \frac{\sum U_j}{(E_r + E_i)/2} + 2 \qquad j = 1-4 \tag{3}$$

and, accordingly, the number average molecular weight can be calculated as

$$M_n = 2\frac{\sum U_j M_{U_j}}{(E_r + E_i)} + 2f_b M_b + (1 - f_b)M_m \qquad j = 1-4 \tag{4}$$

where $M_{U_j}$ are the formula weights of the various $C_j$ internal units and $M_b$ and $M_m$ are the *average* formula weights of the bifunctional and monofunctional end segments; in practice

$$M_b = \text{formula weight of } \frac{(HOCH_2CF_2-) + (-OCF_2CH_2OH)}{2} = 89$$

$$M_m = \text{formula weight of } \frac{(HOCH_2CF_2-) + (-OCF_3)}{2} = 83$$

Equations 1, 2 and 4 applied to the ZDOL base sample data give the following values, which characterize the starting macromonomer:

$$p/q = 1.05 \qquad f = 1.94 \qquad M_n = 2060$$

For the ZDOL–formaldehyde acetal copolymer , the application of eqs 1 and 2 gives $p/q = 1.05$ and $F = 1.23$. The $M_n$ value may be estimated by reference to the compositional formula (IV) and with a proper choice of signals representative of the $m$ repeat units. Thus, as two $-CF_2CH_2OR-$ sequences (whose normalized integrated areas $U_e$ are reported in Table 1) occur for each repeat unit, the $m$ value has to be calculated as

$$m = \frac{U_e/2}{(E_r + E_i)/2} = 13.6 \tag{5}$$

This $m$ value would correspond to a $M_n$ about 30 000, which however should be subjected to an error surely higher than in the case of ZDOL, in that the intensity of the residual end groups ($E_r$ and $E_i$) is much lower. This aspect is, anyhow, common to any other analytical method based on end groups analysis.

About the accuracy and precision in the $M_n$ determination some further considerations may be made.

Experimental conditions were here set up in order to avoid large systematic errors and provide high accuracy: a great number of FT accumulations (see Experimental Part) to maximize the signal-to-noise ratio, and a pulse delay sufficient to allow the complete longitudinal relaxation of the nuclei (with consequent peak integrals representative of the whole resonating atoms). However, an exact quantification of the accuracy is hard to reach without the parallel determination of molecular weight values. For instance, a comparison with another analytical technique was reported in a previous work[8] where the molecular weight of a series of ZDOL fractions was determined by vapor pressure osmometry and NMR, using a method similar to the present one: in fact, the former method showed systematically lower values (5–10%). The accuracy of the NMR method is clearly lower in the case of the acetal copolymer. For this, the intensity of the residual end group signals is very weak and a partial overlapping among the peaks is also present (i.e. the $C_1$ bound $-OCF_2CH_2OH$ signal at −81.3 ppm with the $C_3$ signal at −83.8 ppm). A further source of uncertainty could be represented by the possible presence of cyclics, typical of this class of polymerization, for which NMR would see as infinite the molecular weight, leading to overestimated $M_n$ values.

About the precision, our method revealed a high reproducibility: five independent measurements on the same ZDOL sample gave an $M_n$ value of 2060 ± 35 (mean standard deviation). In light of these observations, a 5% precision may be reasonably assumed in our case (on the order of that estimated for molecular weight determinations of other oligomers[21,22]).

A final remark is about the results of the spectroscopic compositional analysis. With regard to acetal copolymers of ZDOL, NMR proved the largely predominant structure to be that containing the only monoformal link. Despite the formation of a rigorously alternated copolymer by reaction of ZDOL and paraformaldehyde, the "reference" product (II) of the very similar reaction between trifluoroethanol and paraformaldehyde resulted in a mixture surely containing relevant amounts of higher oxymethylene sequences. Such an unexpected behavior has to be clarified by a deeper investigation of the parameters affecting the presence of oligo(oxymethylene) segments.

**Acknowledgment.** The authors would like to thank Prof. F. Danusso for helpful discussions and assistance in the preparation of this paper.

## References and Notes

(1) Sianesi, D.; Zamboni, V.; Fontanelli, R.; Binaghi, M. *Wear* **1971,** *18*, 85.
(2) Caporiccio, G.; Strepparola, E.; Bargigia, G.; Novaira, G.; Peveri, G. *Makromol. Chem.* **1983** *184*, 935.
(3) Strepparola, E.; Caporiccio, G.; Monza, E. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 601.
(4) Edelman, P. G.; Castner, D. G.; Ratner, B. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 314.
(5) Danusso, F.; Levi, M.; Gianotti, G.; Turri, S. *Polymer* **1993**, *34*, 3687.
(6) Danusso, F.; Levi, M.; Gianotti, G.; Turri, S. *Eur. Polym. J.* **1994,** *30*, 647.
(7) Danusso, F.; Levi, M.; Gianotti, G.; Turri, S. *Eur. Polym. J.* **1994,** *30*, 1449.
(8) Gianotti, G.; Levi, M.; Turri, S. *J. Appl. Polym. Sci.* **1994**, *51* , 973.
(9) Levi, M.; Turri, S. *J. Appl. Polym. Sci.* **1995**, *55*, 989.
(10) Ausimont S.p.A. EP 0 587 997 A1, 1993, and EP 0 621 296 A2, 1994.
(11) Shipp, K. G.; Hill, M. E. *J. Org. Chem.* **1966**, *31*, 853.
(12) Trischler, F. D.; Hollander, J. *J. Polym. Sci., Polym. Chem. Ed.* **1967,** *5*, 2343.
(13) Adolph, H. G.; Goldwasser, J. M.; Koppes, W. M. *J. Polym. Sci., Polym. Chem. Ed.* **1987,** *925*, 805.
(14) Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986,** *108*, 2093.
(15) Ciampelli, F.; Tacchi Venturi, M.; Sianesi, D. *Org. Magn. Reson.* **1969**, *1*, 281.
(16) Marchionni, G.; Spataro, F.; De Pasquale, R. J. *J. Fluorine Chem.* **1990**, *49*, 217
(17) Fleischer, D.; Schultz, R. C. *Makromol. Chem.* **1972,** *162*, 103.
(18) Ogawa, T.; Ishitobi, W.; Jinta, K. *J. Appl. Polym. Sci.* **1989,** *38*, 87.
(19) Mazurek, W.; Moritz, A. G. *Macromolecules* **1991,** *24*, 3261.
(20) Fleischer, D.; Schultz, R. C. *Makromol. Chem.* **1975,** *176*, 677.
(21) Yeager, F. W.; Becker, J. W. *Anal. Chem.* **1977,** *49*, 722.
(22) Hammerich, A. D.; Willeboordse, F. G. *Anal. Chem.* **1973,** *45*, 1696.

MA950479T