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On the unperturbed dimensions of perfluoropoly-(oxymethylene-co-oxyethylene)-acetals

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Abstract

Some solution properties of polyacetals containing poly perfluoro (oxymethylene-ran-oxyethylene) macromers (PFPE acetals) were investigated. Of the eight fractions selected dynamic light scattering in 1,1,2 trichlorotrifluoroethane and intrinsic viscosity measurements in four solvents of different thermodynamic quality and polarity, including a theta solvent, were performed. Previous results on chain flexibility of the new polymers could be reanalyzed taking into account non-negligible solvent effects. The characteristic ratio of the new PFPE-acetals was confirmed to be slightly higher than that of the corresponding fully fluorinated polyethers.

Keywords: Perfluoropolyethers acetals; Unperturbed dimensions; Solvent effect

1. Introduction

The term unperturbed state [1] concerns the conformational state exhibited by the amorphous polymers in bulk state with the absence of external forces. In these conditions, chain dimensions mainly depend on the short-range (few units only) conformational energies of the single macromolecule and by their temperature dependence, because bond angles and length are substantially fixed at normal temperatures and without any external (mechanical, electric) constraint.

In Flory's approach polymer dimensions in dilute solution are given by the potential of 'mean force' related to the thermodynamic quality of solvent [1]. Therefore the ratio $\langle r^2\rangle/M$, where $\langle r^2\rangle$ is the mean square end-to-end distance of the chain and M is the molecular weight, is influenced by both short range and long range interactions, the latter given by excluded volume effects caused by the osmotic swelling of 'good' solvents and quantified by the second virial coefficient, A_2. In principle, it is possible to find a temperature for any polymer/solvent pair at which chain expansion as a result of long-range interactions is exactly balanced by chain contraction caused by the lowered thermodynamic quality of the solvent. At that temperature, defined as theta temperature, A_2 vanishes and chain dimensions are substantially unperturbed by long-range interactions [1]. Intrinsic viscosity or light scattering measurements of the radius of gyration in theta solvent or extrapolation methods in moderately good solvents allow the estimate of the unperturbed dimensions and the so called characteristic ratio, C_∞, of the polymer, and that information can be correlated to very important bulk properties like the elastic modulus, the processing-flow characteristics and so on. However, the possibility that the solvent could influence specific conformational energies and equilibrium rotational states of the macromolecule even in the theta state has been confirmed both on experimental and on theoretical grounds [2,3]. Examples concern especially polar systems, or polymers bearing sterically hindered side groups, like poly(vinyl) alcohol [4] and polystyrene [5–7]. Therefore, when a new polymer is characterized, it is advisable to make measurements in various solvents, different in terms of thermodynamic quality and polarity.

In previous papers [8,9] we have described the preparation and molecular characterization of new high molecular weight perfluoropoly-(oxymethylene-oxyethylene)-acetals, briefly indicated as perfluoropolyether-acetals or PFPE-acetals. In particular, the unperturbed dimensions $\langle r^2\rangle_o/M$ and the characteristic ratio C_∞ could be determined [9] by combined light scattering and intrinsic viscosity measurements in a moderately good solvent, that is 1,1,2 trichlorotrifluoroethane (CFC 113) at 20°C. A rather high

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Table 1
Molecular characteristics of PFPE-acetal fractions

Fraction	M_w (LS)[9]	A_2 10^4 (LS) cm(^{3}/g)[9]	M_w/M_n (GPC)[9]	R_h (nm)	R_G (nm)	R_G/R_h
F1	19,000	n.d.	1.2	n.d.	n.d.	n.d.
F2	40,000	1.3	1.2	4.3	n.d.	n.d.
F3	67,000	1.3	1.2	5.2	n.d.	n.d.
F4	116,000	1.3	1.2	7.2	n.d.	n.d.
F5	250,000	1.3	1.3	9.9	n.d.	n.d.
F6	440,000	1.2	1.3	14.6	n.d.	n.d.
F7	1,200,000	0.7	1.4	26.6	43.9	1.65
F8	2,500,000	0.5	1.4	39.9	59.0	1.51

C_∞ was found if compared with the already known properties of Fomblin Z random perfluoropolyether polymers, having substantially the same molecular architecture [10–12]. Quantification of the stiffening provoked by the acetal linkage proved difficult as a result of the glass transition temperature of the polymer. These results led us to a wider investigation of some solution properties of PFPE-acetals by dynamic light scattering in CFC 113 as well as by intrinsic viscosity measurements in four different solvents, including a theta solvent, which we have found. Our previous [9] results on chain flexibility parameters of PFPE-acetals can then be reanalyzed in the light of possible solvent effects on intrinsic viscosity measurement of these new polymers.

2. Experimental part

2.1. Materials

Eight fractions of PFPE acetals were considered for the present work. Synthesis, fractionation, NMR and GPC analysis and molecular weight determination by classical light scattering in CFC 113 has already been reported [9].

2.2. Dynamic light scattering measurements

Dynamic light scattering was performed in CFC 113 using a B1200SM goniometer (Brookhaven) with a Spectra Physics 2020 argon–ion laser operating at 514.5 nm. Solutions and raw scattering intensities were processed as previously described [9].

Diffusion coefficient (D) was calculated from the autocorrelation function using third order cumulant analysis, after applying the Siegert equation [13]. The fraction with M_w lower than 500 000 were characterized at angles such as $kR_h < 0.2$ (R_h is the hydrodynamic radius and $k = 4\pi n \sin(\hat{\theta}/2/\lambda)$. This condition could not be reached with our experimental apparatus for the two fractions with the highest molecular weight, which were characterized at different angles (30–90°) and the reported diffusion coefficients have been extrapolated at zero angle using a procedure analogous to the Zimm method [14]. The radius of gyration was measured by the classical approach [13]. All measurements were performed at 23 ± 0.1°C.

2.3. Intrinsic viscosity measurements

Intrinsic viscosities $[\eta]$ were measured by means of a capillary Desraux–Bischoff glass viscometer kept in a thermostat bath (temperature accuracy of ± 0.1°C), using 4–5 concentrations for each fraction with relative viscosities ranging from 1.6 to 1.2 and keeping the difference between efflux times of solvent and solution larger than 20 s. $[\eta]$ has been obtained as intercept by extrapolation of the η_{red} versus concentration [15] and $\ln\eta_{inh}$ versus concentration [16] relation. Corrections for density effects are negligible ($d_{solution}/d_{solvent} < 1.01$), as the intrinsic viscosity values changed within the experimental error even for the highest concentrations.

Solvents used for $[\eta]$ measurements were 1,1,2 trichlorotricloroethane, perfluoroheptane, perfluorobenzene and 1,3 hexafluoroxylene. They were distilled before use and kept over dry molecular sieves. Fractions F7 and F8 were not completely dissolved in 1,3 hexafluoroxylene, even after very prolonged stirring at room temperature.

3. Results and discussion

The chemical structure of the PFPE-acetals can be represented as follows [8].

$$[-CF_2\ (OCF_2CF_2)_p(OCF_2)_qOCF_2 - CH_2OCH_2OCH_2-]n$$

The composition and chemical homogeneity of all the fractions were previously checked and confirmed by ^{19}F NMR spectroscopy [9]. Some of the molecular features of the fractions considered as weight average molecular weight and second virial coefficient A_2 by light scattering, molecular weight distribution by GPC, as well as the hydrodynamic radius R_h, the radius of gyration R_G and their ratio are summarized in Table 1. F1–F8 fractions span over more than 2 decades of molecular weight. Moreover, they can be considered as sufficiently narrow molecular weight fractions because in our previous work [9] we have shown that corrections for polymolecularity [17] are practically negligible.

The second virial coefficients (Table 1) are positive for all fractions showing that the CFC 113 is better than a theta solvent for polyacetals. On the contrary, in a previous work

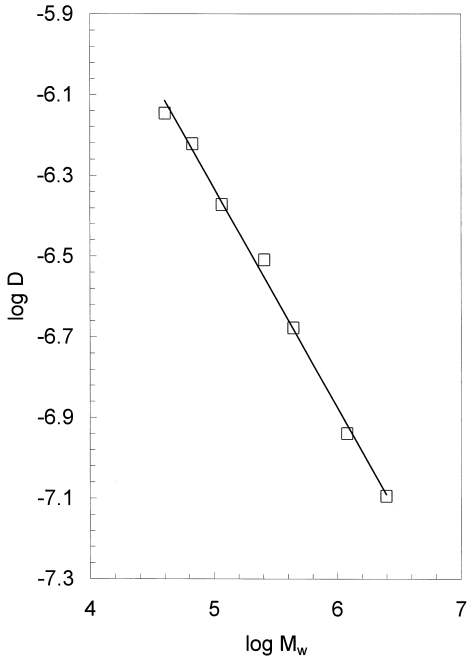

Fig. 1. Dependence of the diffusion coefficient on the molecular weight for the PFPE acetals in CFC 113.

fully fluorinated PFPE polymers were studied in the same solvent, showing $A_2 \approx 0$, at room temperature for molecular weight ranging from 10 [4] to 2.10 [5,12]

The dependence of the diffusion coefficient on the molecular weight is shown in Fig. 1. Least squares regression leads to the following equation:

$$D = 2.66 \times 10^{-4} M^{-0.55}, (R^2 = 0.99). \quad (1)$$

The value of the exponent is higher than the value, 0.5, expected for a theta solvent but lower than the one predicted for good solvents by scaling laws, 0.588 [18]. This, together with the A_2 data, confirms that CFC 113 is a moderately good solvent (at $T = 20$°C) of PFPE-acetals. The hydrodynamic radius R_h reported in Table 1 was calculated from the diffusion coefficients using the Stokes–Einstein equation [13].

Another point of interest is the determination of the radius of gyration R_G which could be measured reliably only for the two fractions of highest molecular weight (Table 1). A too high experimental error was in fact found for the other fractions because of very low refractive index increment and the smaller molecular size. The reliability of measured R_G values can be checked using some different theories, which compare R_G and R_h through R_G/R_h ratio and experimental values obtained for other polymers. The average value of R_G/R_h obtained in this work is 1.58. This value is in agreement with those measured for polystyrene in trans-decalin [18], but larger than those reported for the same polymer in 2-butanone [19], for polyisobutylene [20] and polybutadiene [21].

Moreover, our results are lower than the calculation (1.86) of Ackasu and Han [21], but very close to that (1.56) of Oono [22]; both evaluated taking into account the presence of excluded volume interaction. It useful to recall that our measurements were performed far from theta conditions for fractions having a polydispersity of 1.4, which is small but probably not negligible, and that both excluded volume interaction and polydispersity in molecular weight are reported to affect R_G/R_h. For instance, it increases from 1.504 for monodisperse chain under theta condition to 1.6 for $M_w/M_n = 1.4$ [14] and to 1.66 for solvent interaction similar to the one found in this work [23]. Therefore, both excluded volume and polydispersity can, at least qualitatively, account for the value of this ratio higher than that calculated or measured for monodisperse fraction in theta solvent. Table 2 reports the intrinsic viscosity $[\eta]$ data measured for the fractions in CFC 113, perfluoroheptane, perfluorobenzene and 1,3 hexafluoroxylene, Measurements were carried out at +20°C except for those in perfluorobenzene (+30°C); the very high molecular weight F7 and F8 fractions could not be completely dissolved in hexafluoroxylene and their $[\eta]$ were not included in the table.

The results of the log–log least square linear regressions for all the data according to the well known Mark–Houwink–Kuhn–Sakurada (MHKS) relation (Eq. (2)) are collected in Table 3, while the plots are shown in Fig. 2.

$$[\eta] = K_\eta M^a \quad (2)$$

Very high correlation coefficients were generally found (0.997–0.999), confirming the validity of the Mark–Houwink–Kuhn–Sakurada relation in the whole range of molecular weights explored, as well as the reliability of

Table 2
Intrinsic viscosity ($[\eta]$ in ml/g) of PFPE-acetals in four different solvents

Fraction (temperature)	CFC 113 (20°C)	Perfluoroheptane (20°C)	Perfluorobenzene (30°C)	Hexofluoroxylene (20°C)
F1	8	7.8	7.2	6.2
F2	11.6	11.6	11.2	8.7
F3	16.8	16.8	16.6	11.1
F4	22.3	21.9	24.9	15.3
F5	35.3	37	43	22.4
F6	49.3	50.7	60.7	30
F7	85.1	86	109.3	Partially soluble
F8	124	126	166	Partially soluble

Table 3
Parameters of Mark–Houwink–Kuhn–Sakurada relation of PFPE-acetals in four solvents

Solvent	$K\eta$	a	R^2
CFC 113, 20°	0.029 ± 0.001	0.57 ± 0.01	0.999
Perfluoroheptane, 20°	0.026 ± 0.001	0.58 ± 0.01	0.998
Perfluorobenzene, 30°	0.011 ± 0.002	0.65 ± 0.02	0.997
1,3 hexafluoroxylene, 20°	0.041 ± 0.001	0.51 ± 0.01	0.999

the weight average molecular weight by light scattering, used in Eq. (2) as usual procedure. From the examination of Table 3 data, it appears that a ranges from 0.65 (± 0.01) for perfluorobenzene (rather good solvent) to 0.51 (± 0.01) for hexafluoroxylene, suggesting for this last a 'quasi-theta' behaviour. The value of constant $K\eta$ in this last case is particularly meaningful, because:

$$[\eta] = K_\theta M^{0.5} \tag{3}$$

and K_θ is related to the mean square polymer dimensions according to:

$$(K_\theta/\Phi_0)^{2/3} = \langle r^2 \rangle_o / M \tag{4}$$

being Φ_0 a 'universal' constant equal to $2.6 \times 10^{23}\,g^{-1}$ when $[\eta]$ is expressed in ml/g. The K_θ value obtained by $[\eta]$ measurements in hexafluoroxylene resulted 0.041 (±0.01), significantly lower than $K_\theta = 0.055$ extrapolated by

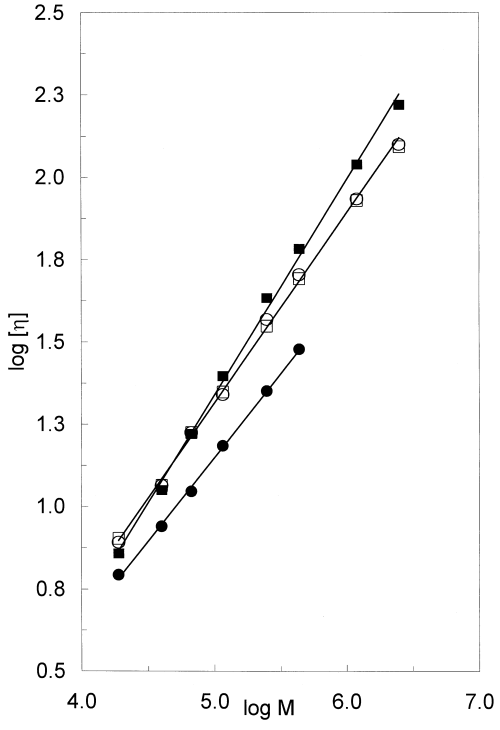

Fig. 2. Mark–Houwink–Kuhn–Sakurada plot of PFPE acetals in (■) perfluorobenzene, (○) perfluoroheptane, (□) CFC 113, (●) hexafluoroxylene. (The straight line relative to CFC 113, very similar to perfluoroheptane one, has been omitted for clarity.)

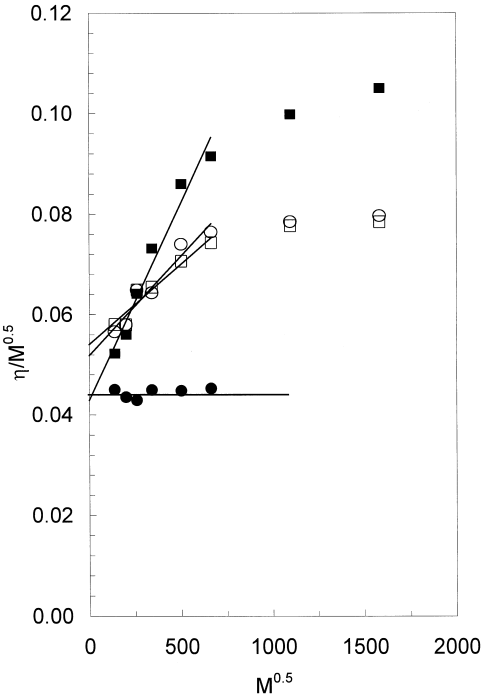

Fig. 3. Stockmayer–Fixman–Burchard plot for the four solvents (symbols like in Fig. 2).

measurements in CFC 113 at the same temperature, a moderately good solvent, and previously reported by us [9].

In order to estimate K_θ from the other measurements in non-theta solvents, all the $[\eta]$ data were then processed according to the Stockmayer–Fixman–Burchared (SFB) equation [24,25]:

$$[\eta] = K_\theta\, M^{0.5} + 0.51\Phi_0\, B\, M, \tag{5}$$

where B is the Flory polymer–solvent interaction parameter [26], representing the interaction energy density typical of the solvent–solute pair.

As is well known [27], only relatively low molecular weights (roughly below 10^6), are suitable for such an extrapolation procedure. The SFB plots (six points) are shown in Fig. 3, while results of least square linear regressions are reported in Table 4. Whilst data regarding CFC113, perfluoroheptane and perfluorobenzene solutions show an acceptable linear interpolation ($R^2 = 0.93$–0.96), the points in 1,3 hexafluoroxylene appear rather scattered giving a substantially flat interpolation curve ($B = 0$), with a mean K_θ value equal to 0.044 ml/g. Since this value is only

Table 4
Parameters of Stockmayer–Fixman–Burchard relation of PFPE-acetals in three solvents

Solvent	K_θ	$B\ 10^{28}$	R^2
CFC 113, 20°	0.054 ± 0.002	2.4 ± 0.3	0.934
Perfluoroheptane, 20°	0.052 ± 0.002	3.0 ± 0.4	0.936
Perfluorobenzene, 30°	0.043 ± 0.003	5.8 ± 0.5	0.966

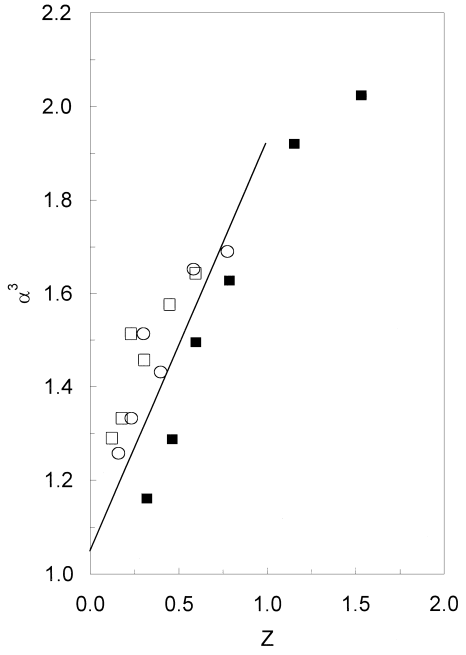

Fig. 4. Viscosity expansion factor versus excluded volume variable for (■) perfluorobenzene, (○) perfluoroheptane, (□) CFC 113. (The straight line represents the universal relation for relatively mild excluded volume conditions — see text.)

slightly higher than that calculated from the MHKS relation, 1,3 hexafluoroxylene at 20°C was, therefore, definitely accepted as a practically theta solvent of PFPE-acetal copolymers.

From an examination of Fig. 3 and Table 4, it seems that some moderately good solvents like CFC 113 (a MHKS = 0.57) and perfluoroheptane ($a = 0.58$) lead to a K_θ value above 0.05 ml/g, confirming our previous findings [9], while perfluorobenzene ($a = 0.65$) and hexafluoroxylene (theta) measurements nicely extrapolate to a common value around 0.043–0.044 ml/g. This difference is significant, of the order of 20%. Such behaviour may be indicative of possible solvent effects on $[\eta]$ measurements. As evident, these solvent effects cannot be justified by the simple difference in thermodynamic quality. Moreover, although intrinsic viscosity measurements in perfluorobenzene were carried out at a temperature slightly higher than the others, the possible temperature effect on K_θ is supposed to be small because:

$$\mathrm{d}\ln K_\theta/\mathrm{d}T = (3/2)\mathrm{d}\ln(\langle r^2\rangle_o/M)/\mathrm{d}T \quad (6)$$

The temperature coefficient $\mathrm{d}\ln(\langle r^2\rangle_o/M)/\mathrm{d}T$ may be positive or negative, but is usually [28] of the order of $10^{-4}/10^{-3}\ \mathrm{K}^{-1}$. Therefore, the variation of K_θ when $\Delta T = 10°$ should be only a few percent. Another way to visualize the solvent effect is shown in Fig. 4, where the viscosity expansion factor $\alpha^3\eta = [\eta]/[\eta]_\theta$, is plotted against the excluded volume variable $z = 2/3(B\Phi_o/K_\theta).M^{0.5}$, calculated from the Stockmayer–Fixman–Burchard plot. The straight lines drawn in Fig. 4 represent the following empirical, 'universal' relation valid for relatively mild excluded volume conditions [29,30].

$$\alpha_\eta^3 = 1.05 + 0.87z \text{ (for } 0 < \alpha_\eta^3 < 2.5). \quad (7)$$

The equation (VI) clearly separates perfluorobenzene points from the others (CFC 113 and perfluoroheptane), which seem to be shifted by a parallel line.

The equation (VI) clearly separates perfluorobenzene points from the other (CFC 113 and perfluoroheptane), which seem to be shifted by a parallel line.

A tentative explanation of this solvent effect might be that more compact chain conformations (smaller K_θ and, therefore, $\langle r^2\rangle_o/M$) of PFPE-acetals have lower energy in presence of relatively hindered solvents like the aromatic haxafluoroxylene and perfluorobenzene. In any case, it is worthwhile to attempt a new estimate of the flexibility of PFPE-acetals through the recalculation of the characteristic ratio C_∞ [1] using an experimental K_θ value directly derived from measurements in theta solvent.

$$C_\infty = (\langle r^2\rangle_O M.\ M_\mathrm{b}/l^2 = (K_\theta/\Phi_o)^{2/3}.M_\mathrm{b}/l^2. \quad (8)$$

Being M_b the average molecular weight of the repeat unit and l the average bond length, calculated using 0.155 nm for C–C and 0.136 nm for C–O bonds [12], the characteristic ratio of PFPE-acetals from $[\eta]$ measurements in 1,3 hexafluoroxylene results:

$$C_\infty = 5.4(\pm 0.3).$$

This value is clearly lower than that previously reported [9] and computed from $[\eta]$ measurements in CFC113 ($C_\infty = 6.3 \pm 0.5$) and confirmed in the present work also by perfluoroheptane data, whilst it is only slightly higher than the characteristic ratio of Fomblin Z perfluorocopolyethers ($C_\infty = 4.8 \pm 0.5$ [12]), having the same perfluorinated polyether repeat unit of the type:

$$-\mathrm{CF_2(OCF_2CF_2)_p(OCF_2)_qCF_2}-$$

without any hydrogenated unit.

Finally, some speculation can be made about the polymer–solvent interactions. The B values reported in Table 4, although their calculation from the Stockmayer–Fixman–Burchard procedure is admittedly a rough approximation, confirm the trend given by the a exponents of the Mark–Houwink–Kuhn–Sakurada relation, being 1,3 hexafluoroxylene a theta solvent, CFC113 and perfluoroheptane moderately good solvents, perfluorobenzene a good one. The solubility parameters δ of PFPE-acetals of the present work is about 11.3 $\mathrm{MPa}^{0.5}$, while δ values of the solvents used have been calculated with the group contribution method [31] from their enthalpies of evaporation according to the known relation $\delta = ((\Delta H_\mathrm{vap} - \mathrm{R}T)/\mathrm{V})^{0.5}$, giving the following set of values:

$$\delta_\mathrm{CFC113} = 14.6\ \mathrm{MPa}^{0.5},\ \delta_\mathrm{perfluoroheptane} = 11.5\ \mathrm{MPa}^{0.5},$$

$$\delta_\mathrm{perfluorobenzene} = 16.3\ \mathrm{MPa}^{0.5},\ \delta_\mathrm{hexafluoroxylene} = 15.3\ \mathrm{MPa}^{0.5}.$$

It is evident that no simple correlation exists between δ and thermodynamic quality of the solvent in our case. In particular, it is somehow surprising that the best solvent among those tested is the one having the larger $\delta_{solvent} - \delta_{polymer}$ value, although perfluorinated, confirming the data obtained by light scattering measurements also on Fomblin Z perfluorocopolyethers and other fully fluorinated polyethers [11].

4. Concluding remarks

The introduction of $CH_2OCH_2OCH_2$ sequences in a random perfluorocopolyether chain is responsible for changed solvent–polymer interactions. A tentative explanation of the improved interaction with CFC 113 due the presence of acetalic groups could follow different lines. First, a simple additivity rule shows that the solubility parameter of the PFPE shifts towards CFC 113 by the addition of acetalic groups. In other words, the increase of the chain polarity because of the acetal group should improve the interaction with a slightly polar solvent as CFC 113. In parallel, a more specific 'copolymer' effect could be invoked; the apparent increase in polymer–solvent interaction after the addition of oxymethylene group could be attributed to the mutual incompatibility of the two alternating blocks of the PEPF acetals, which would lead to an extra contribution to the expansion of the copolymer chain with respect to the parent homopolymers, as argued long ago by Stockmayer and co-workers [32].

Moreover, the intrinsic viscosity measurements of such a new polymer seem affected by not negligible solvent effect which make the estimate of chain stiffness and molecular flexibility parameters subjected to some uncertainty. Actually, taking into account the variability of results derived by the solvent effects, it seems that the characteristic ratio of PFPE-acetals is slightly higher than that of the corresponding fully fluorinated polyethers.

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