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Solution properties of perfluoropolyether polymers

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Solution properties of fractions of a perfluoropolyether copolymer (PFPE Z) having the structure $CF_3-(OC_2F_4)_p-(OCF_2)_q-O-CF_3$ have been studied in two solvents, 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113) and perfluoroheptane, over a large molecular weight range. Two series of fractions having p/q ratio equal to 0.54 and 1.27 were considered. The fractions, which were characterized by light scattering, vapour pressure osmometry and viscosimetry, were found to be narrow. The coefficients of the Mark–Houwink–Sakurada equation, $[\eta] = KM^a$, were determined for both solvents in the molecular weight range between 8000 and 200 000. CFC 113 turned out to be a theta solvent (the Flory polymer–solvent interaction parameter χ is close to 0.5) while perfluoroheptane behaves as a good solvent ($\chi = 0.28$). The coil expansion factor α^3 in perfluoroheptane was also measured. The relationship between the hydrodynamic radius and the molecular weight was determined from dynamic light scattering. Finally, a parameter related to the chain stiffness, the characteristic ratio C_∞, was also determined. In the molecular weight range explored it was found that the stiffness is independent of the p/q ratio. PFPE Z polymer has a chain flexibility similar to that of poly(oxyethylene) and larger than that of poly(tetrafluoroethylene).

(Keywords: perfluoropolyether polymers; solution properties; chain flexibility)

INTRODUCTION

Perfluoropolyether polymers are a family of medium-low molecular weight liquids, which find application in such demanding fields as lubrication, high vacuum and aerospace. They can be homopolymers or copolymers, and can have linear or branched structures as shown below:

$CF_3(OC_2F_4)_p(OCF_2)_qOCF_3$	(Fomblin® Z)
$CF_3CF_2CF_2(OCF_2CF_2CF_2)_nOCF_2CF_3$	(Demnum®)
$CF_3CF_2CF_2(OCF(CF_3)CF_2)_nOCF_2CF_3$	(Krytox®)
$CF_3[(OCF(CF_3)CF_2)_m(OCF_2)_n]OCF_3$	(Fomblin® Y)

Fomblin is the registered trade name of commercial samples produced by Ausimont S.p.A. (Milan, Italy), Demnum by Daikin (Osaka, Japan) and Krytox by Du Pont (Wilmington, DE, USA).

The molecular properties (molecular weight and molecular weight distribution) of these polymers can be determined by conventional techniques such as vapour pressure osmometry (v.p.o.), light scattering, intrinsic viscosity and gel permeation chromatography (g.p.c.)[1–5]. A very accurate study concerning the solution properties of fractions of Fomblin Z and Y was carried out some years ago by Cantow and co-workers, who performed the first known intrinsic viscosity measurements in CFC 113 (1,1,2-trichloro-1,2,2-trifluoroethane), and determined from these data the polymer–solvent interaction parameter and the coil dimensions. The molecular weight range was, however, limited to the low molecular weight side, 9060 and 24 000 being the largest molecular weights investigated for Y and Z polymers, respectively.

As new synthesis techniques are currently available to obtain Z fluids of higher molecular weight[6], it seemed worthy to reconsider the study of solution properties by extending it over a broader field of molecular weight; in such a case, some asymptotic properties of the chain, like the characteristic ratio C_∞, could be determined reliably. Moreover, the present study will also take into account the composition of the copolymer and the influence of the solvent.

EXPERIMENTAL

Materials

Fomblin polymers characterized in this work are random copolymers of oxydifluoromethylene and oxytetrafluoroethylene (Fomblin Z) produced by photooxidation of tetrafluoroethylene (TFE) and successive thermal treatment and neutralization[7]. In this work two copolymers having different p/q ratio (0.54 and 1.27) have been investigated. The polymer with $p/q = 1.27$ (oxygen-to-carbon ratio $O/C = 0.64$) (named polymer A in the following) is a lab-scale sample, obtained by the photooxidation of TFE using CFC 115 as solvent to produce high molecular weights[6]. The raw material, having a peroxide content of about 3% (w/w) was thermally treated until the peroxidic bonds completely disappeared; it was then dissolved in perfluoroheptane and treated with elemental fluorine under u.v. irradiation to transform the acidic terminal groups ($-OCF_2COF$) into stable CF_3O- ones[8]. After distillation of the solvent,

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^{19}F n.m.r. analysis showed the complete absence of acidic terminals. On the other hand, the polymer with $p/q = 0.54$ (O/C = 0.74), named polymer B, is a commercial product.

Moreover, two commercial samples of perfluoropolytrimethyleneoxide (Demnum) were considered (O/C = 1/3), (polymer C).

Two different solvents have been used: CFC 113 (1,1,2-trichloro-1,2,2-trifluoroethane) and perfluoroheptane. CFC 113 was distilled before use, while perfluoroheptane was used as received. Both solvents are Ausimont products, commercialized as Delifrene LS and Galden D80, respectively.

Polymer fractionation was performed by solvent–non-solvent methods using the pair CFC 113–methanol. Polymer A was fractionated at 15°C by successive precipitation (99.4% yield), while fractions of polymer B were obtained at 15°C by a successive solution method (99.9% yield)[9].

Methods

Molecular weight, molecular weight distribution and hydrodynamic properties of fractionated and unfractionated polymers were determined by the following methods.

Number-average molecular weights were measured by v.p.o. in CFC 113 at 25°C, using a Knauer Vapor Pressure Osmometer.

Light scattering measurements were carried out at 20 and 25°C using a BI2030AT correlator and a BI200SM goniometer (Brookhaven Instrument Co.), with a Spectra Physics 2020 argon-ion laser operating at 514.5 nm. All the solutions in CFC 113 were filtered directly into a cylindrical cell with a home-made poly(tetrafluoroethylene) (PTFE) cap through a Millipore GV filtration unit (0.2 μm). As the amount of solvent required to completely fill the cell was small (3 ml), and dust is easily removed from CFC 113, very clean solutions were obtained. It was thus possible to collect the signal for long times, thereby improving its quality, even when the scattered intensity was low. Scattered intensities were measured at five different angles in the range 30–150° and for concentrations $>20\,\mathrm{g\,l^{-1}}$. Raw data were processed by the Zimm method; no angular dependence of scattered intensity was detected, so that the macromolecules under study have been treated as point-like particles.

Intensity autocorrelation functions were measured via homodyne detection at 90, 30 and 20°. Diffusion coefficients and polydispersity index were obtained by third-order cumulant analysis; they are independent of the scattering angle. Hydrodynamic radii were calculated from diffusion coefficients, extrapolated at zero concentration, through Stokes–Einstein formula; CFC 113 viscosities used in calculations were 0.688 mPa s at 20°C and 0.652 mPa s at 25°C, as measured by an Ostwald viscosimeter.

The refractive index increment ($\mathrm{d}n/\mathrm{d}c$) was determined for both solvents at 546 nm by means of a Brice–Phoenix differential refractometer. As the wavelength is slightly different from the laser wavelength, the dependence of the refractive index increment on wavelength was determined for two fractions at 432 and 546 mm; as the dependence was of the same order of magnitude as the experimental error, the correction was not considered necessary. The refractive index increment of perfluoroheptane was very low, as reported in the following; for that reason it was considered unsuitable for light scattering analysis.

G.p.c. was performed at 23°C in CFC 113, using a Waters pump (model 490) and refractive index detector (model R401), and five PL-GEL styrene–divinylbenzene columns of porosity 100, 500, 10^3, 10^4 and 10^5 Å. The calibration was the same as reported in previous papers[3,4].

Intrinsic viscosities in both solvents were determined on fractions of polymers A and B and on unfractionated polymers C at 20°C, using an Ubbelohde viscosimeter coupled with a Schott Gerate AVS automatic viscosimeter. At least three concentrations were used; they were chosen to have relative viscosities in the range between 1.2 and 1.8. All solutions were filtered directly into the viscosimeter. The intrinsic viscosity of the unfractionated polymer A ($p/q = 1.27$) was also determined as a function of temperature between −20 and 50°C.

RESULTS AND DISCUSSION

Refractive index increment

The measured refractive index increments were between 0.01 and $0.02\,\mathrm{ml\,g^{-1}}$ for perfluoroheptane and $-0.046 \pm 0.003\,\mathrm{ml\,g^{-1}}$ for CFC 113; $\mathrm{d}n/\mathrm{d}c$ data determined in CFC 113 on fractions of both copolymers lead to the conclusion that the refractive index increment is practically independent of composition. Moreover, no dependence on molecular weight was found simply because the low molecular weight range, where the effect of chain ends on the refractive index might become evident, was not considered in this work.

The independence of $\mathrm{d}n/\mathrm{d}c$ on both O/C ratio and molecular weight is corroborated by the experimentally observed independence from these variables of the normalized areas under g.p.c. peaks.

It is worth noting that the invariance of the refractive index increment with O/C ratio is predicted not only for Fomblin Z copolymers with different composition, but also for Demnum, if the group contributions to the molar refractivity, recently reported by Groh and Zimmermann[10] for fluorinated structures, are used to calculate the refractive index of the polymers under study.

Molecular properties

The measurements of weight-average molecular weight $\bar{M}_w$ of copolymers by light scattering is generally an involved task; if no simplification is possible, measurements in at least three different solvents are required to determine $\bar{M}_w$. However, it is well known that both composition homogeneity and the independence of $\mathrm{d}n/\mathrm{d}c$ on composition allow the determination of $\bar{M}_w$ from measurements in one solvent[11,12]. Both these conditions are met in this case: the composition of the perfluoropolyether (PFPE) polymers considered in this work is practically independent of molecular weight, as previously reported in ref. 4 on the basis of ^{19}F n.m.r. analysis; and, as shown before, $\mathrm{d}n/\mathrm{d}c$ independence of the O/C ratio seems reasonable from both theoretical and experimental considerations.

Data of $\bar{M}_w$ and of the second virial coefficient A_2 from light scattering, together with number-average

Table 1 Molecular characteristics of the different polymers: A1–A10, fractions with O/C = 0.64; B1–B4, fractions with O/C = 0.74; C1–C2, polymers with O/C = 0.33 (Demnum). All data obtained in CFC 113 at 20°C, except when (*) at 25°C

	M_w (g mol^{-1}) (light scattering)	M_n (g mol^{-1}) (v.p.o.)	$A_2 \times 10^4$ (mol cm^3 g^{-2})	M_w (g mol^{-1}) (g.p.c.)	M_n (g mol^{-1}) (g.p.c.)	M_w/M_n (g.p.c.)
A1	374 000			187 000	141 000	1.32
A2	164 000		−0.2	175 000	132 000	1.25
A3 (*)	149 000		−0.1	130 000	109 000	1.19
A4 (*)	125 000		−0.1	118 000	107 000	1.11
A5 (*)	94 000		0.0	93 000	79 500	1.17
A6	84 500		−0.3	78 000	66 000	1.17
A7	71 000		−0.1	61 000	52 000	1.16
A8 (*)	53 000		−0.1	46 000	39 000	1.16
A9	35 000		−0.4	33 000	27 000	1.21
A10 (*)	17 500		−0.2	17 000	14 000	1.26
B1	8 970	7 010	0.1	8 300	7 700	1.08
B2	12 000	9 970	−0.4	11 400	10 300	1.10
B3	19 600	18 300	−0.5	16 800	15 300	1.10
B4	32 800	24 500	−0.2	23 400	21 200	1.10
C1		4 200		5 500	4 800	1.15
C2		7 200		7 000	6 600	1.10

Table 2 Intrinsic viscosity ([η]) and Huggins coefficient (k') in CFC 113 and perfluoroheptane (same fractions as in *Table 1*)

	[η] (ml g^{-1}) CFC 113	k' CFC 113	[η] (ml g^{-1}) perfluoroheptane	k' perfluoroheptane
A1	21.4	0.33	42.1	0.35
A2	19.0	0.56	34.1	0.38
A3	15.6	0.77	30.1	0.35
A4	14.7	0.61	27.9	0.38
A5	13.2	0.77	23.6	0.43
A6	11.4	0.80	19.9	0.37
A7	10.9	0.66	17.6	0.32
A8	9.5	0.57	14.0	0.27
A9	8.0	0.50	13.8	0.32
A10	5.0	0.80	6.9	0.31
B1	3.2	1.00	4.8	0.30
B2	4.0	1.00	5.5	0.32
B3	5.8	0.62	7.8	0.29
B4	7.0	0.78	10.9	0.28
C1	2.9		3.0	
C2	3.8		4.0	

molecular weights $\bar{M}_n$ from v.p.o., and $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ from g.p.c. are collected in *Table 1* for fractions and unfractionated polymers studied in this work. With the exception of the first fraction of polymer A, which has the largest molecular weight, fraction polydispersity is always <1.4 from both g.p.c. and 'absolute' $\bar{M}_w/\bar{M}_n$ ratios, clearly indicating that fractionation procedures have been effective. The good agreement between M data measured by the different methods also reveals the reliability of light scattering measurements. Second virial coefficients are slightly negative, suggesting that PFPE solutions in CFC 113 at 20 or 25°C are close to the theta condition.

The standard g.p.c. calibration curve used in previous works[3,4], and which was based on PFPE fractions of lower molecular weight, nicely superimposes in the common range of molecular weights on that determined by means of the present fractions.

Hydrodynamic properties

Hydrodynamic properties have been investigated by intrinsic viscosity and photon correlation spectroscopy.

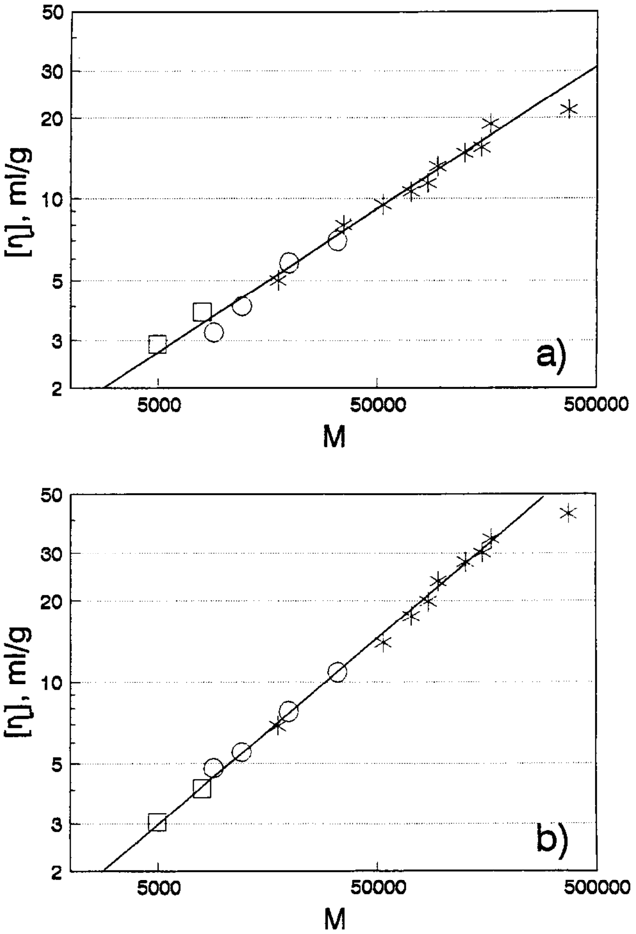

Figure 1 Intrinsic viscosity *versus* weight-average molecular weight in CFC 113 (a) and in perfluoroheptane (b): *, fractions of polymer A (O/C = 0.64); ○, fractions of polymer B (O/C = 0.74); □, polymers C (O/C = 0.33)

Intrinsic viscosities ([η]) and Huggins coefficients (k') in both solvents are collected in *Table 2*, while intrinsic viscosities for the fractionated samples and polymers are plotted *versus* molecular weight (M) in *Figure 1*. It is

Table 3 Parameters of the Mark–Houwink–Sakurada relationship

	K ($\times 10^2$)	a
CFC 113	3.8 ± 0.3	0.51 ± 0.03
Perfluoroheptane	0.95 ± 0.2	0.68 ± 0.02

Table 4 Diffusion coefficient (D), hydrodynamic radius (R_h), second virial coefficient of the diffusion coefficient (k_D), polydispersity index from dynamic light scattering (v) and viscometric radius (R_η) in CFC 113. A1–A10, fractions with O/C = 0.64; B1–B4, fractions with O/C = 0.74. Light scattering data at 20°C, except when (*) at 25°C

	M_w (g mol^{-1})	$D \times 10^7$ (cm^2 s^{-1})	R_h (nm)	k_D (ml g^{-1})	v	R_η (nm)
A1	374 000	2.6	12.2		0.33	
A2	164 000	4.2	7.5	−18.3	0.03	8.1
A2 (*)	164 000	4.4	7.7	−13.8	0.03	
A3 (*)	149 000	4.5	7.5	−9.4	0.05	7.2
A4 (*)	125 000	4.9	6.8	−8.1	0.06	6.7
A5 (*)	94 000	6.1	5.5	−6.2	0.03	5.8
A6	84 500	5.9	5.3	−10.2	0.04	5.4
A7	71 000	6.6	4.7	−8.4	0.03	4.9
A8 (*)	53 000	7.7	4.3	−4.2	0.01	4.3
A9	35 000	9.1	3.5	−6.3	0.03	3.7
A10 (*)	17 500	13.1	2.6	−3.8	0.07	2.4
B1	32 800	9.2	3.4	−3.6	0.09	3.3
B2	19 600	11.7	2.7	−2.5	0.06	2.6
B3	12 000	13.9	2.1	−1.7	0.08	2.0
B4	8 970	19.1	1.6	−1.1	0.03	1.7

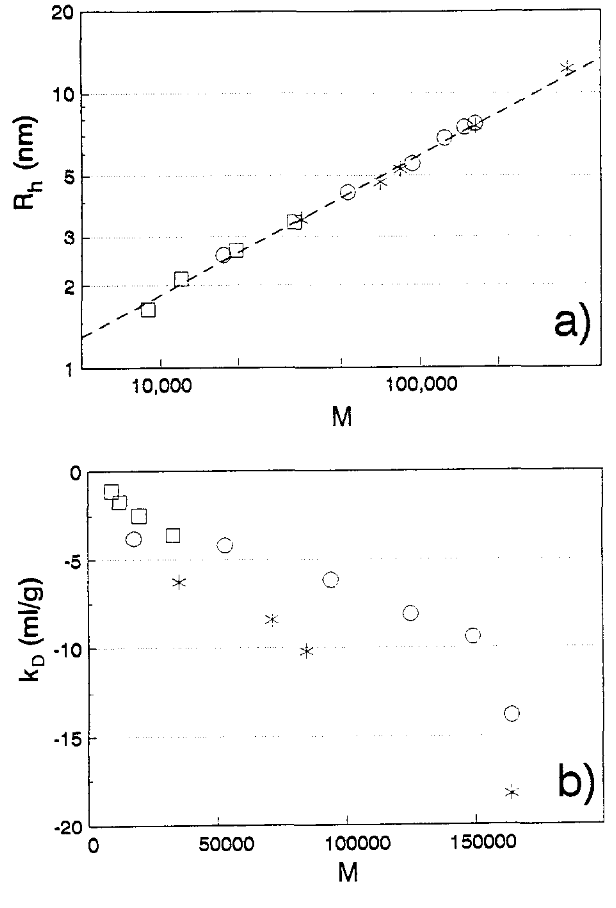

Figure 2 Hydrodynamic radius R_h (a) and second virial coefficient k_D of the diffusion coefficient (b) *versus* weight-average molecular weight. Symbols in *Figure 2a* as in *Figure 1*. *Figure 2b*: *, ○, polymer A fractions (O/C = 0.64) at 25 and 20°C, respectively; □, polymer B fractions (O/C = 0.74) at 20°C

apparent that not only experimental points pertaining to fractions of copolymers with different O/C ratio lie on a common line, but also that data for Demnum homopolymers are fitted by the same line. At first sight it would seem that the hydrodynamic volume is independent of the backbone structure; however, such a conclusion must be considered with some care because the molecular weight range for Demnum does not extend towards high molecular weights.

The values of K and a obtained by the application of the Mark–Houwink–Sakurada relationship, $[\eta] = KM^a$, are shown in *Table 3*. The value of the A exponent (close to 0.5) for CFC 113 confirms that this solvent behaves as a theta solvent at 20°C. It is worth noting that the K and a values are in good agreement with those reported previously[2] and obtained over a smaller molecular weight range. The larger value of the exponent obtained in perfluoroheptane indicates that this is a better solvent for PFPEs than CFC 113. The fraction with the highest molecular weight was not considered in data analysis, because its intrinsic viscosity was lower than expected. As the molecular weight was measured in CFC 113, we cannot exclude the possibility of aggregation on increasing molecular dimension and the consequent overestimation of molecular weight. This hypothesis is confirmed by the large polydispersity indices obtained for the same fraction by both g.p.c. and dynamic light scattering (*Table 4*), and for that reason this fraction is not considered in the following.

A further confirmation of the different solvent quality is given by the Huggins coefficients. The average over the data of *Table 2*, neglecting any molecular weight dependence, leads to 0.73 ± 0.16 in CFC 113 and 0.33 ± 0.04 in perfluoroheptane. These values agree with those generally found for polymer solutions in theta and good solvents, respectively[13–17]. The larger standard deviation obtained in CFC 113 simply reflects the difficulty in performing viscosity measurements in this solvent because of its high vapour pressure at 20°C.

Diffusion coefficients can be measured by dynamic light scattering performed on dilute macromolecular solutions, if proper experimental conditions are observed[18,19]. All the results reported in this work have been obtained with $kR_h < 0.2$ (where R_h is the hydrodynamic radius and $k = 4\pi n \sin(\theta/2)/\lambda$), and therefore the influence of internal macromolecular motions on the diffusion coefficient can be safely neglected.

The decrease in diffusion coefficient, and the corresponding increase in hydrodynamic radius, with molecular weight is evident from the results collected in *Table 4*. The molecular weight dependence of hydrodynamic radius in CFC 113 is shown in *Figure 2a*; least-squares regression leads to the following equation:

$$R_h\,(\text{nm}) = (1.74 \pm 0.1) \times 10^{-2} M^{(0.50 \pm 0.02)} \qquad (1)$$

The exponent is close to 0.5, as expected for a theta solvent[20]; measurements carried out at two slightly different temperatures show that the influence of this variable on the hydrodynamic radius is negligible.

The concentration dependence of the diffusion coefficient is generally quantified by the 'virial coefficient' k_D (*Figure 2b*), which may be written as a combination of osmotic, frictional and volumetric contributions[21,22]. The following equation is generally used:

$$k_D = 2A_2M - k_f - v_2 \qquad (2)$$

where k_f is the second virial coefficient of the friction coefficient and v_2 is the partial specific volume of the polymer.

Although the data are somewhat scattered, the decrease of k_D with increasing molecular weight, typical of polymer solutions in theta solvents[14,20–25], is evident in *Figure 2b*. Another interesting point is associated with the temperature dependence of k_D, which decreases in a more evident way than R_h when the temperature is lowered from 25 to 20°C. A more quantitative comparison with literature data can be made by computing k_f^* through the following expression[14,15,21,22]:

$$k_f^* = k_fM/(N_AV), \qquad V = 4\pi R_h^3/3 \qquad (3)$$

where N_A is Avogadro's constant.

Using $v_2 = 0.55\,\mathrm{ml\,g^{-1}}$ in equation (2), k_f^* values of 1.3 ± 0.2 and 1.0 ± 0.3 are obtained at 20 and 25°C, respectively, for fractions with O/C = 0.64, while k_f^* is 0.6 ± 0.2 at 20°C for fractions with O/C = 0.74. These values agree with those found for other polymers under the theta condition in the same molecular weight range[14,23], and are close to those predicted by the theories of Yamakawa[23] and Imai[24]. This last result supports the reliability of the present dynamic light scattering data carried out in critical conditions, i.e. on medium-low molecular weight polymers with a low dn/dc.

Table 4 reports also the values of the 'viscometric radius' R_η, measured in the same solvent (CFC 113), which, in a hard sphere framework, can be calculated[13,14] as

$$R_\eta = \{3[\eta]M/(10\pi N_A)\}^{1/3} \qquad (4)$$

It is found that R_η is close to the hydrodynamic radius, and the average value of the ratio R_η/R_h is 1.00 ± 0.05, in good agreement with the values obtained for other polymers (1.03 ± 0.05) and also not so far from the value of 1.07 predicted by recent theoretical calculations[13,14]. As the ratio R_η/R_h is believed to be poorly dependent on polymer structure, the agreement between this work and the literature gives further proof of the reliability of the present results.

As a final remark on photon correlation spectroscopy, it is worthy to observe that the polydispersity index v (*Table 4*) is always lower than 0.09, except for the highest molecular weight fraction of polymer A (see above). A polydispersity value lower than 0.1 is generally considered an indication that the molecular weight distribution of fractions is narrow, as already observed by g.p.c.

Coil expansion and conformation

The exponents of the molecular weight dependence of both intrinsic viscosity and diffusion coefficient, together with the values of the virial coefficients k_D and A_2, are in agreement with the assumption that CFC 113 is a theta solvent for all practical purposes. Therefore, we have computed the viscosity expansion factor ($\alpha^3 = [\eta]/[\eta]_\Theta$, where $[\eta]_\Theta$ is the intrinsic viscosity under theta conditions) in perfluoroheptane with respect to CFC 113.

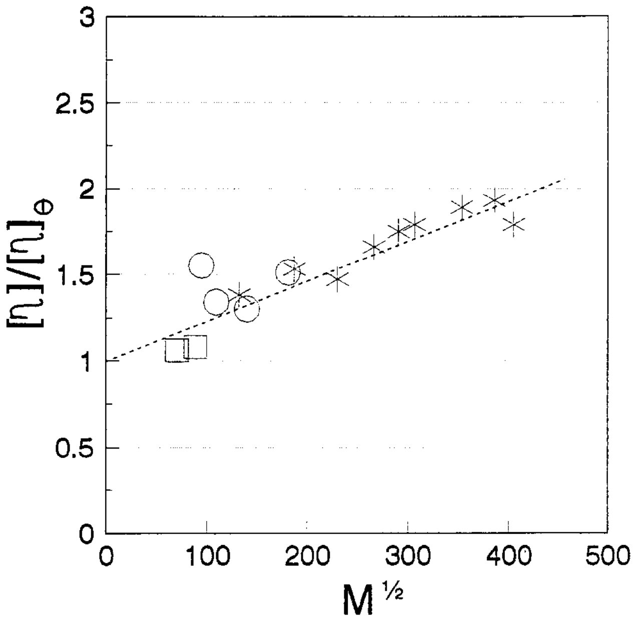

Figure 3 Viscosity expansion factor $\alpha^3 = [\eta]/[\eta]_\Theta$ *versus* $M^{1/2}$ for all fractions and polymers in perfluoroheptane. Symbols as in *Figure 1*

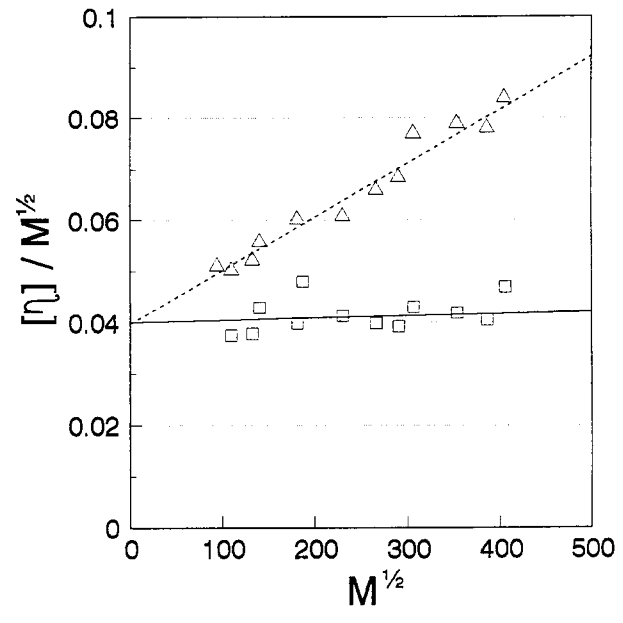

Figure 4 Stockmayer–Fixman–Burchardt plot for fractions of polymers A and B in CFC 113 (□) and in perfluoroheptane (△)

Figure 3 shows that α^3 depends linearly on $M^{1/2}$, as theoretically predicted[26] for $\alpha^3 < 2$.

Intrinsic viscosities in both solvents have been arranged in *Figure 4* according to the Stockmayer–Fixman–Burchardt (SFB) method[27,28]. In particular, $[\eta]/M^{1/2}$ depends on $M^{1/2}$ according to the following equation

$$[\eta]/M^{1/2} = K_\Theta + K'\phi_0BM^{1/2} \qquad (5)$$

where K_Θ is the Mark–Houwink pre-exponential factor under theta conditions, K' is a numerical constant equal to 0.51 in the original SFB formulation or equal to 0.346 according to more recent theories[29,30], ϕ_0 is a universal constant equal to $(2.6 \pm 0.1) \times 10^{23}$, and finally B is related to the Flory–Huggins polymer–solvent

Table 5 Unperturbed dimension and characteristic ratio of perfluoropolyethers and other polymers

	$\langle r_0^2 \rangle / M \times 10^3$ (nm^2 mol g^{-1})	C_∞	Ref.
PF-PEO	2.57	4.9	5
PF-PEO/MO	2.8 ± 0.3	4.8 ± 0.5	this work
PF-PEO/MO	3.1	5.2^a	2
PF-PEO/MO	4.08	7.5	5
PF-P3 MO	2.8 ± 0.3	5.3 ± 0.5	this work
PF-P3 MO	2.72	5.4	5
PTFE	3.3–4.3; 11.5	7–9; 24	32, 33, 34; 33
PE	8.8–17.4	5.3–10.5	33
POM	14.4 ± 1	10.5	33
PEO	5.6–7.1	3.8–4.8	33
P3MEO	6.3	4.2	33

PF-PEO = poly($-OCF_2CF_2$); PF-PEO/MO = poly[$-(OCF_2CF_2)_p-(OCF_2)_q$], Fomblin Z; PF-P3 MO = poly[$-OCF_2CF_2CF_2$], Demnum

[a] Calculated from $\langle r_0^2 \rangle / M$ using standard bond lengths

interaction parameter χ through the relation:

$$B = 2(1/2 - \chi)\bar{v}^2/(V_1 N_A) \tag{6}$$

where $\bar{v}$ is the specific volume of polymer and V_1 is the molar volume of solvent.

As easily seen in *Figure 4*, SFB plots extrapolate to the same value of $K_\Theta = (3.8 \pm 0.3) \times 10^{-2}$ for both solvents. This fact leads us to believe that solvent-specific effects are negligible, and that K_Θ can be safely used to obtain structural information on PFPE chain configuration. Moreover, as a further confirmation, the intrinsic viscosity at 20°C of the unfractionated polymer A ($O/C = 0.64$) in a PFPE having molecular weight equal to 410 is identical to the one measured in perfluoroheptane (22.6 and 22.4 ml g^{-1}, respectively). Therefore perfluoropolyethers and other polymers can be compared through the characteristic ratio C_∞, defined as[31]

$$C_\infty = \frac{\langle r_0^2 \rangle / M}{\langle l^2 \rangle / M_b} \tag{7}$$

where $(\langle r_0^2 \rangle / M) = (K_\Theta / \phi_0)^{2/3}$, M_b and $\langle l^2 \rangle$ are the average molecular weight and the average quadratic bond length of the structural unit, respectively (both weighed over bond number). Calculations have been carried out using 0.153 and 0.143 nm as bond length for C–C and C–O bonds, respectively.

$\langle r_0^2 \rangle / M$ and C_∞ values calculated for Fomblin Z copolymers and Demnum samples are reported in *Table 5*, where they are compared with literature data for PFPEs[2,5], poly(tetrafluoroethylene) (PTFE)[33,34], polyethylene (PE) and hydrogenated polyoxides[33,35]. Two very different values are reported for PTFE; the largest one was determined from intrinsic viscosity measurements in a good solvent[33], while the lowest, which seems the most reliable, was recently determined by light scattering[32–34].

It is evident from the tabulated data that the introduction of an ethereal oxygen either in a linear paraffin or in a linear perfluorinated chain has the same effect; the flexibility of the chain is increased and is dependent on the O/C ratio as pointed out in a previous paper[32].

Mark[33] reports that the chain flexibility reaches a maximum (or a minimum for C_∞) for poly(trimethylene oxide) in the case of the hydrogenated series. A similar trend cannot, at present, also be soundly stated for the perfluorinated series; C_∞ for perfluoro poly(methylene oxide) is indeed unknown and some discrepancies among data reported in the present paper and by Cotts[5] are evident.

In any case it can be concluded that the chain flexibility of linear PFPEs is only slightly lower than that of their hydrogenated homologues.

Polymer–solvent interaction

The polymer–solvent interaction parameter χ can be estimated through equations (5) and (6); χ is equal to 0.49 in CFC 113, whatever K' value is used, and in perfluoroheptane is equal to 0.17 or 0.28 using the original (0.51) or the more recent (0.346) value for K'. The interaction parameter is usually considered as the sum of an enthalpic (χ_h) and an entropic (χ_s) contribution[36]; the enthalpic part is directly related to solubility parameter through the relation:

$$\chi_h = V_1(\delta_p - \delta_s)^2/RT \tag{8}$$

where δ_p and δ_s are the solubility parameters of polymer and solvent, respectively, R is the gas constant and T absolute temperature.

Therefore the entropic contribution in both solvents can be calculated using 11.9, 12.1 and 14.8 (J cm^{-3})$^{1/2}$ as solubility parameters of Fomblin Z[32], perfluoroheptane and CFC 113[37], respectively. As the solubility parameters of PFPE and perfluoroheptane are very close, it is evident that χ_h is very small and therefore $\chi_s = \chi = 0.17$ (or $= 0.28$). The similarity of solubility parameters suggests athermal mixing for this polymer–solvent pair. As a matter of fact, the temperature dependence, between -20 and 50°C, of the intrinsic viscosity of polymer A in perfluoroheptane is very small[38]. χ_h turns out to be 0.41 in CFC 113, and therefore $\chi_s = 0.08$. It is worth noting that this last pair of values (χ_h, χ_s) is in good agreement with the data reported in the literature (*Figure 2* in ref. 39) for a number of polymer–solvent systems having the theta temperature close to room temperature, as occurs for PFPE–CFC 113.

CONCLUSIONS

Solution properties of perfluoropolyether polymers have been investigated using static and dynamic light scattering, vapour pressure osmometry and viscosimetry. Two solvents have been considered: 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113) and perfluoroheptane. Their thermodynamic interaction with PFPE polymers at room temperature was found to be different: CFC 113 is close to a theta solvent, while perfluoroheptane is a better solvent. The chain characteristic ratio, C_∞, was determined using the Stockmayer–Fixman–Burchardt procedure, and the same value (close to 5) was found in both solvents. This ratio is independent of composition, in the investigated range, and shows that PFPE chain flexibility is similar to that of poly(oxyethylene) and larger than that of poly(tetrafluoroethylene).

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