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Solution Properties of a Group of Perfluoropolyethers: Comparison of Unperturbed Dimensions

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ABSTRACT: A group of three different perfluoropolyethers (PFPE) has been studied in dilute solution using static and dynamic light scattering, and size exclusion chromatography with a viscometric detector (SEC/η). The polymers studied were perfluoropoly(ethylene oxide) (PF-PEO), perfluoropoly(trimethylene oxide) (PF-3MO), and a copolymer of perfluoropoly(ethylene oxide) and perfluoropoly(methylene oxide) (PF-PEO/MO). The polymers were separated into narrow molecular weight distribution fractions by supercritical fluid extraction. Molecular weights of the fractions obtained spanned a range from 1500 to 50 000. Molecular weights of several of the fractions and whole polymers were determined by low-angle light scattering and used as calibration standards for the SEC. The intrinsic viscosities in dilute solutions of 1,1,2-trichlorotrifluoroethane were determined using SEC/η. Excluded volume interactions are negligible due to the very low molecular weights and the poor thermodynamic quality of the solvent. Deviations from Gaussian chain statistics at these very low molecular weights were observed and the viscometric data were evaluated to obtain unperturbed dimensions using a graphical procedure based on the wormlike cylinder model. Characteristic ratios estimated from the slopes of these plots are 4.9, 5.1, and 5.6 for PF-PEO, PF-P3MO, and PF-PEO/MO, respectively.

Introduction

Despite the widewpread use of perfluoropolyethers as lubricants in disk files, as high-performance vacuum pump oils, and in a variety of applications, there have been only a few studies reported of the bulk rheological properties[1-5] and even fewer studies of the molecular configurations.[5,6] The insolubility of the perfluoropolyethers in most organic solvents is an advantage in their applications, but a limiting factor in their dilute solution characterization. These materials are only soluble in fluorinated solvents such as 1,1,2-trichlorotrifluoroethane, perfluorohexane, hexafluorobenzene, or trifluoroethanol. In these solvents, the differential refractive index increment, (dn/dc), is very small, about −0.04 mL/g or less. The molecular weights of these polymers are quite low ($2000 < M < 20\,000$), and thus light scattering measurements of the molecular weight can require concentrations as high as 20% by weight.

The very limited studies on the solution properties of PFPE indicate that these polymers are quite flexible, with characteristic ratios which are similar to those observed for the hydrogen-substituted analogs, poly(ethylene oxide), poly(propylene oxide), etc.[5,6] This suggests that rotational barriers about the CF_2 groups are not substantially higher than those found for CH_2 groups. A low *dynamic* barrier in fluorocarbons was indicated by the NMR studies of poly(decamethylene perfluorosebacate) in chloroform solution.[7] Several theoretical and experimental measurements on perfluorinated alkanes,[8-10] and the recent theoretical treatment[11] and measurements of poly(tetrafluoroethylene),[12-14] indicate that the fluorinated polymer chain is not highly extended. In the perfluoropolyethers, as in poly(ethylene oxide) and poly(methylene oxide), the presence of the ether oxygens prevents the high degree of crystallinity observed in the pure hydrocarbon or fluorocarbon polymers. Studies on these soluble oxygen-containing polymers can contribute to the understanding of the molecular and intermolecular effects in the intractable highly crystalline fluorocarbon polymers. Several studies in the literature have correlated the oxygen to carbon ratio with bulk properties related to the molecular flexibility such as T_g.[3,4] In this study we compare characteristic ratios and statistical segment lengths among three different perfluoropolyethers with varying oxygen to carbon ratios. Narrow molecular weight distributions were obtained by supercritical fluid extraction in CO_2.[15] The molecular weight and intrinsic viscosity of each fraction in solution in 1,1,2-trichlorotrifluoroethane were determined by size exclusion chromatography with a viscometric detector (SEC/η). Calibration of the SEC was accomplished with several fractions for which molecular weights were determined by low-angle light scattering in the same solvent. The unperturbed dimensions of the various perfluoropolyethers were then determined using a wormlike cylinder model to address the non-Gaussian chain statistics at these low molecular weights.[16-19]

Experimental Methods

Materials. Of the three different PFPE structures investigated, two were available commercially and were obtained directly from the manufacturer: (1) perfluoropoly(trimethylene oxide), $(CF_2CF_2CF_2O)_n$ (PF-P3MO) was available under the tradename Demnum, from the Daikin Industry; and (2) a copolymer of perfluoropoly(ethylene oxide) and perfluoropoly(methylene oxide), $(CF_2CF_2O)_m(CF_2O)_n$, $m/n = 2/3$ (PF-PEO/MO), was available under the tradename Fomblin Z from Montedison Co. The perfluoropoly(ethylene oxide), $(CF_2CF_2O)_n$ (PF-PEO), was a gift from Dr. M. Guerra, 3M Fluorochemical Technology Center, St. Paul, MN. The PF-PEO, PF-P3MO, and PF-PEO/MO polymers were fractionated by supercritical fluid extraction in CO_2 (Phasex Corp., Lawrence, MA).

Light Scattering. The intensity of light scattered from dilute solutions of several whole polymers and fractions in 1,1,2-trichlorotrifluoroethane and/or hexafluorobenzene was measured using a KMX-6 low-angle light scattering photometer (Thermo-Separation Products). Generally, five to six concentrations $0.05c^* < c < 0.5c^*$ where c^* is the overlap concentration (taken as $[\eta]^{-1}$) were prepared. Solutions were filtered through a 0.5 μm Fluoropore filter (Millipore Corp.) directly into the KMX-6 cell.

The weight-average molecular weight M_w and second virial coefficient A_2 were calculated from the concentration dependence of the reciprocal scattering at low angle ($\theta = 4°$) in the usual manner:

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$$\frac{Kc}{R_\theta} = \frac{1}{M_w} + 2A_2c + \ldots \qquad (1)$$

where R_θ is the measured excess Rayleigh factor for a solution of concentration c at a scattering angle θ,

$$K = \frac{4\pi^2n^2(\mathrm{d}n/\mathrm{d}c)^2}{\lambda^4N_A} \qquad (2)$$

with dn/dc the refractive index increment, n the refractive index, and λ the vacuum wavelength of light (632.8 nm). The M_w, A_2, and dn/dc for each fraction or unfractionated polymer measured are listed in Table 1. At these low molecular weights, a significant molecular weight dependence is observed in the dn/dc, as was reported previously.[6] The unfractionated polymer PF-PEO/MO was also measured in hexafluorobenzene, as shown in Figure 1. While $A_2 < 0$ in 1,1,2-trichlorotrifluoroethane, indicating a poor solvent thermodynamically, $A_2 > 0$ in hexafluorobenzene, indicating a favorable polymer–solvent interaction. Previous light scattering studies also indicated that 1,1,2-trichlorotrifluoroethane is a thermodynamically poor solvent for PFPE polymers.[6] Heats of solution of PFPE polymers measured by microcalorimetry indicated that perfluoroalkanes are also better solvents than 1,1,2-trichlorotrifluoroethane;[20] however, in these solvents, dn/dc is less than 0.02.

Size Exclusion Chromatography with a Viscometric Detector. SEC measurements were accomplished using a modular instrument consisting of a Waters 6000 pump, a Waters WISP automatic sample injector, a Viscotek Model 200 differential viscometer/refractometer, and a set of four size exclusion columns (PLGel, Polymer Laboratories) of sizes 10^5, 10^4, 10^3, and 500 Å. The columns were housed in an oven thermostated at 27 °C. The mobile phase was Aldrich HPLC grade 1,1,2-trichlorotrifluoroethane, which was filtered and degassed by vacuum filtration through a 0.5 μm Fluoropore filter and used within 1 day. Calculations of the intrinsic viscosity were accomplished with the Unical software provided by Viscotek. In this instrument, the specific viscosity of the eluting polymer solution is measured by a differential pressure transducer, using the solvent as a reference. The intrinsic viscosity of each slice is calculated using a single-point equation derived from the usual Huggin's and Kramers' relations. The concentration used in the calculation is measured by the refractive index detector and the known injected mass and flow rate. The average $[\eta]$ is then calculated by summation over all the slices in the distribution. Prior to the PFPE measurements, standard narrow distribution polystyrenes were measured in tetrahydrofuran and the results compared with literature values. It was found that $[\eta]$ and M of polystyrene as low as M = 580 could be measured using the SEC/η technique. The polydispersity of the PFPE fractions was very narrow: $1.01 < M_w/M_n < 1.07$. Injection volumes were in the range 100–300 μL, and concentrations were 6–10 mg/mL. The flow rate was 1 mL/min and was monitored using an internal standard. Figure 2 shows a typical dual chromatogram obtained for one of the fractions, and a composite concentration chromatogram of one of the PFPE polymers and some of its fractions.

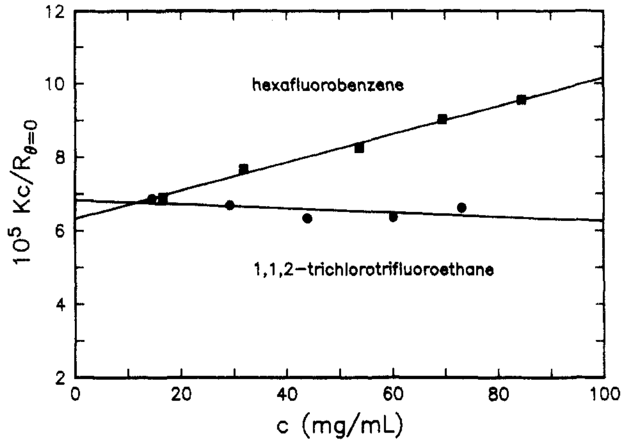

Figure 1. Low-angle light scattering of the whole polymer PF-PEO/MO in 1,1,2-trichlorotrifluoroethane and in hexafluorobenzene.

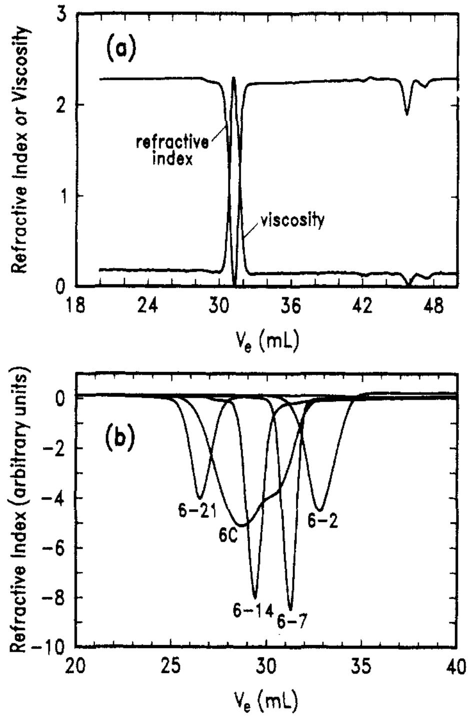

Figure 2. (a) Dual chromatogram obtained for a fraction of PF-PEO/MO: (negative peak) refractive index; (positive peak) viscosity. (b) Composite concentration (refractive index) chromatogram for unfractionated PF-PEO/MO and four of its fractions.

Table 1. Molecular Parameters Determined by Light Scattering

sample	M_w (±5%)	$10^4 A_2$ mL/(mol g^2) (±10%)	dn/dc, mL/g (±1.5%)
PF-P3MO*	10 400	−0.69	−0.0394
PF-P3MO (5–6)	10 900	−0.66	−0.0394
PF-P3MO (3-2)	1 960		−0.0454
PF-PEO/MO (6-18)	20 800	−1.2	−0.0428
PF-PEO/MO (6-15)	11 800	−1.3	−0.0426
PF-PEO/MO (6–21)	52 500	0	−0.0432
PF-PEO/MO (6C)	14 200	−0.6	−0.0434
PF-PEO/MO (6C) in hexafluorobenzene	15 800	2.44	−0.0487

Results and Discussion

Light Scattering. The low molecular weight and very small dn/dc result in very low light scattering intensities for PFPE in the solvents available. Light scattering measurements of the molecular weight required concentrations as high as 20% by weight. However, due to the low molecular weights and the high density of fluorine, concentrations were always less than $c^*/2$, where c is the overlap concentration (taken as $[\eta]^{-1}$), and may still be considered "dilute".

Table 1 lists the M_w and A_2 measured by light scattering for several fractions and whole polymers. The values for A_2 in 1,1,2-trichlorotrifluoroethane were negative, indicating that it is a thermodynamically poor solvent for the PFPE polymers. Since the excluded volume interactions are long-range, the solvent quality is expected to have a minimal effect on the polymer dimensions for these low degrees of polymerization. The unfractionated PF-PEO/MO polymer was also measured in hexafluorobenzene, which exhibited a positive A_2. The equivalent M_w obtained in the good and poor solvents is evidence that no aggregation contributes to the scattering in the poor solvent

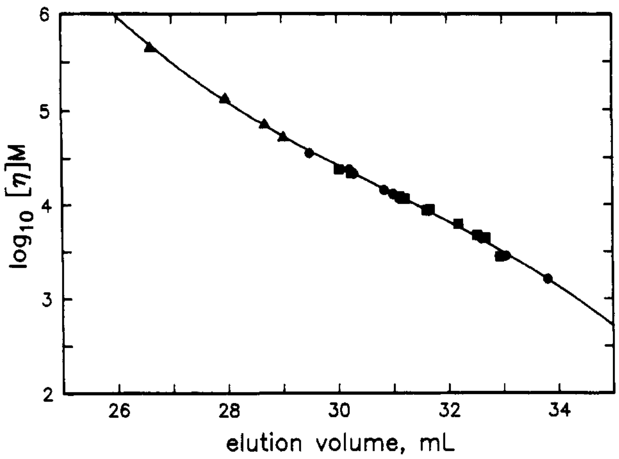

Figure 3. "Universal calibration" $[\eta]M$ versus elution volume, V_e, obtained with PF-PEO (■), PF-3MO (●), and PF-PEO/MO (▲) fractions.

1,1,2-trichlorotrifluoroethane despite the negative A_2.

Size Exclusion Chromatography with Viscometric Detection. The SEC/η measurement determines $[\eta]$ independent of any column calibration. At the lowest molecular weights measured, values of $[\eta]$ were 1.0–1.5 mL/g, which are in the range of the Einstein hard sphere value, $2.5v_{sp}$, where v_{sp} is the specific volume of the polymer in the solvent, 0.53 ± 0.04 mL/g. Measured values of $[\eta]$ were used along with M determined by light scattering for PF-P3MO, PF-PEO, and PF-PEO/MO fractions to construct a so-called "universal calibration", which is shown in Figure 3. This type of calibration is based on the assumption that SEC separates by molecular *size* and that different polymers may all be placed on the same calibration curve if a measure of molecular volume is used rather than molecular weight.[21] For Gaussian coil polymers, the molecular volume may be expressed in terms of the product $[\eta]M$ through the Fox–Flory relation:[22]

$$[\eta] = \Phi\frac{\langle r^2\rangle^{3/2}}{M} \tag{3}$$

where Φ is the universal Flory viscosity constant, and $\langle r^2\rangle$ is the mean-square end-to-end distance. While the use of this type of calibration is still controversial, it is generally accepted as valid when polymers of similar structure in the same solvent are compared. A calibration of the same column set based on $[\eta]M$ of a series of narrow distribution polystyrene standards in tetrahydrofuran produced a curve substantially shifted from the one shown in Figure 3. This indicates the large error that may occur when using a "universal calibration" obtained for dissimilar polymers in a different solvent. The PFPE in 1,1,2-trichlorotrifluoroethane calibration was then used to determine M for all the other PFPE polymers and fractions, with $[\eta]$ measured independently using the viscometric detector. Several of the common sources of error in using this technique have been avoided in this study: (1) the "standards" used to construct the "universal calibration" are of similar or identical structure to the samples measured, (2) the column conditions (mobile phase, temperature, etc.) are identical for calibration and measurement, and (3) the $[\eta]M$ relation is determined from a series of fractions, so that band-broadening corrections are avoided. While in principle a broad distribution polymer can be used to obtain the parameters of the $[\eta]M$ relation using SEC/η, in practice this can be very hazardous. The so-called "universal calibration" is constructed from narrow distribution standards, for which the peak elution volume is used. When calculating from broad distribution polymers, parts of the distribution removed from the peak maximum have undergone diffusion, or broadening, as well as separation on the column. In traditional SEC measurements of molecular weight and distribution, this broadening can be reflected in a larger apparent polydispersity, but the effect is relatively minor. When molecular weight sensitive detectors are used with a "universal calibration" to construct a $[\eta]M$ relation, broadening can have an enormous effect on the exponent a which is obtained. For example, while the measured specific viscosity near the ends of the distribution is independent of the elution volume, the molecular weight taken from the "universal calibration" can be in error due to broadening, too high at the beginning of the peak and too low at the end, producing an apparent exponent a which is erroneously small. Standard broad distribution polymers may be used to obtain a band-broadening correction, but the exponent is very sensitive to this effect, and a series of narrow distribution samples should be used if possible.

Table 2. M_w and $[\eta]$ for PFPE Fractions

PF-PEO		PF-PEO/MO	
M_w	$[\eta]$, mL/g	M_w	$[\eta]$, mL/g
2150	1.3	2300	1.5
2620	1.7	3600	2.2
2780	1.7	3900	2.3
3280	1.9	4000	2.4
4140	2.1	4300	2.6
4240	2.1	4600	2.7
5020	2.3	5400	2.9
5070	2.4	6800	3.2
7800	2.8	7400	3.4
7940	3.0	7800	3.6
		8800	3.8
PF-P3MO		11 600	4.6
		13 800	5.1
1620	1.0	16 700	5.9
2200	1.3	19 900	6.6
2900	1.5	25 800	7.6
5240	2.2	35 600	8.9
5670	2.3	51 300	10.3
6000	2.4		
7630	2.8		
8240	2.9		
10 900	3.3		

The $[\eta]$ and M_w results for the fractions of the three PFPE polymers are listed in Table 2. Since the fractions are of narrow polydispersity, hereafter we simply use M. Figure 4 shows log–log plots of $[\eta]$ *versus* M for the three PFPE polymers. The PF-PEO/MO polymer was broader in distribution than the other two, and thus fractions were obtained which encompassed a much wider range in M. In all three cases, the data cannot be adequately fit with the standard Mark–Houwink relation, $[\eta] = KM^a$, even for this limited range of molecular weight. This behavior is expected at the low molecular weights studied here and indicates that, despite their high flexibility, Gaussian statistics are not attained until higher M for the PFPE polymers. At the highest molecular weights, where the number of backbone bonds, N, is greater than about 200, the exponent d ln $[\eta]$/d ln M does approach the value of $^1/_2$ expected for unperturbed Gaussian coils. Below this molecular weight range, a downward curvature is observed, as has been observed at low M for other unsubstituted polymers. The mean-square end-to-end distance of the polymer chain in this region no longer scales with $M^{1/2}$, and a more complex model is needed.

Unperturbed Dimensions. Estimation of the unperturbed dimensions ($\langle r^2\rangle_0/M$), in the high M limit, or the

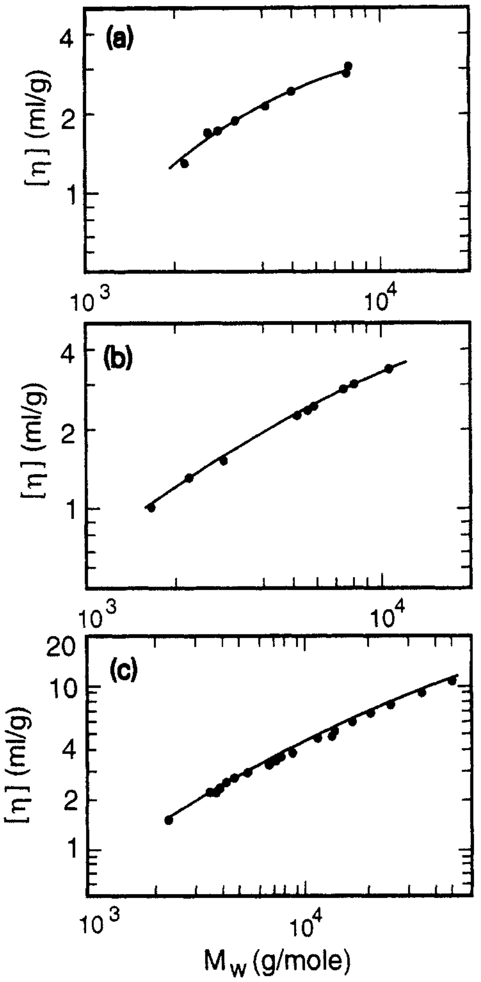

Figure 4. Mark–Houwink–Sakurada relations, $[\eta]$ versus M: (a) PF-PEO, (b) PF-P3MO, and (c) PF-PEO/MO. The lines through the data are least-squares fits.

characteristic ratio, C_∞, can be done in a number of ways: (1) consideration of data only at higher M where $[\eta]/M^{1/2}$ is independent of M; (2) use of a graphical procedure which accounts for non-Gaussian statistics at the lower molecular weights;[23-25] (3) a best fit of the experimental data with the analytical expressions developed by Yamakawa and Fujii for the intrinsic viscosity of a continuous wormlike cylinder (Kratky–Porod chain).[19]

Estimation of $\langle r^2\rangle_0/M$ from the data at higher M where $[\eta]/M^{1/2}$ is independent of M was done using the Fox–Flory equation (eq 3), valid for nondraining Gaussian coils in a Θ solvent. A viscosity constant Φ of 2.5 × 10^{23} was used for these calculations. The characteristic ratio may then be calculated:

$$C_\infty = \frac{\langle r^2\rangle_0}{n l_{av}^2} \tag{4}$$

with n the number and l_{av} the root-mean-square average lengths of backbone bonds. The mean-square average bond lengths were calculated using a bond length of 0.136 nm for C–O and 0.155 nm for C–C, calculated for model compounds.[26-28] The average values of $\langle r^2\rangle_0/M$ and C_∞ for the three PFPE polymers measured are listed in Table 3 under "Fox/Flory". Although the PFPE polymers appear to be sufficiently flexible for the Gaussian coil model to be valid at higher M, it should be noted that an exponent of 0.5 over a limited range in M cannot be regarded as a sufficient criterion for the Gaussian coil, since wormlike chains can also display this exponent over quite extended ranges of M.

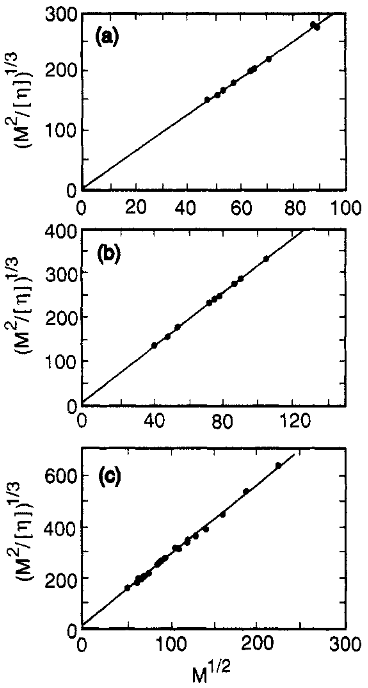

Figure 5. Plots of $(M^2/[\eta])^{1/3}$ versus $M^{1/2}$ according to eq 5: (a) PF-PEO, (b) PF-P3MO, and (c) PF-PEO/MO.

There have been numerous graphical procedures used in the literature to evaluate $\langle r^2\rangle_0/M$ from intrinsic viscosity data where non-Gaussian statistics are observed.[23-25] Of these, we use a recent method proposed by Bohdanecky[25] based on the theory of Yamakawa and Fujii[19] for the intrinsic viscosity of a continuous wormlike cylinder:

$$(M^2/[\eta])^{1/3} = A_\eta + B_\eta M^{1/2} \tag{5}$$

where

$$A_\eta = A_0 M_L \Phi^{-1/3} \tag{6}$$

and

$$B_\eta = B_0 \Phi^{-1/3}(\langle r^2\rangle_0/M)^{-1/2} \tag{7}$$

Equations 5–7 are valid over limited but useful ranges of L/l_k, where L is the contour length of the polymer chain, and l_k is the Kuhn statistical segment length. The plots of the data according to eq 5 are displayed in Figure 5. The parameters A_η and B_η depend on the ratio of the cylinder diameter d to l_k. B_0 is within <1% of unity for $d/l_k \approx 1$, as here, so that $\langle r^2\rangle_0/M$ may be evaluated from the slope of the plots in Figure 5, using a Φ of 2.86 × 10^{23}.[19]

Table 3. Unperturbed Dimensions of PFPE Polymers

	"Fox/Flory"		"Yamakawa/Fujii"			
	$10^3\langle r^2\rangle_0/M$, nm^2	C_∞	$10^3\langle r^2\rangle_0/M$, nm^2	C_∞	M_L, nm^{-1}	l_k, nm
PF-PEO	2.6 ± 0.2	5.0 ± 0.4	2.5 ± 0.2	4.8 ± 0.4	324	0.8
PF-P3MO	2.5 ± 0.2	5.0 ± 0.4	2.6 ± 0.2	5.2 ± 0.4	346	0.9
PF-PEO/MO	3.0 ± 0.15	5.5 ± 0.3	3.1 ± 0.15	5.7 ± 0.3	311	1.0

Values of $\langle r^2\rangle_0/M$ and C_∞ obtained by this method are listed in Table 3 under "Yamakawa/Fujii". In principle, the intercept, A_η, may be used to estimate the mass per unit length (shift factor), M_L. However, the parameter A_0 depends strongly on the ratio d/l_k in the region where this ratio is near unity, such as the flexible PFPE chains. Instead, we estimate M_L as m_0/l_0, with m_0 the molecular weight of the repeat unit, and l_0 the length of the projection of the repeat unit along the chain backbone at its maximum extension. These values of M_L (also listed in Table 2) were used to calculate l_k from $\langle r^2\rangle_0/M$.

The KP chain model was developed to address the properties of long, semirigid polymers, and the hydrodynamic theories of Yamakawa and Fujii have been used successfully with highly extended polymers such as polypeptides, poly(alkyl isocyanates), and polymers containing aromatic groups in their backbone.[29,30] For short flexible chains such as the PFPE polymers, where l_k is similar in magnitude to the cylinder diameter, Yoshizaki and Yamakawa have shown that the more complex helical-wormlike (HW) chain is preferred, due to significant end effects, as well as a need for a different hydrodynamic model at low M.[31] Using $[\eta]$ data in various Θ solvents which encompassed 3 or more decades in M, Yamakawa and co-workers compared experimental data for the flexible polymers poly(dimethylsiloxane) and poly(methyl methacrylate) with both the HW and KP models.[32] Their results showed that unreasonably large values for the mass per unit contour length, M_L, and/or unreasonably small values of the statistical segment length, l_k, were obtained using a "best fit" with the KP model, whereas the HW model yielded appropriate values of these parameters. However, the HW model requires two additional parameters, so that use of this model for $[\eta]$ as a function of M over only 1 decade in M without independent measures of some of the five parameters of the model would be unreasonable.

The results in Table 3 are virtually the same for either method of analysis and indicate that the PFPE polymers are quite flexible, with characteristic ratios similar to those observed for the hydrogen analogs, poly(ethylene oxide) and poly(trimethylene oxide). The copolymer, PF-PEO/MO, although it contains the largest percentage of ether oxygens, has the *largest* C_∞. These results may be compared with the few other experimental results reported for these polymers. Cantow et al. reported $\langle r^2\rangle_0/M$ of 3.14×10^{-3} nm^2 for a single PF-PEO/MO polymer,[6] which is in agreement with our result listed in Table 3. Marchionni and co-workers have tabulated the steric factor, σ, the ratio of the unperturbed dimensions to those of a chain with free rotation, for PFPE polymers with varying oxygen to carbon ratios.[5] They report $\sigma = 1.69$ for PF-P3MO and $\sigma = 1.64$ for PF-PEO/MO, using their own $[\eta]$ and M data for PF-P3MO and the data of Cantow et al.[6] for PF-PEO/MO. Although Marchionni and co-workers do not report their experimental value of $\langle r^2\rangle_0/M$ for PF-P3MO, the reported σ suggests a value similar to that of PF-PEO/MO. In the hydrogen analogs of these materials, poly(methylene oxide) exhibits a substantially larger C_∞ than poly(ethylene oxide). This is attributed to the preference for sequences of *gauche* rotational states of the same sign in poly(methylene oxide), leading to helical sequences. Recent rotational isomeric state calculations on PF-PEO based on ab initio calculations on the model compound perfluorodiethyl ether indicate that PF-PEO is indeed at least as flexible as PEO.[28] Further RIS calculations may elucidate whether the copolymer PF-PEO/MO is expected to be slightly more extended than PF-PEO.

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