Molecular Weight Characterization of Fluoropolyoxyalkylenes by Gel Permeation Chromatography

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SYNOPSIS

Conditions required for the molecular weight and molecular weight distribution determination of fluoropolyoxyalkylenes by gel permeation chromatography are reported and discussed. Experimental work was carried out with three series of narrow fractions of oligomers having the same perfluorinated copolymeric body and three different types of chain ends. The same calibration curve describes very well the behavior of the three series of samples, so that a "size-exclusion" mechanism of the molecular separation can be postulated practically. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The recent increasing interest in the study and development of various classes of oligomeric compounds frequently involves new or specific problems on their accurate molecular characterization. This is particularly true in the lower range of molecular weights and when the chemical nature of such compounds entails the use of uncommon solvents.

In this work, three series of fluorinated oligomer fractions have been prepared and studied, having the following general constitution:

$$E\text{—}CF_2O[(CF_2CF_2O)_p(CF_2O)_q]CF_2\text{—}E$$

in which a perfluorinated copolymeric body, namely, a random chain substantially consisting of p perfluorooxyethylene and q perfluorooxymethylene units (with $p/q \approx 1$), is endcapped by two equal end groups E of one of the following types:

$$\text{—}CH_2OH \quad \text{—}CH_2O(CH_2CH_2O)_mH \quad \text{—}CH_2OCOCF_3$$

where m has an average value around 1.5.

The aim of this article was to report the interesting results obtained in applying gel permeation chromatography (GPC) to the determination of molecular weight (MW) and molecular weight distribution (MWD) of such oligomeric fluorinated polyoxyalkylene copolymers.

It is well known that the GPC method, when used to measure MWs, involves a calibration that allows to turn the retention volume V_R, recorded in the experimental chromatogram, into the corresponding molecular weight M of the eluted polymer.[1] Such a calibration is specific in every polymer system, depending on its chemical nature and molecular structure, as well as on the solvent used and on the temperature at which the measurements were performed.

An approach to a somewhat general calibration relation between V_R and M was suggested by Benoit et al.,[2] based on a postulated pure "size-exclusion" mechanism of the macromolecules' separation. By this, the macromolecule hydrodynamic volume, assumed to be proportional to the $[\eta] \cdot M$ product, is taken as a "universal calibration parameter."

In the case of fluorinated polymers, considered here, the requirements for such an approach are lacking, mainly because of their solubility characteristics and the MW range of interest. As a matter of fact, even in the presence of a size-exclusion mechanism, their MWs ($1\text{–}5 \cdot 10^3$) would be rather low for good limiting viscosity number measure-

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ments. In addition, it would be surely difficult to find solvents common to fluorinated polymers and reference polystyrene samples. Furthermore, in the chemical structure of the studied compounds, the end groups E have physicochemical interaction properties fairly different from those of the perfluorinated body: On the one hand, a "copolymer end effect"[3] could work in, perturbing a simple size-exclusion separation in the chromatographic gel; on the other hand, the rather polar main chain could govern the whole molecular interaction. Specific experimental calibrations are therefore necessary.

EXPERIMENTAL

Materials

The oligomeric samples of the two diol series were prepared by solvent/nonsolvent fractionation of some samples of ZDOL (E = CH_2OH) and ZDOLTX (E = $CH_2O(CH_2CH_2O)_{1.5}H$), kindly supplied by Ausimont, Milan. Those of the third series (E = CH_2OCOCF_3) were synthesized by esterifying six ZDOL fractions with trifluoroacetic anhydride. All the solvents and reagents used were freshly distilled commercial pure products; in particular, as fluorinated solvent used was 1,1,2-trifluorotrichloroethane, available under the commercial name DELIFRENE LS® (Ausimont).

Molecular Characterization

The number-average molecular weight, M_n, of all the samples was determined following an Ausimont proprietary method of ^{19}F-NMR band integration from VARIAN 200 MHz spectra (as a ratio of body-to-end group contents). With the same method, the p/q ratio was also evaluated for every sample.[4] For comparison, vapor-pressure osmometry (VPO) was also used to measure M_n of several samples; the latter was carried out with a Perkin-Elmewr Model 115 VPO, at 50°C, in perfluoroctane. The retention volumes (V_R) in the calibration experiments were determined by a Waters Model 5900 GPC instrument, equipped with four "Ultrastyragel" columns of 10^5, 10^4, 10^3, and $5 \cdot 10^2$ Å porosity at 30°C using an azeotropic mixture of DELIFRENE LS/acetone as eluent (87.5/12.5 w/w), also available as the commercial product DELIFRENE AC® (Ausimont).

RESULTS AND DISCUSSION

Fractionation

To prepare fractions of narrow MWD in the widest MW range, four base samples of ZDOL (here named A, B, C, and D) and two of ZDOLTX (E and F) were carefully fractionated. Several fractions were then conveniently selected as samples for GPC calibration.

DELIFRENE LS was used as a solvent and methanol as a nonsolvent, at the equilibrium temperature of 25°C. A typical scheme[5-7] followed for fractionation and refractionation may be seen in the example reported in Scheme 1, relative to a base sample of ZDOL.

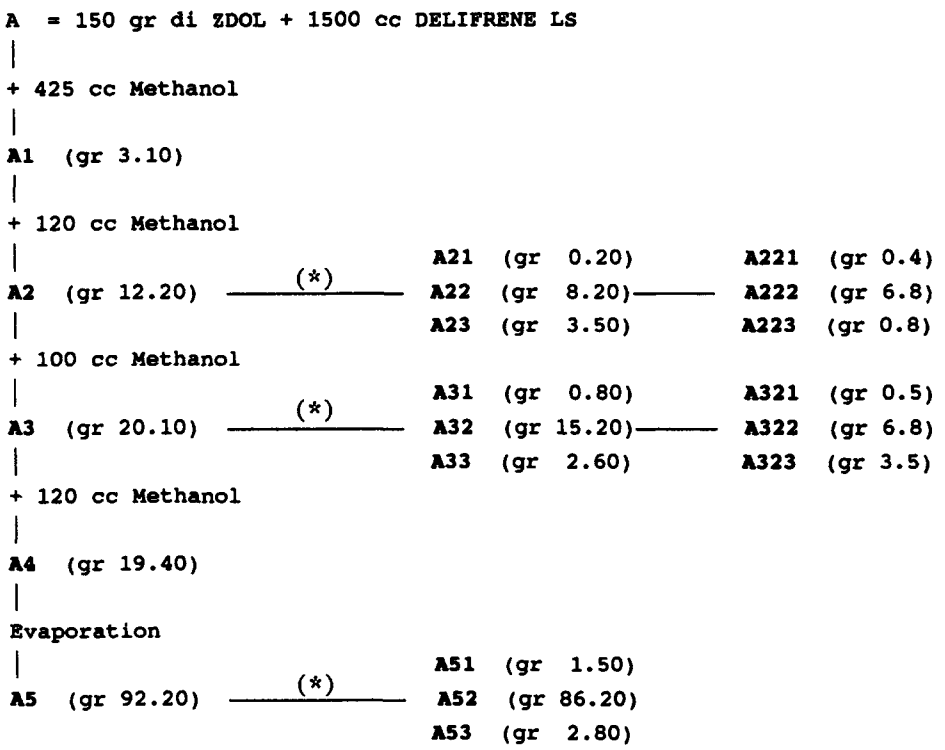
It may be noted that particular care was taken in narrowing the refractionated fractions by eliminating preferably consistent amounts of the lowest MWs (see, e.g., a comparison between A21 and A23 fractions).

The molecular separation appears to have been prevalently guided by the molecular mass. No noticeable systematic variations were observed in the p/q copolymeric composition of the fractions of the different base samples; this may also be seen in Tables I and II, which collect all the data relative to the selected fractions.

The fractionation efficiency could be verified as satisfactory by the subsequent GPC evaluation of the M_w/M_n ratio (next paragraph). It is interesting to note that this ratio would be hardly obtainable by direct M_w light scattering determination because of the relatively small molecular masses, but also, in our case, because of the particularly low dn/dc value practically realizable with highly fluorinated compounds.[8]

From GPC measurements, after calibration, another interesting feature of the fractionation efficiency could be singled out: In spite of the particular fractionation pattern used, the MWD curves of all the fractions showed some "dissymmetry" (as shown in Fig. 1), due to a slightly higher proportion of residual low MWs. Such a "dissymmetry" was, however, substantially accepted, mainly because of the particular nature of these perfluoropolyoxyalkylenic oligomers and their unusual solubility characteristics.

Six ZDOL fractions, covering an MW range from 1400 to 10,700, were derivatized using trifluoroacetic anhydride (see Table III) to obtain a different system (ZDOL–ACF) having the same perfluorinated



Scheme 1 Fractionation Scheme of ZDOL A Sample

(*) All the new fractions were obtained from the previous one dissolved in DELIFRENE LS (500 cc) and addition of appropriate quantities of methanol.

body and different, however, partially fluorinated end groups ($-CH_2OCOCF_3$).

GPC calibration

DELIFRENE LS has to be considered one of the best solvents of highly fluorinated compounds, but, in our preliminary attempts of using it as eluent in GPC, it failed expectation. This was mainly because its solutions showed a refractive index increment dn/dc too low to be accurately measured by the RI detector of the instrument. Consequently, a specific appropriate solvent choice was necessary.

The best results were obtained using a mixture of DELIFRENE LS and acetone in the ratio 87.5/12.5 (w/w). This was suggested basically by the following considerations:

(a) The solutions show reliably measurable RI increments dn/dc and a better resolution,

Table I Molecular Characterization of the Samples of the ZDOL Series

Fraction	p/q	M_n (NMR)	M_n (VPO)	M_w/M_n
A222	0.99	10,600	10,000	1.17
A322	1.01	7,950	7,700	1.16
B222	1.09	4,300	3,900	1.16
B42	1.10	3,900	3,400	1.05
B52	1.11	3,500	3,200	1.10
B6	1.12	2,700	2,400	1.11
C212	0.80	11,450	—	1.14
C42	0.87	5,650	—	1.18
C6	0.92	3,050	—	1.17
C7	0.95	2,150	—	1.20
C8	0.96	1,250	—	1.17
D312	0.80	16,950	—	1.05
D322	0.82	13,200	—	1.05

Table II Molecular Characterization of the Samples of the ZDOLTX Series

Fraction	p/q	M_n (NMR)	M_w/M_n
E322	1.03	6250	1.21
E42	1.04	5800	1.17
E6	1.04	5050	1.12
E9	1.04	4600	1.17
F32	1.01	4300	1.19
F42	1.01	3800	1.18
F5	1.02	2750	1.16

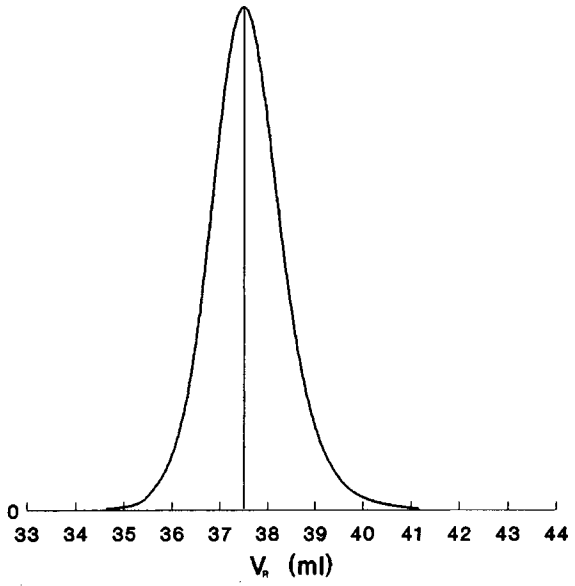


Figure 1 A typical shape of a GPC chromatogram showing a light "tail effect."

especially if compared with those of pure DELIFRENE LS; the recorded chromatograms have well-defined peaks, about twice the intensity.

(b) The calibration curve has a slope sufficient to assure good molecular resolution and manageable peak widths for the interpolation of the base line.

(c) The solvent mixture composition is azeotropic and assures a good reproducibility of its preparation.

In Table III (columns 2 and 3) are reported, in particular, for every selected fraction of the three series, the retention volumes, V_R, taken exactly at the peak of the chromatographic pattern, and the number-average M_n determined by NMR.

From the analysis of the experimental data, it results that, for any series of samples, the relation between V_R and M_n is well represented by a linear equation of the usual type:

$$\log M_n = A - BV_R \qquad (1)$$

For the diolic ZDOL series, the mean-square fitting, graphically illustrated in Figure 2, gives $A = 11.433$ and $B = 0.211$, with a correlation coefficient $cc = 0.995$. With the same procedure, for the diolic-oxyethylene ZDOLTX series, $A = 11.527$ and $B = 0.214$, with $cc = 0.959$, and for the trifluoroacetate series, $A = 11.546$ and $B = 0.215$, with $cc = 0.997$.

A very interesting result is that the three just-found linear relations are very close to each other. It is thus possible to represent all the data, with a reasonable accuracy, with the following single equation, resulting from the collective fitting of all the data:

$$\log M_n = 11.467 - 0.213V_R \qquad (2)$$

with $cc = 0.994$.

Using this equation as a first calibration relationship, the ratio M_w/M_n of all the samples has been calculated and reported in the last column of Tables I and II.

A final remark is, however, in order. The above calibration was based on the experimental M_n value of every fraction measured by NMR. Now, the values of M_n subsequently obtained by the GPC instrument integration of the chromatographic patterns relative to the same fractions are systematically slightly

Table III Physicochemical Data of All the Fractions Used for GPC Calibration

Fraction	M_n (NMR)	V_R (mL)	M_n (GPC) [Eq. (2)]	M_n (GPC) [Eq. (3)]
D312	16,950	34.16	15,300	16,750
D322	13,200	34.42	13,200	14,600
C212	11,450	34.80	9,650	10,550
G(A222)	10,792[a]	35.03	9,450	10,350
A222	10,600	35.13	8,900	9,700
G(A322)	8,142[a]	35.57	6,950	7,650
A322	7,950	35.70	6,950	7,600
E322	6,250	36.04	5,550	5,900
G(C42)	5,842[a]	36.11	5,350	5,850
E42	5,800	36.28	5,200	5,700
C42	5,650	36.22	4,850	5,300
E6	5,050	36.58	4,500	4,900
E9	4,600	36.74	4,300	4,600
F32	4,300	36.58	4,050	4,350
B222	4,300	36.67	3,650	4,000
B42	3,900	36.86	3,500	3,800
F42	3,800	36.97	3,460	3,750
B52	3,500	37.20	3,100	3,400
G(C6)	3,242[a]	37.28	3,050	3,300
C6	3,050	37.50	2,700	2,950
F5	2,750	37.74	2,550	2,750
B6	2,700	37.76	2,400	2,600
G(C7)	2,342[a]	37.98	2,250	2,400
C7	2,150	38.32	1,850	2,000
G(C8)	1,442[a]	39.13	1,350	1,500
C8	1,250	39.52	1,180	1,450

[a] The M_n of trifluoroacetylated G fractions was calculated by adding two trifluoroacetyl units to the M_n of the corresponding ZDOL (in parentheses).

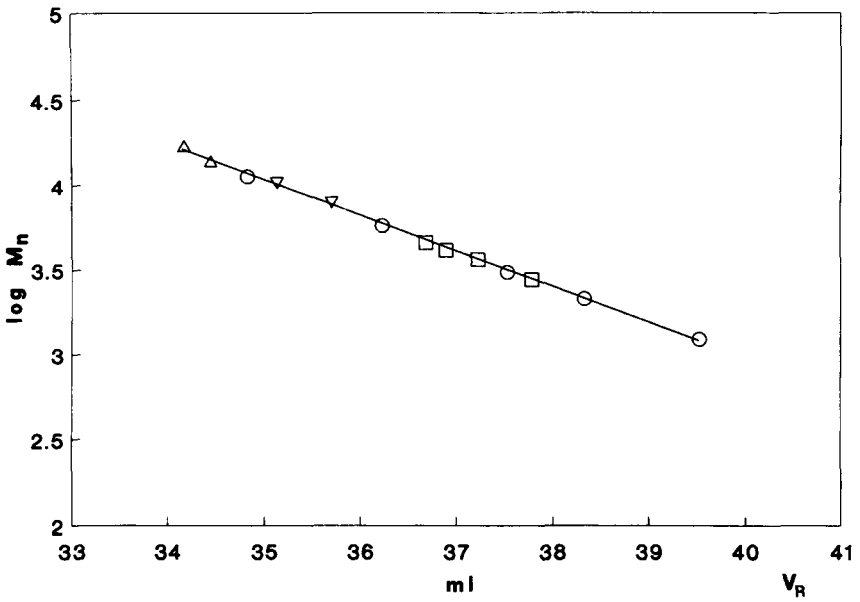


Figure 2 GPC calibration for the ZDOL series (Log $M_n = 11.433 - 0.211V_R$): (▽) fraction A; (□) fraction B; (○) fraction C; (△) fraction D.

lower than those obtained by ^{19}F-NMR and used for calibration. This fact can be explained by the observed (and previously discussed) slight "dissymmetry" of the MWD curves of all the fractions toward lower MWs, which causes an average difference between V_r of the peak and that corresponding to the calculated M_n value of about 0.15 mL. Then, for a more correct calibration, an empirical adjustment of eq. (2) is possible by simply shifting the corresponding straight line of Figure 3 upward, in such a way that only coefficient A is changed as follows:

$$\log M = 11.498 - 0.213\ V_R \qquad (3)$$

Table III confirms a good agreement between all M_n values experimentally determined by ^{19}F-NMR

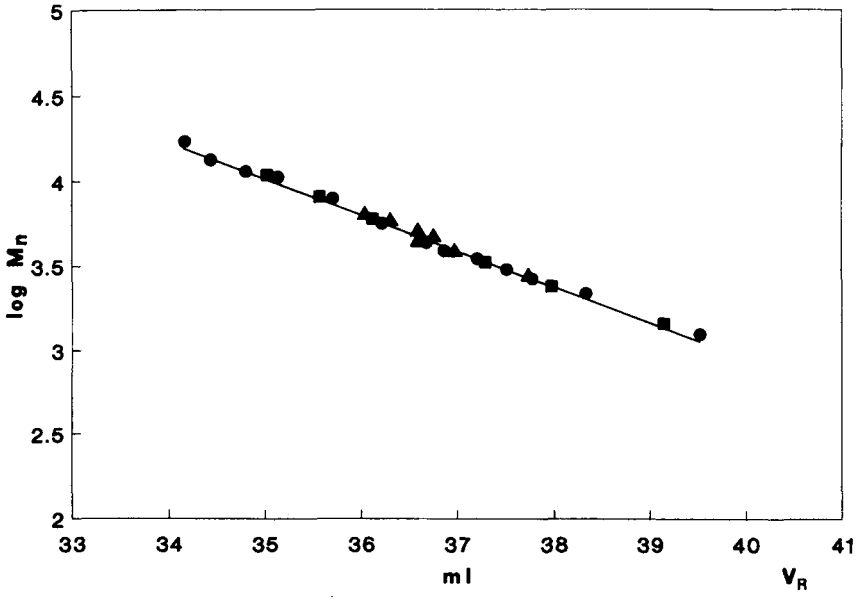


Figure 3 GPC calibration for three series [Eq. (2): Log $M_n = 11.467 - 0.213V_R$): (●) ZDOL (fractions A, B, C, D); (■) ZDOLTX (fractions E, F); (▲) ZDOL–ACF (fraction G).

and those calculated using the calibration, by Eq. (3), compared to the experimental ones of Eq. (2) for all the fractions used in this work.

CONCLUSIONS

The strict similarity of the GPC behavior of the studied compounds, represented by Eq. (2), can be taken as the demonstration, in the limits of the realized experimental conditions and structural characteristics, that the molecular separation has been practically insensitive to the great chemical nature dissimilarity: (a) between end groups and the perfluorinated molecular body, and (b) between the end groups of the three different series of samples with a common molecular body. This leads to a twofold result:

1. The absence of a noticeable "copolymer end effect"; and
2. A practical "size-exclusion" mechanism of the molecular separation.

Point 2 allows the conclusion that a "size-exclusion" mechanism of the chromatographic separation (SEC) can take place also when the GPC technique is applied to families of very special compounds like those studied in this work. As for the copolymer end effect, it is to note that, if it was present, it would be more and more important as the molecular weight is lowered, so that it should modify the V_R–M relation with different intensities, as a function of M, with the three different series of compounds. By contrast, such an effect was very recently found to be relevant on the T_g–M relation of series of fluorinated oligomers, whose structure was equal or similar to those considered in this work.[3]

REFERENCES

1. J. C. Moore, *J. Polym. Sci. A*, **2,** 835 (1964).
2. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci. B*, **5,** 753 (1967).
3. F. Danusso, M. Levi, G. Gianotti, and S. Turri, *Polymer*, **34,** 3687 (1993).
4. Unpublished results, CRS Ausimont, Bollate, MAN PF 30/1E/88.
5. M. J. R. Cantow, *Polymer Fractionation*, Academic Press, New York, London, 1967.
6. F. Danusso and G. Moraglio, *Ist. Lomb.*, **A92,** 591 (1958).
7. G. Meyerhoff, *Makromol. Chem.*, **19,** 7 (1954).
8. M. J. R. Cantow, R. B. Larrabee, E. M. Barral, R. S. Butner, P. Cotts, F. Levy, and T. J. Ting, *Macromol. Chem.*, **187,** 2475 (1986).

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