Fractionation of Reactive Perfluoropolyoxyalkylene Oligomers

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SYNOPSIS

Fractional distillation, solubility fractionation, and column chromatographic separation have been applied in the study of fractionation of perfluoropoly(oxymethylene-*co*-oxyethylene) oligomers with $-CH_2OH$ end units, containing mono and bifunctional species. With a suitable choice of conditions, all three techniques proved to be useful for the preparation of fractions with narrow molecular weight distribution. Column chromatography allowed the separation of fractions having, in addition, sharp mono and bifunctionality. On the basis of the experimental results, general indications for designing reactive oligomers fractionation procedures are discussed, prevalently centered on the copolymer end effect, which is typically present in this kind of compound. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Reactive oligomers are an increasingly important class of compounds, mainly used as reagents, for the synthesis of complex molecule compounds, and frequently, as macromonomers, for that of various macromer-segmented copolymers.[1]

It is known that for accurate oligomers preparation, a typical problem is that of their individual separation from synthetic reaction polydisperse mixtures. This is, in general, performed by designing appropriate fractionation procedures to be applied to the original synthetic mixtures of homologous compounds, in order to reach a sufficiently narrow molecular weight distribution in the individual final products. With reactive oligomers, however, it can be very important to reach high functionality degree in the final product of interest, so as to obtain it in a form close to that of a pure chemical substance. This clearly implies a more complex fractionation procedure.

Of a particular, practical interest is the preparation of bifunctional reactive oligomers, whose synthesis in general involves, besides molecular weight dispersity, the presence of related mono and heterofunctional species in the final reaction mixture.

In this work we shall report on results obtained in studying fractionations leading to the preparation of the following bifunctional hydroxyl-terminated perfluoropoly(oxymethylene-*co*-oxyethylene) oligomers:

$$HOCH_2CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2CH_2OH$$

produced by AUSIMONT S.p.A. (Milan) with the commercial name ZDOL.

These diols are currently synthesized by photocopolymerization of oxygen and perfluorinated monomers, followed by chain scission and reduction of dicarboxy derivatives, as originally described by Sianesi et al.[2]

The experimental base samples fractionated in this work were intentionally chosen of a moderately high degree of bifunctionality (functions per molecule $F = 1.93$–1.96), medium polydispersity, and relatively different average molecular weights. They contained some monofunctional species (the foreign end units mainly being "inert" $-OCF_3$ instead of "reactive" $-CH_2OH$), and a practically negligible amount of zero-functional ones (i.e., species having a pair of trifluoromethoxylic end units).

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Journal of Applied Polymer Science, Vol. 55, 989–995 (1995)
 CCC 0021-8995/95/070989-07

The aim of this study is to provide concerned operators with some useful information about the fractionation behavior of the above very special fluorinated samples, from which generalizable indications may also be drawn for designing fractionation procedures in other comparable cases of reactive oligomer mixtures.

EXPERIMENTAL

Materials

Experiments were carried out starting with three raw ZDOL samples that were fractionated with different techniques. Their molecular characteristics are summarized in Table I.

1,1,2-Trichlorotrifluoroethane (Delifrene-LS AUSIMONT) and the other solvents (Fluka) were distilled before use.

Molecular Characterization

NMR Spectroscopy

^{19}F-NMR spectroscopy was used (VARIAN 300 MHz) to evaluate p/q ratio, molecular weight M_n, and functionality F (end functions per molecule) of each sample. Calculations were made by analyzing spectra with an AUSIMONT proprietary method, on the basis of literature assignments.[3,4]

It follows from the working hypothesis, in this case quite acceptable, that the photooxidative synthesis process leads only to mono and bi-hydroxylated species (the zero-functional species being negligible). Consequently, if U_1 and U_2 are the normalized areas of signals corresponding to the internal units $-OCF_2-$ and $-OCF_2CF_2O-$, and E_r and E_i those of $-CF_2CH_2OH$ and $-OCF_3$ end units, the p/q ratio can be calculated as U_2/U_1, and the number-average polymerization degree as follows:

$$x_n = \frac{2(U_2 + U_1)}{E_r + E_i} + 2$$

Table I Characterization of ZDOL Base Samples

Sample	p/q (NMR)	M_w/M_n (GPC)	M_n (NMR)	F (NMR)[a]
Z1	0.94	1.28	1150	1.96
Z2	0.92	1.60	2150	1.95
Z3	1.03	1.40	3700	1.93

[a] Hydroxylic functions per molecule.

The fraction of bifunctional species is

$$f_B = \frac{E_r - E_i}{E_r + E_i}$$

and the average hydroxylic functionality F simply:

$$F = 2f_B + (1 - f_B)$$

Gel Permeation Chromatography (GPC)

M_n and M_w/M_n ratio of raw samples and fractions were determined by GPC, with a WATERS 5900 instrument equipped with an ULTRASTYRAGEL set of columns (10^5–10^4–10^3–5×10^2 Å), at 30°C, using as solvent Delifrene–LS/acetone azeotropic mixture (8/2 v/v). As the calibration curve the one previously determined with ZDOL narrow fractions in the molecular weight range 1000–17000[5] was used.[5]

Fractionation

Distillation

ZDOL narrow fractions were obtained by vacuum distillation of the raw samples at 0.5×10^{-2} torr, with a gradual heating up to 300°C, using a 10-cm Vigreux column.

Solubility Fractionation

Fractionations of the raw samples were also carried out by liquid–liquid separation from 10% w/v Delifrene-LS solutions, by adding, as a rule, methanol as nonsolvent, at 30°C. They essentially followed the conventional procedure for high polymers, as already described in a preceding work for the same type of fluorinated oligomers.[6] Other nonsolvents were also used for the lowest molecular weights in order to try to obtain a sufficiently clear separation of the two phases (see Results).

Column Chromatography

Chromatographic separations were also performed in 2.5 and 7 cm (internal diameter) glass columns, filled with 150 and 250 g, respectively, of silica gel. Columns with different length–diameter ratios L/d (2, 4, 25) were intentionally used in the development of this work (see Results). The silica (Merck 9385) was washed with methanol, dried at 130°C, and then packed and conditioned in the elution solvent. The fluorinated samples, 20–30% w/w referred to silica, were loaded at the top of the columns, and eluted under moderate pressure (1.5 bar). The eluent vol-

ume was about 7 L; several portions of sample were collected according to the planned schemes.

RESULTS AND DISCUSSION

Fractional Distillation

Fractional distillation proved to be, in this case, a very simple and effective means of preparing fractions in a relatively wide range of M_n, having a narrow molecular weight distribution (average M_w/M_n = 1.14).

Table II reports the main data of the fractions obtained from the three base samples Z1, Z2, and Z3. M_n values up to about 5000 could be separated by simple vacuum distillation up to 300°C. This relatively high M_n value has to be related to a low cohesive energy of these oligomers, which was recognized as typical of perfluorinated polyethereal molecular chains.[7]

A slight, regular change can also be observed in the molecular p/q ratio and functionality F of the sequential fractions. These data cannot, however, be surely attributed to resolution in that they could derive from a possible relation between F and M_n of the base samples used.

Table II Molecular Characterization of the Fractions Obtained by Vacuum Distillation

Sample	Fraction	p/q	M_w/M_n	M_n	F
Z1	D11	0.97	1.21	750	1.93
	D12	0.95	1.10	850	1.95
	D13	0.93	1.08	1000	1.96
	D14	0.93	1.06	1250	1.96
	D15	0.91	1.07	1500	1.95
Z2	D21	0.98	1.18	750	1.99
	D22	0.97	1.10	1095	1.99
	D23	0.96	1.18	1395	1.97
	D24	0.95	1.13	1830	1.96
	D25	0.95	1.13	2200	1.95
	D26	0.94	1.13	2800	1.95
	D27	0.92	1.15	3410	1.94
	D28	0.91	1.10	3960	1.92
	D29	0.89	1.14	5020	1.89
	Residual	0.82	1.30	10100	1.77
Z3	D31	1.05	1.13	2250	1.96
	D32	1.05	1.12	2450	1.95
	D33	1.04	1.11	2950	1.94
	D34	1.04	1.13	3900	1.93
	D35	1.03	1.12	4250	1.94
	D36	1.03	1.12	5450	1.93
	Residual	1.01	1.28	11850	1.80

Table III Molecular Characterization of the Main Fractions Obtained by Solubility Fractionation

Sample	Fraction	p/q	M_w/M_n	M_n	F
Z1	P11[a]	0.94	1.18	1300	1.96
	P12[a]	0.94	1.25	950	1.96
Z2	P21	0.80	1.14	11450	1.75
	P22	0.84	1.15	7500	1.81
	P23	0.87	1.18	5650	1.85
	P24	0.92	1.17	3050	1.93
	P25	0.95	1.20	2150	1.95
	P26	0.96	1.14	1500	1.98
	P27[a]	0.97	1.16	900	1.99
Z3	P31	0.96	1.18	13000	1.74
	P32	0.99	1.13	10600	1.77
	P33	1.01	1.16	7950	1.82
	P34	1.02	1.13	5500	1.87
	P35	1.04	1.15	3250	1.96
	P36	1.04	1.15	2000	1.97

[a] Fraction obtained using dichloromethane as nonsolvents.

Solubility Fractionation

Good fractions were also prepared by fractional separation with the chosen solvent–nonsolvent system, however, in a range of molecular weights not below about 1500.

In Table III it may be seen that: (1) the average M_w/M_n index of the fractions is satisfactory (about 1.16); (2) the fractionation is very sensitive to molecular weight; (3) a noticeable, regular change is also observed for p/q and F, with the trend already seen in Table II for the fractional distillation; (4) the results of fractional distillation and solubility fractionation appear to be essentially equivalent (except for the possible range of the molecular weights).

With the procedure used for solubility fractionation, it has in fact been observed that, starting with a 10% (w/v) solution of the base samples in Delifrene–LS, and stepwise adding methanol, fractions of M_n from 13000 to 1500 were regularly separated. Below the latter value methanol, as well as predictably, other polar solvents like ethylacetate, acetone, and chloroform were not able to work as nonsolvent. Some results were on the contrary obtained by adding dichloromethane, with which very long times (likely due to the very small differences in density) and large nonsolvent amounts are, however, required to afford a clean separation of a sufficiently large amount of fractions. No practical results could be obtained using n-hexane as nonsolvent, due to the poor oligomer content invariably found in the separated hexonic phase.

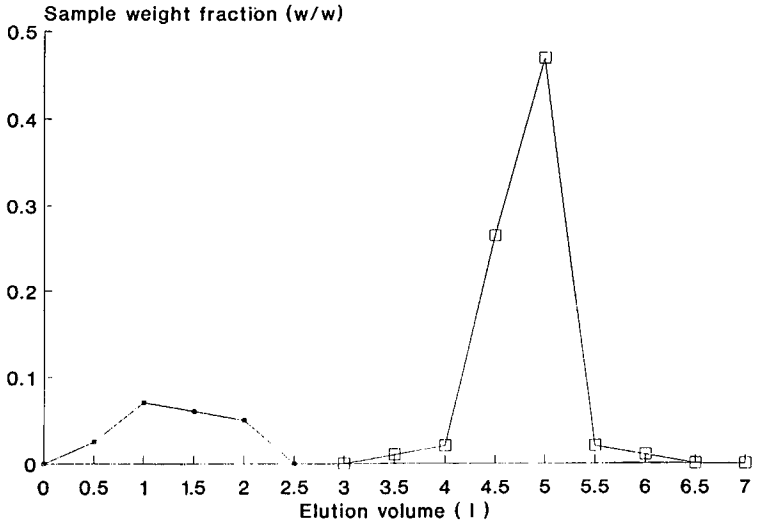

Figure 1 Elution profile of column chromatography of Z2 sample (■) eluted with Delifrene-LS, (□) eluted with Delifrene-LS–methanol 9/1 (v/v).

This behavior, i.e., a marked change of solubility when the molecular weight decreases below about 1000–1500, may appear to be peculiar to the examined class of oligomers. It is on the other hand interesting to recall that, with similar oligomers, marked changes have also been observed[6] of other physical properties (glass transition temperature, specific volume, and viscosity); and that this phenomenological feature can be generally attributed to a dominant "copolymer end effect."[6,8] This is due to the difference of chemical nature (in our case very marked) between body monomeric units and end units, whose concentration becomes dominant, in oligomeric systems, when the molecular weight is lowered below certain values.

Column Chromatography

Preliminary chromatographic experiments were performed in order to select suitable solvents, or solvent mixtures, as eluents.

Using a column with $L/d = 2$ and Delifrene-LS as eluent, all the base samples released a fraction (A) in a reasonable time; a second fraction (B), covering the remaining amount of the samples, could be released comparatively well only using a mixture Delifrene-LS–methanol 9/1 v/v, with a higher eluotropic power. Other binary eluent mixtures were also tested: Delifrene-LS with acetone, ethylacetate, dichloromethane, and chloroform, for which a decreasing eluotropic strength can be in the order estimated with a simplified method proposed by Snyder.[9] The above methanol-based eluent seemed, however, to be more effective.

Figure 1 shows, as an example, the two chromatographic bands of sample Z2. Table IV reports the data characterizing all the A and B fractions obtained, compared to those of the corresponding original base samples (Table I).

In these preliminary chromatographic separations the functionality F appears to play a more definite role, in spite of the relatively low efficiency of

Table IV Column Chromatography Separation of ZDOL Raw Samples

Sample	Fraction	wt %	p/q	M_w/M_n	M_n	F
Z1	—	100	0.94	1.28	1150	1.96
	A	10.7	0.93	1.20	1850	1.35
	B	89.3	0.94	1.12	1100	> 1.995
Z2	—	100	0.92	1.60	2150	1.95
	A	11.3	0.92	1.63	3500	1.36
	B	88.7	0.92	1.40	1950	> 1.995
Z3	—	100	1.03	1.40	3700	1.93
	A	22.0	1.02	1.34	6900	1.41
	B	78.0	1.03	1.25	3100	> 1.995

the column used. The bifunctional species are predominantly released in fractions B, which are practically pure, whereas the monofunctional ones are in fractions A, mixed to the remainder of the bifunctional ones. As for the molecular weights, Figure 2 shows, as an example, the analytical GPC bands of sample Z2 and its A and B fractions: fraction B, of the major amount, is monomodal, similar to the initial sample, whereas fraction A is clearly bimodal, likely because of different average molecular weights of the two mixed bifunctional and monofunctional species.

On the basis of these results, a more accurate chromatographic fractionation of greater amounts of base samples was then performed in two steps, according to the scheme reported, as an example, in Figure 3, relative to Z2 base sample. For this, the first step, made with a procedure similar to that described above, yielded two raw fractions: AA, wt % = 15, F = 1.49; and BB, wt % = 85, F = 2.0. The second step was a refractionation of both these fractions made with a more efficient column using pure Delifrene-LS as eluent for AA (d = 2.5 cm, L/d = 25), and a gradient elution for BB (d = 7 cm, L/d = 4), using Delifrene-LS–methanol mixtures with increasing eluotropic strength, i.e., containing from zero to 1/9 v/v methanol. The results of the whole operation may be seen in Figure 3.

The fractionation of sample BB appears to be very regular; it demonstrates that, at constant bifunctionality, the fractions are released in a decreasing order of molecular weight. This fact is easily understandable in terms of copolymer end effect in that it is reasonably due to the greater affinity of the polar end units, compared to that of the perfluorinated body, with the stationary phase: the molecules are eluted in order of increasing compositive ratio of end units, and therefore of decreasing molecular weight. Such a state of things might also be expressively described in terms of a "drawing effect" that, in every molecule, the "dissolved" molecular body exerts on its polar end units, "retained" by the stationary phase. Of course, in this case the fractionation could in practiced be favored by an appropriate parallel gradient increase of the solvent eluotropic power.

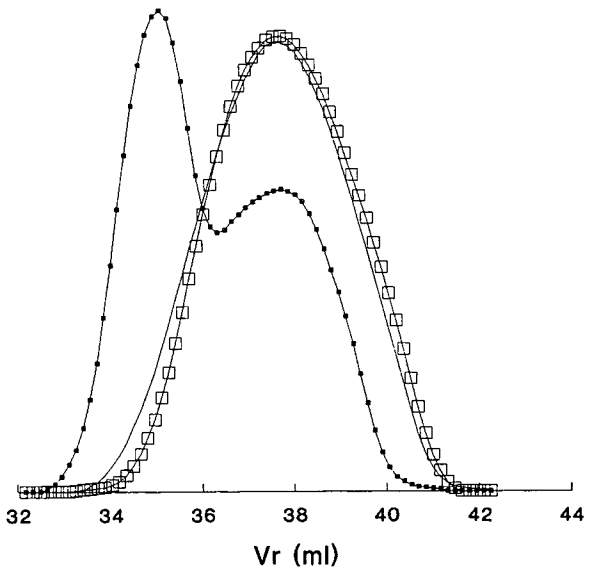

Figure 2 Analytical GPC chromatograms of (———) Z2 sample, (■) A fraction, (□) B fraction.

More complex, but equally understandable in terms of copolymer end effect, is the fractionation of sample AA. Fractions AA1 and AA4 happened to consist of pure mono and bifunctional species, respectively; their molecular weights are different, nevertheless in a way which can now be expected: in fact, for monofunctional species the drawing effect of the perfluorinated body had to be more effective than for bifunctional ones, so that, at not too dissimilar molecular weights, the former species were in fact eluted before.

Supporting evidence for this statement could be found in a deeper analysis of the mixed fraction AA3. Its GPC chromatogram, reported in Figure 4, demonstrates that it consisted of two clear-cut component fractions having very different molecular weights. These could be well separated by a subsequent solvent–nonsolvent fractionation of AA3: the first one consisted of essentially monofunctional species with M_n = 13,000 and F = 1.1; the second one of essentially bifunctional species with M_n = 2000 and F = 1.9.

CONCLUSIONS

The experimental results of the specific case considered in this work show that vacuum distillation and solubility fractionation separated the raw samples substantially in terms of molecular size. The two methods appear to be in some way complementary; in fact the former was more effective just in the molecular weight range where the fractional precipitation failed (M < 1500–2000). The adsorption chromatography, if properly used, allowed on the contrary a good separation both by molecular weight and by functionality, and it may be seen as a more versatile technique.

On the basis of the reported results, some interesting, more general considerations may also be done about fractionation problems of reactive oligomers.

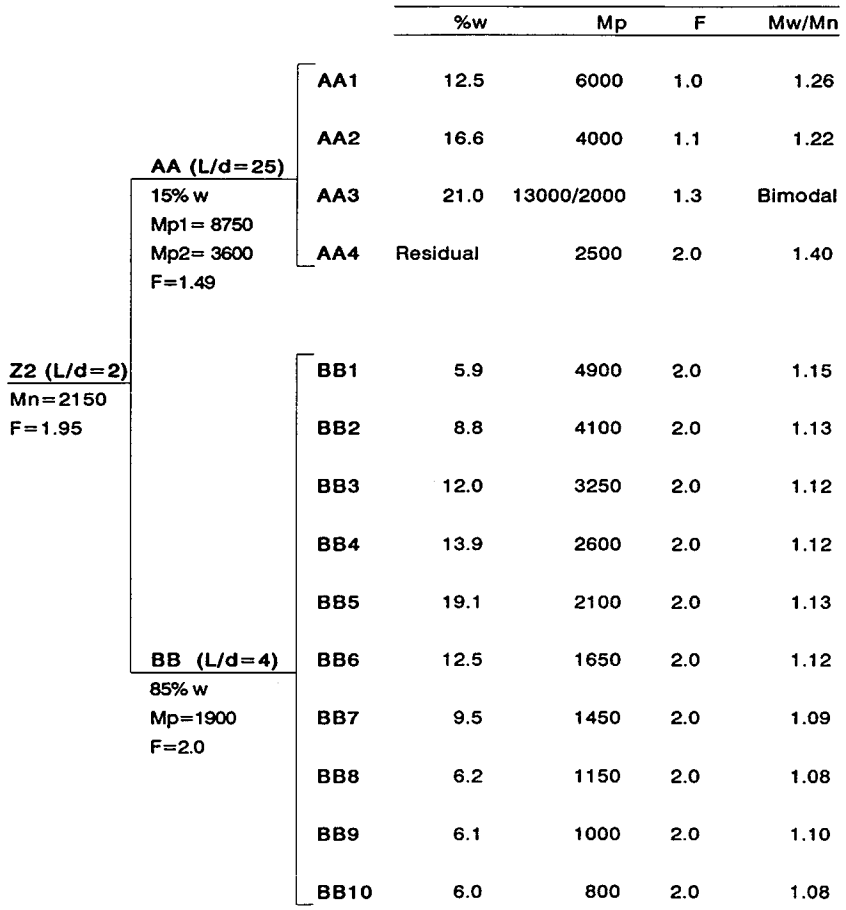

Figure 3 Chromatographic step-fractionation scheme relative to Z2 sample.

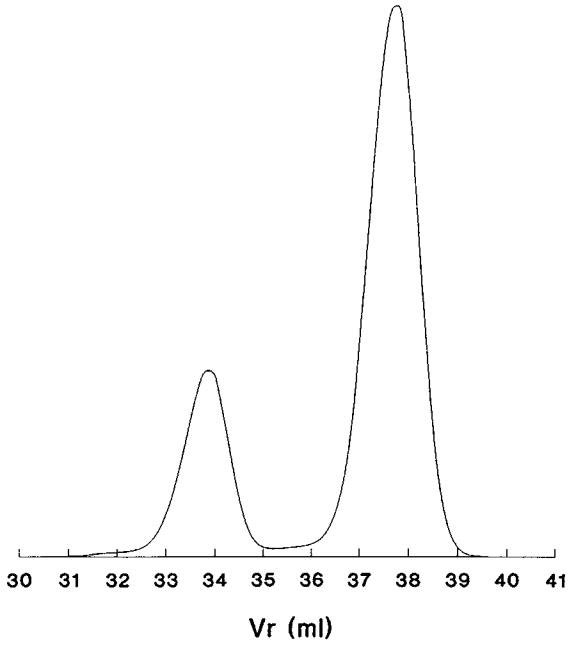

Figure 4 GPC chromatogram of AA3 fraction.

Clearly, when dealing with high polymers, molecular end unit effects are negligible, and fractionation techniques are applicable on the basis of properties that homogeneously depend on molecular weight. In oligomers, on the contrary, copolymer end effects are generally present, with a possible heterogeneous response of properties. In reactive oligomers they can indeed by particularly effective, due to a probably more marked chemical nature difference between functional end units and molecular body units. In addition the fractionation can in practice be further complicated by an heterogeneous influence of nature and relative amounts of different units present in the system, which is frequently a mixture of oligomers of different functionality. As a consequence, for every specific case of structural differences of the oligomeric species that have to be separated, an appropriate, balanced evaluation has to be done of the possible counteracting factors brought about by the changes of molecular composition bound to the changes of molecular weight.

The case of fluorinated oligomers presented in

this work is a particular, but an expressive, example of a practical situation, and the described results may offer suggestions for an appropriate simple or orderly combined use of known traditional fractionation techniques in other comparable cases.

The authors are indebted to Prof. F. Danusso, and to Prof. G. Gianotti for the helpful discussions regarding this present work. This work has been partially supported by University MURST (60%).

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Received February 23, 1994
Accepted July 20, 1994