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Viscosity *versus* molecular weight and temperature of diolic perfluoro-poly(oxyethylene-*ran*-oxymethylene) oligomers: role of the end copolymer effect

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Viscosity was measured at various temperatures (10-60°C), of a series of oligomer fractions constituted by a perfluoro-poly(oxyethylene-*ran*-oxymethylene) chain with two $-CH_2OH$ end units (FOMBLIN ZDOL®, Ausimont S.p.A.), with molecular weights ranging from 400 to 9050. An unusual non-monotonic trend of the η–M relation, which cannot be described by the typical Debye–Bueche equation $\eta = KM$ below M_c, has been observed at every temperature. An empirical equation $\eta = \eta(M,T)$ is simply derived, which provides a good quantitative description of the experimental results. From an end copolymeric view, this results in a simple composition equation, in which the logarithm of the ratio η/M is isothermally additive with regard to the weight fraction of end units of the members of the homologous series. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: viscosity; fluorinated oligomers; homologous series)

INTRODUCTION

In preceding papers[1–6] results were reported on fractionation, molecular characterization and some physical properties of series of random copolymer fractions having the following constitution with various end units E:

$$E - CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2 - E$$

which were obtained by end functionalization of oligomeric base samples having $E = -CH_2OH$.

The members of these series, characterized by a random disposition of the perfluorinated oxyethylene and oxymethylene units with a uniform p/q ratio around unity, are non-crystallizable liquids down to very low temperatures.

Of special interest appeared to be the dependence on the molecular weight of main physical properties, whose values, in the oligomeric range, are influenced by the chemical nature and content of the end units in the system.

In particular, isothermal viscosity (at 30°C) of two of these series was studied[2] in a molecular weight range from about 350 to 17 500, and for that possessing $E = -CH_2OH$ (ZDOL series) an unexpected non-monotonic behaviour was found with a minimum at a molecular weight of about 1100.

It is known that for the large majority of polymers the viscosity can be related to the molecular weight by the following exponential equation:

$$\eta = KM^a$$

and that, when M is lower than a critical value M_c, for the relevant theory the exponent a should be constant and equal to unity. Isothermal experimental measurements have, however, shown that for $M < M_c$ the linear dependence $\log\eta$–$\log M$ is not always strictly obeyed and that the parameter a may also be significantly different from unity[7–9].

The completely anomalous non-monotonic behaviour of the ZDOL series was attributed to the physico-chemical structure forming interactions of the alcoholic end units, which are chemically greatly dissimilar from the molecular body units[2].

In the present paper we report new experimental data of viscosity of fractions of the same ZDOL series, measured in a temperature range from 10 to 60°C. We will then suggest a possible way of interpretation of the peculiar viscosimetric behaviour of this series, leading to relations able to quantitatively describe the dependence of viscosity on molecular weight and temperature in the studied regions.

EXPERIMENTAL

Eight FOMBLIN ZDOL® samples were prepared by fractionation of some polydispersed base samples (kindly supplied by AUSIMONT S.p.A. Milan, Italy), following a procedure already described in preceding papers[5,10].

The molecular characterization of these samples was carried out by $^1H-^{19}F-^{13}C-NMR$ (Varian spectrometers) and GPC (Waters 5900) analyses, by which molecular weights, p/q and M_w/M_n ratios were determined following methods previously described[6,10]. The results are reported in *Table 1*. In subsequent calculations the M_n value will be used as M, being the polydispersity index of the samples fairly close to unity.

The rheological characterization of the samples was carried out by a stress-controlled dynamic rheometer (DSR Rheometrics Scientific), using parallel plates (40 mm diameter) with a 0.5 mm gap. Preliminary tests were performed in a shear rate range of $10-10^2\,s^{-1}$ (with

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Table 1 Molecular characteristics of the ZDOL fractions[a]

Fraction	M_n	M_w/M_n	p/q	w_E
F1	400	1.13	1.13	0.155
F2	510	1.20	1.26	0.122
F3	860	1.10	0.95	0.072
F4	2250	1.17	0.94	0.027
F5	3250	1.17	1.04	0.019
F6	3900	1.16	0.90	0.016
F7	4610	1.18	0.89	0.013
F8	9050	1.26	0.97	0.007

[a] M_n, M_w—number and weight average molecular weights; p/q—mole ratio of tetrafluorooxyethylene to difluorooxymethylene units; w_E—weight fraction of end units ($-CH_2OH$).

Table 2 Viscosities of the fractions of *Table 1* (in mPa s)

Fraction	10°C	20°C	30°C	40°C	50°C	60°C
F1	365	190	105	59	35	21
F2	325	170	93	53	31	19
F3	180	100	59	35	22	14
F4	205	125	77	49	33	22
F5	260	165	105	70	48	33
F6	260	165	110	73	50	36
F7	275	180	120	80	56	40
F8	450	290	195	135	94	68

corresponding stresses up to 10 Pa) at temperatures from 10 to 60°C. In these conditions the behaviour of all the samples was demonstrated to be substantially Newtonian. Definite viscosity measurements were then made at temperatures of 10, 20, 30, 40, 50 and 60°C.

RESULTS AND DISCUSSION

Table 2 reports the viscosities of the ZDOL fractions at every considered temperature. All the viscosity values are represented in a $\log\eta$–$\log M$ plot in *Figure 1*, which also includes previous experimental data[2] at 30°C, obtained by a capillary viscometer, of other various ZDOL fractions. Our present data confirm that the non-monotonic dependence on molecular weight is clearly exhibited in the whole temperature range considered.

As already mentioned, theory predicts that in the range of molecular weights lower than the critical M_c value, the $\log\eta$–$\log M$ relation should be represented by a straight line of unit slope; it is, however, well known that experimental results on various homologous series frequently show slopes different from unity and possibly non-constant. In any case, to our knowledge non-monotonic trends have never been previously reported.

For a further analysis of the data, it is usual to make reference to the simple Debye–Bueche theory on viscosity of polymers. By this, the viscosity can be expressed as[11]

$$\eta = \frac{r_0^2}{M}\frac{\rho A}{36}Nf \qquad (1)$$

where r_0^2 is the average square chain end-to-end distance, A is the Avogadro number, ρ is the density of polymer, M the molecular weight, N the number of chain segments per molecule and f is the so-called segmental friction factor. Following Bueche, at constant temperature, below M_c, in an homologous series ρ and f as well as r_0^2/M may be considered as roughly constant and N proportional to the molecular weight M[11]; consequently the viscosity should be (roughly) proportional to the first power of M, that is $\eta = KM$.

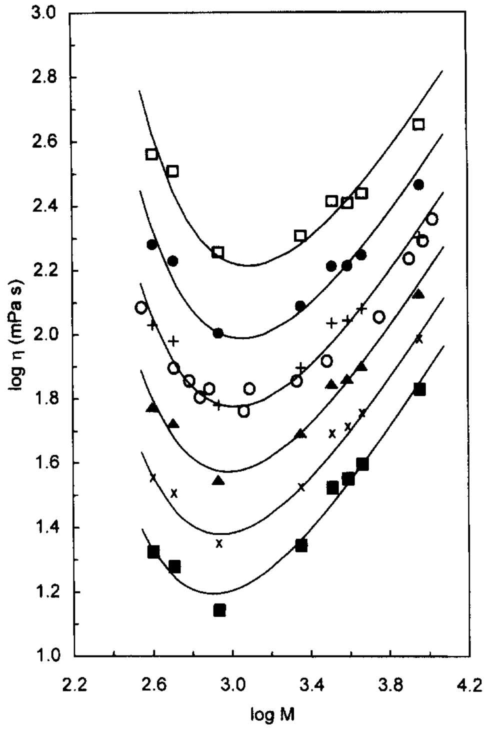

Figure 1 Logarithmic plot of viscosity *versus* molecular weight of the ZDOL fractions of *Table 1* at different temperatures: (□) 10°C; (●) 20°C; (+) 30°C; (▲) 40°C; (×) 50°C; (■) 60°C. Viscosity data of other ZDOL fractions at 30°C from a previous work[2] are also shown (○). Solid curves are calculated from equation (4).

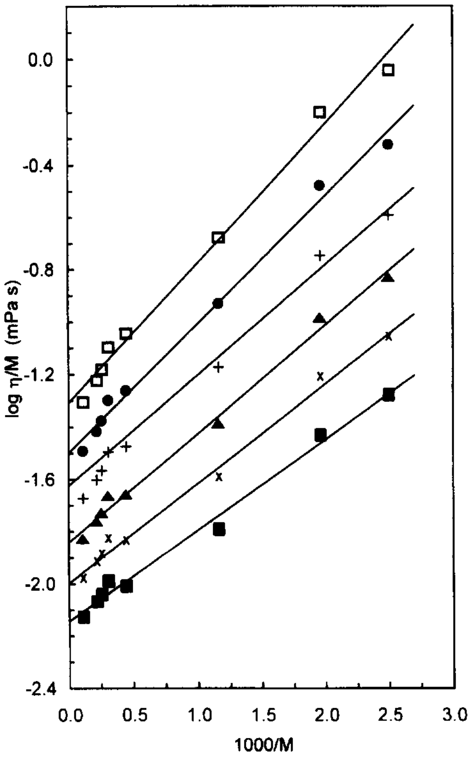

Figure 2 Plot of $\log(\eta/M)$ *versus* $1/M$. Straight lines according to equation (3a) and *Table 3* (data marks as in *Figure 1*).

The reason why the proportionality to M is not found to be experimentally true may be that r_0^2/M and ρ are in fact in some way functions of the molecular weight, and in particular that the friction factor f may be affected by a different behaviour of the end units, which in the oligomeric range becomes dominant with the decrease in molecular size.

Table 3 Calculated values of the parameters of equation (3a)

T (°C)	A	B
10	− 1.31	533
20	− 1.50	491
30	− 1.68	452
40	− 1.84	415
50	− 2.00	380
60	− 2.14	348

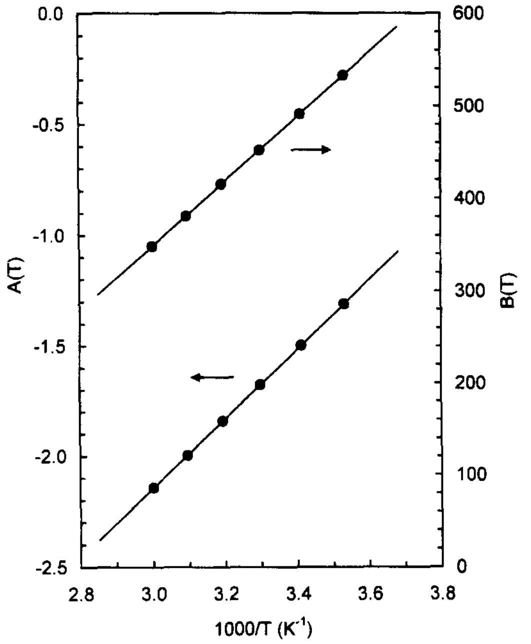

Figure 3 Dependence of parameters A and B of equation (3a) and *Table 3* on the inverse absolute temperature. Straight lines from best fitting of the data.

Now, by generally considering the possible dependence of viscosity on molecular weight and temperature, instead of equation (1) we can write

$$\eta = K(M,T)M \tag{2}$$

$K(M,T)$ being some function of M and T. It is then interesting to present, as a particular function, the ratio

$$\frac{\eta}{M} = K(M,T)$$

which can be directly calculated from the experimental data, and to find how it depends on M and T.

By plotting, as in *Figure 2*, the logarithm of η/M against $1/M$, it can be seen that, within a reasonable approximation, the outcome at every temperature is linearly dependent on $1/M$, i.e.

$$\log\left(\frac{\eta}{M}\right) = A(T) + \frac{B(T)}{M} \tag{3a}$$

The values of the parameters A and B, determined by linear regression at every temperature, are reported in *Table 3*. In *Figure 3* they are plotted as a function of the inverse absolute temperature $1/T$, and it may also be seen that here a linear relation results in a fairly good approximation, leading to the expressions

$$A(T) = a + \frac{b}{T},\ B(T) = c + \frac{d}{T}$$

with the following values of the constants: $a = -6.87$, $b = 1.57 \times 10^3$, $c = -697$, $d = 3.48 \times 10^5$.

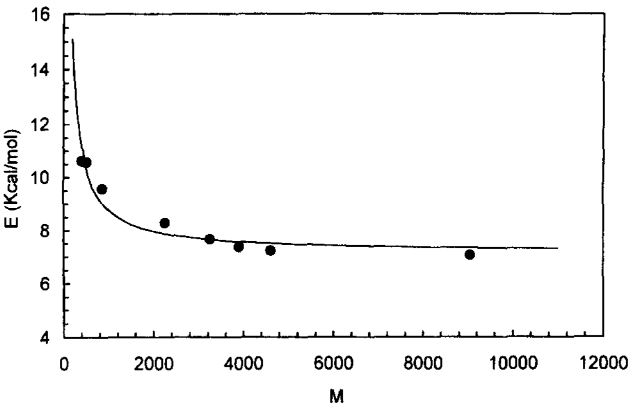

Figure 4 Activation energy of viscous flow of the ZDOL fractions *versus* molecular weight. Solid curve calculated from equation (6).

Thus, from equation (3a), we have the complete relation

$$\log\left(\frac{\eta}{M}\right) = \left(a + \frac{b}{T}\right) + \left(c + \frac{d}{T}\right)\frac{1}{M} \tag{3b}$$

and for the viscosity:

$$\log\eta = \left(a + \frac{b}{T}\right) + \log M + \left(c + \frac{d}{T}\right)\frac{1}{M} \tag{4}$$

which provides at every temperature a very good fit of the experimental data, as it can be seen in *Figure 1*.

Equation (4) can also be written in the Arrhenius type form:

$$\log\eta = \left(a + \log M + \frac{c}{M}\right) + \left(b + \frac{d}{M}\right)\frac{1}{T} \tag{5}$$

from which the dependence of the activation energy of viscous flow on molecular weight can be derived:

$$E = 2.3R(b + \frac{d}{M}) \tag{6}$$

In *Figure 4* the activation energy calculated by equation (6) is plotted against molecular weight. For comparison, the values directly determined by an Arrhenius plot from the experimental viscosity data of every fraction in the same temperature range 10–60°C are also reported.

The behaviour of the ZDOL series turns out to be quite unusual, since in the region of lower molecular weights the activation energy decreases with the increase of molecular weight. In the literature, only a few experimental data can be found on the dependence of the activation energy on molecular weight in homologous series of linear oligomers, but an increase with the molecular weight should normally be expected. This is for example the case of the well-studied series of poly(styrene)[8] and poly(dimethylsiloxane)[12]. The peculiar behaviour of the ZDOL series may clearly be attributed, as already pointed out in a previous paper[4] on thermovolumetric properties, to particular cohesive interactions due to the hydroxyl end groups, whose effect increases with the end units content.

An interesting interpretation of the observed dependence of viscosity on molecular weight can be obtained if we privilege an 'end copolymeric view'[1,3,4] of the structure of these oligomers.

Generally, the constitution of a linear oligomer (or polymer) series can be represented as:

$$\mathrm{E} - \mathrm{B}_{x-2} - \mathrm{E}$$

where B are the monomeric units of the molecular body (possibly in turn copolymeric, but with the more usual meaning of the term), and E the two (equal or different) end units, necessarily having more or less a different chemical structure from the body units. Any member of the series, of molecular weight M, can thus be considered as an 'end copolymer' of units B and E, belonging to a system having two extreme homocomponents: the pure infinite homopolymer B_∞ and the dimer E_2 (of molecular weight $2M_E$). The composition of any oligomer may then be suitably expressed by the end units weight fraction $w_E = 2M_E/M$ (see *Table 1*), or by the complementary body units weight fraction $w_B = 1 - w_E$.

Following this line of reasoning, in our case equation (3b) may be rewritten as

$$\log\left[\frac{\eta}{M}\right] = \left(a + \frac{b}{T}\right) + \left(c + \frac{d}{T}\right)\frac{w_E}{2M_E} \qquad (7)$$

from which, for $M = \infty$ ($w_E = 0$), that is for the pure infinite homopolymeric component, the function

$$\log\left[\frac{\eta}{M}\right]$$

takes the limiting value

$$\log\left[\frac{\eta}{M}\right]_{B_\infty} = \left(a + \frac{b}{T}\right) \qquad (8)$$

and for $M = 2M_E$ ($w_E = 1$), that is for the dimeric E_2 component,

$$\log\left[\frac{\eta}{M}\right]_{E_2} = \left(a + \frac{b}{T}\right) + \left(c + \frac{d}{T}\right)\frac{1}{2M_E} \qquad (9)$$

By substitution, from equation (7) the following simple end copolymeric composition equation of the series under study can finally be obtained:

$$\log\left[\frac{\eta}{M}\right] = w_B \log\left[\frac{\eta}{M}\right]_{B_\infty} + w_E \log\left[\frac{\eta}{M}\right]_{E_2} \qquad (10)$$

which endows the function η/M with a particular significance, deserving further study.

It is to note that, following a Bueche's approximation[11], itis frequently assumed that the deviations from the simple η–M law, below M_c, may be substantially attributed to the non-constancy of the friction factor, whose variability with the molecular weight, due to the presence of the end units, is expected to be largely predominant on that of the parameters ρ and r_0^2/M of equation (1). Under this assumption, at constant temperature the friction factor can be considered as proportional to the ratio η/M, so that equation (3a) gives its dependence on the molecular weight, and the end copolymeric composition equation (7) may be substantially interpreted in terms of friction factor.

A final consideration may be of some interest. The value of

$$\left[\frac{\eta}{M}\right]_{E_2}$$

as given by equation (9), should correspond to that of the extreme dimeric component E_2, which in our case is formally ethylene glycol. In fact, the viscosity value obtainable by equation (9) (for ex. at 20°C about 4.09×10^4 mPa s) is different from that directly measurable for ethylene glycol (19.8 mPa s). A similar behaviour has already been observed[4] for the end copolymeric composition equations derived for the specific volume and glass transition temperature of the same homologous series. It is clearly due to the great chemical nature difference between units B and E, whose interactions pass from a regime of dominant E–B to one of dominant E–E interactions, so that a severe change of trend for certain properties has to be expected towards the lowest oligomers. In other words,

$$\left[\frac{\eta}{M}\right]_{E_2}$$

of equation (9) has to be considered as a traditionally defined 'apparent quantity', whose value has to be in this case referred to the physical state of end units E completely subjected to E–B interactions, i.e. of units E completely surrounded by B units. This state is clearly different from that of units E completely subjected to E–E interactions.

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