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Molecular Interactions in Perfluorinated and Hydrogenated Compounds: Linear Paraffins and Ethers

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ABSTRACT: The cohesive energy density (CED) of linear hydrogenated and perfluorinated paraffins and ethers has been investigated with regards to its dependence on chain length and oxygen content. For high molecular weight compounds (i.e., polymers) the CED has been obtained by extrapolation or by the group contribution method. The oxygen contribution to cohesive energy is found to be very different in the hydrogenated ethers with respect to the perfluorinated ones, and, correspondingly, the dependence of CED on the oxygen to carbon ratio (O/C) is the opposite for the two series. A similar trend, previously described for the glass transition temperature (T_g) is therefore roughly interpretable as related mostly to CED, although intramolecular flexibility parameters also play a role.

Introduction

The genesis of the present work can be traced to the results of our research group in which the molecular weight and composition dependences of some physical properties of different linear perfluoropolyethers have been reported.[1-3] A typical family recently investigated is represented by the linear perfluorocopolyethers $CF_3[(OCF_2CF_2)_p(OCF_2)_q]OCF_3$ (Fomblin Z) first described by Sianesi et al.[4]

A peculiar result of the above work is that the glass transition temperature (T_g) of the fluorohomo- and fluorocopolymers (at infinite molecular weight) decreases regularly with an increase in the oxygen to carbon ratio (O/C) of the copolymer, the limiting value for O/C = 0 [corresponding to poly(tetrafluoroethylene) (PTFE)] being about 200 K and that extrapolated for O/C = 1 (the homopolymer $(CF_2O)_n$, never studied up to now) being 120 K, as shown in Figure 1.[2] Since T_g is interpreted as a parameter which is mostly dependent on chain flexibility and/or molecular interactions, the influence of an increasing oxygen content on T_g appears to be of interest, and a comparison with similar data relative to the correspondent hydrogenated polyethers, also shown in Figure 1, reveals indeed the peculiarity of the perfluorocopolymers' behavior.

As a matter of fact, when the group contribution analysis is applied to the glass transition of the homologous series, one obtains a negative contribution for the ethereal oxygen in perfluoropolyethers, while for the hydrogenated compounds the group contribution is positive.[2]

In the present paper, we report the results of additional studies carried out on the above polymers by measuring or calculating the molecular weight and composition dependence of the enthalpy of vaporization (ΔH_v) and the related cohesive energy density (CED) and by comparing with different families of perfluorinated and hydrogenated linear compounds. The aim of the work is that of clarifying the role played by fluorine and oxygen in the intra- and intermolecular interactions of the above perfluoro linear-chain compounds.

Experimental Section and Methods

The synthesis, fractionation, and characterization of the perfluorinated linear Fomblin copolymers, as well as the characterization of polymers belonging to similar families, have been described previously.[1-3] The values of T_g plotted in Figure 1 refer to polymers of very large (infinite) molecular weight. For polyethylene, the T_g datum corresponds to the experimental dynamic-mechanical value found by Lam and Geil[5] for a wholly amorphous ultraquenched linear sample. The T_g pertaining to different hydrogenated polyethers were gathered from the work of Cheng,[6] Williams,[7,8] and Read.[9] For PTFE, the T_g is given by Cheng[6] as 200 K and is the approximate midpoint of a rather broad calorimetric glass transition. The same value can be obtained by extrapolation of the perfluoropolyoxide data plotted in the same figure. The difference between the two series of polymers appears to be striking.

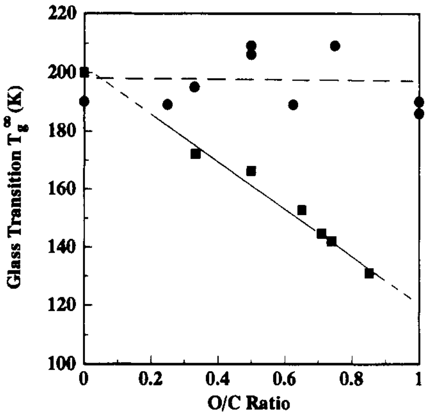

Figure 1. Composition dependence of the glass transition temperature (T_g) for two series of polyethers: (●) hydrogenated polyethers, copolyethers, and polyethylene; (■) perfluorinated polyethers, copolyethers, and poly(tetrafluoroethylene).

According to theoretical models, the glass transition of polymers of high molecular weight ($M = \infty$) should be directly related to various thermodynamic or molecular parameters,[10-14] which are considered to be representative of inter- and intramolecular interactions.

The most important intermolecular thermodynamic parameter is the vaporization enthalpy (ΔH_v), which however is difficult to measure with the accuracy required for structural interpretation and cannot anyway be measured for high molecular weight substances, for which therefore it must be calculated.[15] Directly related to ΔH_v is the well-known cohesive energy density CED, defined as:

$$\mathrm{CED} = \frac{\Delta H_v - RT}{V_m} \qquad (1)$$

where V_m is the molar volume.

A simple way of obtaining the CED value of a high molecular weight polymer is that of extrapolating it from the known CED of low molecular weight compounds belonging to a homologous

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Table I
Properties of Hydrogenated Compounds

N	O/C	formula	T_b (K)	ΔH_v^{298} (kJ/mol)	ΔH_v^{298} (kJ/mol)[a]	ρ (g/cm^3)	ref 37
(a) Ethers							
3	0.50	$(CH_3)_2O$	248.3	19.30	19.1		a, e, –
4	0.33	$CH_3OCH_2CH_3$	280.6	26.70	23.24	0.725	a, c, c
5	0.25	$CH_3CH_2OCH_2CH_3$	307.6	27.37	27.11	0.714	a, e, c
5	0.25	$CH_3OCH_2CH_2CH_3$	311.7	27.90	27.73	0.738	a, e, c
5	0.67	$CH_3OCH_2OCH_3$	315.0		28.21	0.860	a, –, c
6	0.50	$CH_3OCH_2CH_2OCH_3$	358.0	36.47	35.31	0.863	a, e, c
6	0.20	$CH_3CH_2OCH_2CH_2CH_3$	336.4	31.57	31.64	0.739	a, e, c
6	0.20	$CH_3(CH_2)_3OCH_3$	343.3	32.53	32.79	0.744	a, e, c
7	0.17	$CH_3(CH_2)_4OCH_3$	372.0	36.91	37.82	0.767	e, e, c
7	0.40	$CH_3CH_2O(CH_2)_2OCH_3$	375.2	39.87	38.41	0.853	e, e, c
7	0.17	$CH_3CH_2O(CH_2)_3CH_3$	365.4	36.41	36.63	0.749	a, e, c
7	0.17	$CH_3(CH_2)_2O(CH_2)_2CH_3$	363.2	35.79	36.23	0.736	a, e, c
7	0.40	$CH_3CH_2OCH_2OCH_2CH_3$	360.5	35.74	35.75	0.832	a, e, c
8	0.33	$CH_3O(CH_2)_2OCH_2CH_2CH_3$	397.7	43.67	42.68	0.847	e, e, f
8	0.14	$CH_3O(CH_2)_5CH_3$	399.2	42.10	42.97	0.772	e, e, f
8	0.14	$CH_3CH_2O(CH_2)_4CH_3$	390.7	41.06	41.32	0.762	e, e, c
8	0.33	$CH_3CH_2O(CH_2)_2OCH_2CH_3$	392.5	43.27	41.67	0.848	e, e, c
9	0.50	$CH_3CH_2O(CH_2O)_2CH_2CH_3$	413.7	44.70	45.88		e, e, –
9	0.29	$CH_3(CH_2)_3OCH_2CH_2OCH_3$	419.7	47.84	47.11		e, e, –
9	0.29	$CH_3CH_2O(CH_2)_3OCH_2CH_3$	413.7	45.92	45.88		e, e, –
9	0.29	$CH_3CH_2O(CH_2)_2O(CH_2)_2CH_3$	406.7	46.80	44.46		e, e, –
9	0.13	$CH_3(CH_2)_6OCH_3$	424.2	46.92	48.04	0.786	c, e, c
9	0.13	$CH_3(CH_2)_2O(CH_2)_4CH_3$	405.2	42.81	44.16		e, e, –
9	0.13	$CH_3(CH_2)_3O(CH_2)_3CH_3$	413.0	45.00	45.73	0.769	a, e, c
9	0.50	$CH_3O(CH_2CH_2O)_2CH_3$	435.0		50.29	0.927	d, –, d
10	0.25	$CH_3(CH_2)_2OCH_2CH_2OCH_2CH_3$		50.94			–, e, –
10	0.25	$CH_3(CH_2)_2OCH_2CH_2O(CH_2)_2CH_3$		50.62			–, e, –
10	0.11	$CH_3O(CH_2)_7CH_3$		52.29			–, e, –
10	0.11	$CH_3(CH_2)_3O(CH_2)_4CH_3$		49.41			–, e, –
11	0.22	$CH_3(CH_2)_3OCH_2CH_2O(CH_2)_2CH_3$		54.68			–, e, –
11	0.10	$CH_3O(CH_2)_8CH_3$		57.13			–, e, –
11	0.10	$CH_3CH_2O(CH_2)_7CH_3$	459.3	55.62	55.69	0.785	c, e, c
11	0.10	$CH_3(CH_2)_4O(CH_2)_4CH_3$	463.0	54.50	56.54	0.783	c, e, c
11	0.38	$CH_3CH_2O(CH_2CH_2O)_2CH_2CH_3$	458.0		55.36	0.909	d, –, d
12	0.20	$CH_3(CH_2)_3OCH_2CH_2O(CH_2)_3CH_3$		58.76			–, e, –
12	0.09	$CH_3O(CH_2)_9CH_3$		62.30			–, e, –
12	0.09	$CH_3CH_2O(CH_2)_8CH_3$		60.34			–, e, –
12	0.50	$CH_3O(CH_2CH_2O)_3CH_3$	489.0		62.61	0.986	d, –, d
13	0.08	$CH_3CH_2O(CH_2)_9CH_3$		65.89			–, e, –
13	0.08	$CH_3(CH_2)_5O(CH_2)_5CH_3$	499.6	64.10	65.25	0.794	a, e, c
15	0.25	$(CH_3(CH_2)_3OCH_2CH_2)_2O$	529.0		72.68	0.885	d, –, d
(b) *n*-Paraffins							
1		CH_4	111.6				a, –, –
2		C_2H_6	184.6	9.76	12.48		a, e, –
3		C_3H_8	231.1	16.25	17.11		a, e, –
4		C_4H_{10}	272.7	21.05	22.18		a, b, –
5		C_5H_{12}	309.2	26.75	27.35	0.626	a, e, c
6		C_6H_{14}	341.9	31.73	32.55	0.660	a, e, c
7		C_7H_{16}	371.6	36.66	37.75	0.684	a, e, c
8		C_8H_{18}	398.8	41.53	42.90	0.703	a, e, c
9		C_9H_{20}	424.0	46.43	48.00	0.718	a, e, c
10		$C_{10}H_{22}$	447.3	51.39	53.01	0.730	a, e, c
11		$C_{11}H_{24}$	469.1	56.43	57.94	0.740	a, e, c
12		$C_{12}H_{26}$	489.5	61.51	62.78	0.749	a, e, c
13		$C_{13}H_{28}$	508.7	66.43	67.49	0.756	a, e, c
14		$C_{14}H_{30}$	526.7	71.30	72.13	0.763	a, e, c
15		$C_{15}H_{32}$	543.8	76.11	76.67	0.769	a, e, c
16		$C_{16}H_{34}$	560.0	81.39	81.10	0.773	a, e, c
17		$C_{17}H_{36}$	575.2	86.02	85.33	0.777	a, e, c
18		$C_{18}H_{38}$	589.5	90.71	89.52	0.777	a, b, c
19		$C_{19}H_{40}$	603.1	95.72	93.55	0.777	a, b, c

[a] ΔH_v^{298} values calculated from eq 2.

series. For example, CED data on linear paraffins of increasing chain length may constitute the basis for calculating the CED of polyethylene.

In the present work, CED values were obtained for the following series of chemically different compounds: (a) linear paraffins, (b) linear perfluorinated paraffins, (c) linear ethers, and (d) linear perfluorinated ethers and polyethers.

To obtain the CED value for each compound at 298 K, both the ΔH_v^{298} and the molar volume V_m at the same temperature are needed. The above data were generally taken from the literature (see Tables I and II), and were first used to derive, following the suggestion of Hildebrand and Scott,[15] an empirical relation between ΔH_v^{298} and the boiling point (T_b), a relation which is common to the four series examined here and which is shown in Figure 2.

Analytically, the above empirical relation is given, in the range of T_b from 180 to 630 K, by the equation:

$$\Delta H_v^{298} = 4.914 - 0.00573T_b + 0.000253T_b^2 \qquad (2)$$

(ΔH in kJ/mol, standard error 1.340 kJ/mol) which has been obtained by a least-squares regression of 52 experimental couples of ΔH_v^{298} and T_b data, given in Tables I and II.

Table II
Properties of Perfluorinated Compounds

N	O/C	formula	T_b (K)	ΔH_v^{298} (kJ/mol)	ΔH_v^{298} (kJ/mol)[a]	ρ (g/cm^3)	ref 37
			(a) Ethers				
3	0.50	$(CF_3)_2O$	214.0		15.27		h, –, –
5	0.25	$CF_3CF_2OCF_2CF_3$	274.0		22.33		h, –, –
5	0.66	$CF_3OCF_2OCF_3$	263.0	19.75	20.92	1.411	t, t, –
6	0.20	$CF_3(CF_2)_3OCF_3$	309.0		27.30	1.590	h, –, h
6	0.50	$CF_3OCF_2CF_2OCF_3$	289.7		24.49		m, –, –
7	0.17	$CF_3(CF_2)_2O(CF_2)_2CF_3$	329.0		30.41		l, –, –
8	0.14	$CF_3(CF_2)_5OCF_3$	355.0		34.76	1.750	h, –, h
8	0.33	$CF_3CF_2OCF_2CF_2OCF_2CF_3$	349.0		33.73		n, –, –
9	0.29	$CF_3CF_2O(CF_2)_3OCF_2CF_3$	364.0		36.35		n, –, –
9	0.50	$CF_3O(CF_2CF_2O)_2CF_3$	334.5		31.31		n, –, –
9	0.13	$CF_3(CF_2)_3O(CF_2)_3CF_3$	375.0	40.55	38.46	1.710	h, k, h
10	0.25	$CF_3CF_2O(CF_2)_4OCF_2CF_3$	379.0		38.08		n, –, –
10	0.43	$CF_3O(CF_2CF_2O)_2CF_2CF_3$	358.0		35.29		p, –, –
11	0.22	$CF_3CF_2O(CF_2)_5OCF_2CF_3$	393.0		41.74		n, –, –
11	0.38	$CF_3CF_2O(CF_2CF_2O)_2CF_2CF_3$	371.0		37.61	1.630	h, –, h
11	0.10	$CF_3(CF_2)_4O(CF_2)_4CF_3$	412.0	47.23	45.53	1.780	h, k, h
12	0.50	$CF_3O(CF_2CF_2O)_3CF_3$	378.0		38.90		p, –, –
13	0.44	$CF_3O(CF_2CF_2O)_3CF_2CF_3$	391.0		41.35		p, –, –
13	0.08	$CF_3(CF_2)_5O(CF_2)_5CF_3$	452.0		54.01	1.810	h, –, h
15	0.50	$CF_3O(CF_2CF_2O)_4CF_3$	411.0		45.30		q, –, –
16	0.45	$CF_3O(CF_2CF_2O)_4CF_2CF_3$	420.0		47.14		p, –, –
18	0.50	$CF_3O(CF_2CF_2O)_5CF_3$	437.0		50.73		p, –, –
19	0.46	$CF_3O(CF_2CF_2O)_5CF_2CF_3$	447.0		52.90		p, –, –
21	0.50	$CF_3O(CF_2CF_2O)_6CF_3$	459.0		55.59		r, –, –
22	0.47	$CF_3O(CF_2CF_2O)_6CF_2CF_3$	466.5		57.30		r, –, –
			(b) n-Paraffins				
1		CF_4	145.1				a, –, –
2		C_2F_6	194.9				a, –, –
3		C_3F_8	236.5		17.71	1.350	a, –, g
4		C_4F_{10}	271.2	23.32	21.98	1.543	a, i, g
5		C_5F_{12}	302.4	28.45	26.33	1.620	a, j, g
6		C_6F_{14}	329.8	31.73	30.56	1.680	a, j, g
7		C_7F_{16}	355.6	36.36	34.89	1.733	a, k, g
8		C_8F_{18}	376.0	40.96	38.55	1.770	g, k, g
9		C_9F_{20}	396.0		42.32	1.800	g, –, g
10		$C_{10}F_{22}$	417.2		46.56		s, –, –
11		$C_{11}F_{24}$	433.8		50.04		s, –, –
12		$C_{12}F_{26}$	448.0		53.03		g, –, –
13		$C_{13}F_{28}$	467.5		57.53		s, –, –
16		$C_{16}F_{34}$	512.0		68.30		s, –, –

[a] ΔH_v^{298} values calculated from eq 2.

The basis of the correlation and its limits is clearly discussed in the volume of Hildebrand and Scott,[15] where a similar equation, obtained by the above authors for a variety of chemical compounds, was also given. Lawson et al.[16] recently have published a slightly different equation based on 19 perfluorinated compounds. Both are shown for the purpose of comparison in Figure 2. It has to be noted that they differ sensibly from our relation only at the extremes of the ΔH_v^{298} and T_b ranges.

For some fractionated copolyethers belonging to the Fomblin Z family, for which no ΔH_v^{298} data are available, they were evaluated experimentally from the T dependence of the vapor pressure via the well-known Antoine equation with the procedure suggested by Fishtine.[17]

The samples used were found to be substantially very little disperse by high-resolution gas-chromatographic analysis in the sense that peaks of the main component and of the neighboring oligomers, differing no more than 20–30 units in molecular weight, were well resolved, the main peak area being equal or higher than 80% of the total area.

The range of experimental P–T data was such that it was unnecessary to apply the correction for nonideal gases; the maximum error arising from this approximation was estimated to be equal or lower than 1.5% in the vaporization enthalpy value. The results are collected in Table III; a comparison with the relative values calculated from T_b via eq 2 shows a reasonable agreement.

Table III
Properties of PFPE $[CF_3O(CF_2CF_2O)_p(CF_2O)_qCF_3]$
Narrow Fractions

N	O/C	p/q	T_b (K)	ΔH_v^{298} (kJ/mol)	ΔH_v^{298} (kJ/mol)[a]	ρ (g/cm^3)
18.5	0.58	2.70	451	61 ± 2	54	1.737
19.9	0.67	0.97	459	60 ± 2	56	1.739
20.7	0.64	1.26	471	61 ± 2	59	1.743
21.8	0.64	1.25	480	68 ± 3	61	1.746

[a] ΔH_v^{298} values calculated from eq 2.

Results and Discussion

The boiling point T_b is basically determined by the forces of molecular attraction within the saturated liquid and the vapor phases. For the compound families here examined, no strong hydrogen bonds should be present, association in the gas and liquid phase should not play a major role, and the intermolecular forces present should be therefore mostly of the van der Waals and dipole–dipole types. The dependence of T_b on structure can be interesting, and a plot of T_b against the number of backbone chain atoms N for the four different series is shown in Figure 3.

It is seen that all the linear hydrogenated and perfluorinated compounds for which $N \leq 4$ lie on the same T_b–N line, so that the fluorine and hydrogen atoms appear to be interchangeable. As observed by Liebman[18] "both atoms are small, univalent, and contribute rather little to total molecular polarizabilities".

It has to be noted that, for partially fluorinated hydrocarbons, intermolecular hydrogen bonding with

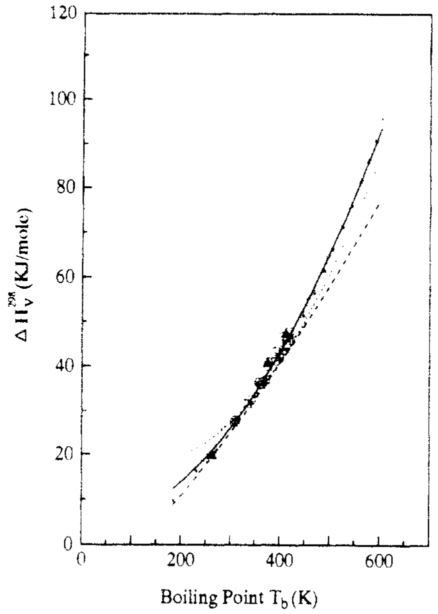

Figure 2. Relation between experimental standard vaporization enthalpies (ΔH_v^{298}) and boiling points (T_b) for 52 compounds belonging to the four series investigated: (*) paraffins, (□) ethers, (○) perfluoroparaffins, (▲) perfluoroethers. The relations of Hildebrand and Scott (dashed line)[15] and of Lawson et al. (dotted line)[16] are also shown.

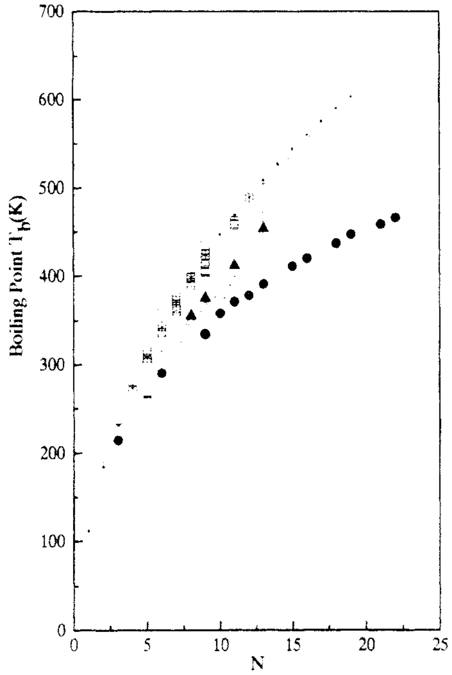

Figure 3. Boiling point (T_b) as a function of the chain atoms number (N) for 89 linear molecules: (*) paraffins, (□) ethers, (○) perfluoroparaffins, and perfluoroethers having an O/C ratio ≈ 0.11 (▲), ≅ 0.25 (△), ≅ 0.44 (●), ≅ 0.66 (▬).

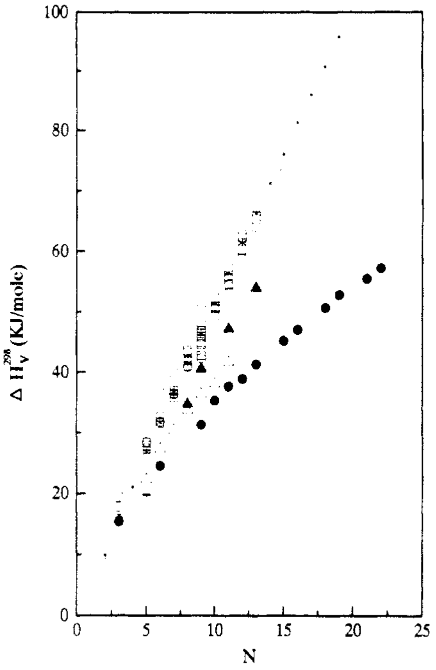

Figure 4. Standard vaporization enthalpy (ΔH_v^{298}) as a function of the chain atoms number (N) for 96 linear molecules (see Tables I and II). Symbol key as in Figure 3. 62 points are experimental, and 34 are calculated from eq 2.

fluorine is present, and T_b is strongly affected.[19] For the normal paraffins and the hydrogenated ethers (containing up to four oxygen atoms in the chain), the T_b–N relation is substantially identical up to $N = 15$, so that the boiling point appears to depend only on N and not on the oxygen atoms number and position within the straight chain.

The perfluoroparaffins, for which data are available up to $N = 16$, have T_b lower than the corresponding paraffins for N larger than 5, the difference increasing with increasing N, and the above-mentioned Liebman's notation cannot be extended to such long molecules. As far as the perfluorinated ethers are concerned, it is clearly seen that, at a given chain atom number N, the boiling point T_b is lower than that of the fluoroparaffinic compound, and the more so the higher the oxygen content and the length of the chain, the difference of T_b being about 90 °C when $N = 16$ and O/C = 0.45.

The data plotted in Figure 3 can be briefly summarized as follows. For linear-chain molecules with $N > 5$:

(1) The presence of oxygen atoms in the chain does not modify strongly the intermolecular forces in the paraffin series; i.e., the atom of oxygen acts largely as a substitute of the CH_2 group.

(2) The substitution of all the H atoms with F atoms in the alkane series results in a lowering of T_b, the difference increasing with increasing N, indicating that for long-chain molecules, at constant chain length, the forces of attraction between fluoroparaffins are lower than those between hydroparaffins.

(3) The presence of oxygen atoms in the perfluoroparaffinic chain strongly decreases the intermolecular attractive forces, the effects increasing with oxygen content and chain length.

Given the close correspondence between boiling points and standard enthalpies of vaporization at 298 K (Figure 2, eq 2), the plot of ΔH_v^{298} vs N shown in Figure 4 gives, of course, the same information with regard to the structural dependence of intermolecular forces. It may be interesting to note that for hydroparaffins and their ethers, ΔH_v^{298} is a linear function of N which extrapolates to the origin of the axes; again for perfluoroparaffins and their ethers the vaporization enthalpies are lower than those of hydrocarbons, the difference being an increasing function of the oxygen to carbon ratio O/C and of the number of chain atoms N. As an example, when $N = 16$, the perfluoroether with O/C = 0.45 has ΔH_v^{298} which is 31% lower than that of the corresponding perfluoroparaffin.

While ΔH_v^{298} is a measure of the intermolecular energy that binds a whole molecule to its neighbors and includes the volume work RT, the cohesive energy density CED (eq 1) measures the intermolecular energy of the unit volume of liquid and is more appropriate for fundamental comparisons.[15]

For some of the samples whose data are collected in Tables I and II and for the perfluoropolyethers described

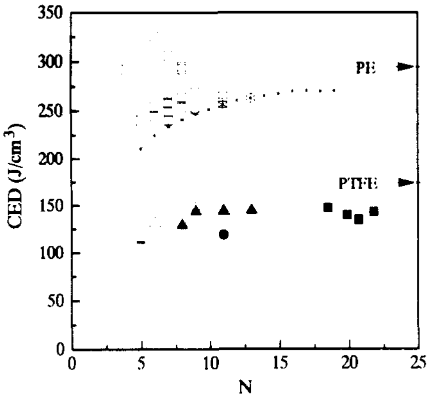

Figure 5. Cohesive energy density (CED) as a function of the number of chain atoms (*N*) for some selected compounds. Key of symbols as in Figure 3; data for perfluoropolyethers (■) (see Table III) are also shown. CED data for PE and PTFE were extrapolated from hydro- and fluoroparaffins (see text).

in Table III, i.e., for those compounds for which density data at 298 K are available, CED values have been calculated and are plotted, as a function of *N*, in Figure 5. The CED data of hydrogenated ethers at low values of *N* are rather scattered, being higher than those of the paraffins. The latter, after an initial increase, level off. A similar increase of CED with increasing *N* is found for fluoroparaffins.

Arrows indicate, on the right-hand side, the CED of polyethylene and poly(tetrafluoroethylene) obtained by linear extrapolation at $N \rightarrow \infty$ of the CED vs $1/N$ plot of the corresponding homologue series data. For PE and PTFE the CED values obtained by extrapolation (295 and 173 J/cm^3, respectively) are close to those obtained from experimental values of the respective solubility parameters[20] and practically identical to those obtained via the group contribution method of the same author.[20]

The few data pertaining to perfluoropolyethers appear indicative of the fact that the presence of oxygen, in lieu of CF_2 groups, in the main chain, has a small influence on CED, lowering it.

The relevant fact of Figure 5 is that the CED of linear perfluorocarbons of sufficiently high molecular weight appears to be much lower (ca. 0.6 times) than that of the corresponding hydrocarbons, independent from the presence of oxygen atoms in the main chain.

The greater van der Waals radius of fluorine and the greater polarity of the C–F bond,[21] due to the strong electron-withdrawing power of the F atoms, are usually invoked as an explanation of the difference between hydroparaffins and fluoroparaffins. In hydrocarbons not only H–H interactions but also H–C and C–C interactions are present, due to the small radius of the H atom, and the concentration of "molecular centers" among which the attractive forces are active is larger. The critical parameters are indicative: the critical density of hydroparaffins is 0.6 times that of fluoroparaffines, and this ratio (at the respective critical temperatures) is close to the ratio of the corresponding CED.[22]

In order to analyze the influence of oxygen independently from that of chain length, one has to consider samples of high chain length, i.e., high polymers, for which of course no experimental ΔH_v^{298} data are available, albeit one can sometimes obtain them by suitable indirect methods or by extrapolation procedures.

Often, the CED of polymers is calculated by the method of group contribution, as described for example by Van Krevelen[20] and Fedors.[23]

The data collected in Tables I and II, and partially plotted in Figure 5, allow calculation of the contribution of several groups to the cohesive energy at 298 K, $\Delta E°$, and therefore the CED of the various polymers.

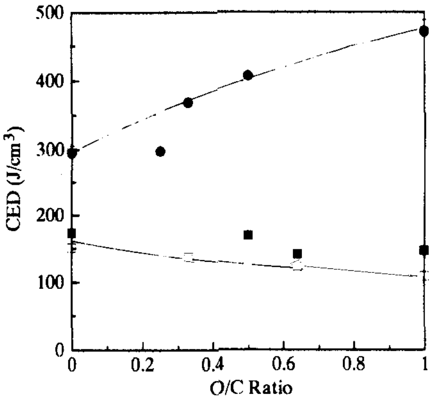

Figure 6. CED dependence on the oxygen to carbon ratio (O/C) for hydrogenated (○,●) and perfluorinated (□,■) polymers of high molecular weight. Open symbols: calculated by the group contribution. Full symbols: experimental data.

By means of the simple linear equation

$$\Delta E° = 2\Delta E°(\mathrm{CH_3}) + x_1\Delta E°(\mathrm{CH_2}) + x_2\Delta E°(\mathrm{O}) \quad (3)$$

where x_1 and x_2 are the number of $-CH_2-$ and $-O-$ groups in the chain, a multiple linear regression analysis has been carried out on the experimental cohesive energy data of linear hydrogenated paraffins and ethers. An excellent correlation is found (coefficient of determination R^2 = 0.999 16; standard error (SE) on the dependent variable = 1.47 kJ/mol) with the $\Delta E°$ values of 5.26 ± 0.29 kJ/mol for the $-CH_3$ group, of 4.81 ± 0.06 kJ/mol for the $-CH_2-$ group, and of 4.80 ± 0.28 kJ/mol for the $-O-$ group.

The group contributions for the $-CH_3$ and $-CH_2-$ are not too far from those reported by Fedors,[23] but the value of the ethereal oxygen contribution is substantially higher than that reported by this author (3.35 kJ/mol). It has to be noted that the two group contributions of $-CH_2-$ and $-O-$ appear to be rather close to each other.

As far as the perfluoro compounds are concerned, the same procedure was applied to the experimental data and the values of 6.74 ± 0.30, 4.04 ± 0.11, and −0.22 ± 0.35 kJ/mol were obtained for the contributions of the $-CF_3$, $-CF_2-$, and $-O-$ groups, respectively (R^2 = 0.999 70, SE = 0.70). It must be noted that the group contribution of the ethereal oxygen is now rather small and negative.

When the multiple regression analysis is applied to a larger amount of data, i.e., to the $\Delta E°$ data calculated from the $\Delta H_v^{298} - T_b$ relationship (eq 2), the $\Delta E°(\mathrm{O})$ = −0.47 ± 0.13 is again small and negative; one finds that $\Delta E°$ values for the $-CF_3$ and $-CF_2-$ groups are found to be 7.17 ± 0.27 and 3.66 ± 0.08 kJ/mol, respectively (R^2 = 0.998 50, SE = 1.56).

Thus, in the intermolecular interaction the oxygen role appears to be reversed when one passes from the hydrogenated to the perfluorinated linear ethers: in the first series the oxygen contribution is positive and quantitatively as large as that of a $-CH_2-$ group, whereas in the second series its contribution is small, as previously reported by Lawson,[16] and perhaps negative.

The recent molecular structure work of Pacansky et al.[24] on model compounds for perfluoropolyethers has shown that the oxygen atoms in the chain have a net negative charge of about 0.8*e* and the carbon atom a large positive charge of 1.0–1.5*e*, a situation very different from that existing in the hydrogenated ethers.

From the group contributions to $\Delta E°$ and the corresponding molar volumes, the CEDs of polymers investigated in the present work have been calculated, and they are plotted in Figure 6 for the two series of hydrogenated and perfluorinated polymers and copolymers.

First of all, it has to be noted that there appears to be an excellent agreement between the CED literature data[20,25,26] that have some form of experimental origin and those calculated by the group contribution method.

Second, it is seen that the intermolecular interactions per unit volume measured by the cohesive energy density for a given polyether—of infinite molecular weight—are the result of two factors, the first related to the chemical nature of the substituents, hydrogen or fluorine, and the second to the opposite effect on the two series of the oxygen content, that strongly increases the CED of hydrogenated chains whereas it decreases, although less strongly, that of perfluorinated chains.

The authors are aware that the use of CED data obtained at a standard reference state (298 K, 1 atm) can be considered a rather rough approach; the more correct one would be to obtain CED data at a given reduced temperature (e.g., at the T_gs of each material considered); however, the dependence of ΔH_v and of specific volume on T unfortunately is unknown for almost all materials, so that the present approach is the only one which can be used in practice.

In light of the strong differences between the CED of perfluoro compounds and hydrogenated compounds shown in Figure 6, some features of the glass transition T_g of the same polymers (Figure 1) could now at least qualitatively be interpreted as related to intermolecular interactions. In other words, the T_g decrease of perfluoropolyethers with an increase in the O/C ratio should be, partly, a consequence of a decrease of the relative CED. However, the constancy of the T_g of hydrogenated polyethers, as well as the fact that PE and PTFE have nearly the same T_g, in spite of their rather different CED values, cannot be understood by referring only to the above controlling parameter, and a more complex interpretation requires that also intramolecular interactions be taken into account.

The chain flexibility of macromolecules is usually considered to depend mostly on a well-known parameter, called the "steric factor", or the steric hindrance parameter, defined as

$$\sigma = (\langle r^2\rangle_o/\langle r^2\rangle_{of})^{1/2} \qquad (4)$$

where $\langle r^2\rangle_{of}^{1/2}$ is the mean-square end-to-end distance of the freely rotating macromolecule and $\langle r^2\rangle_o^{1/2}$ the corresponding unperturbed distance.

The steric factor is known to be an essentially intramolecular parameter.[27]

For the series of samples belonging to the hydrogenated polyethers for which the first term is polyethylene, O/C = 0, the steric factors are found in the literature (see Table IV).[13,25,27-29] For the perfluorocopolyethers Fomblin Z, whose p/q ratio is 0.67, corresponding to a O/C ratio of 0.71, the σ value was calculated in the course of the present work from the $\langle r^2\rangle_o$ datum reported recently by Cantow et al.,[30] making use of the $\langle r^2\rangle_{of}$ derived from simple molecular modeling (bond distances and angles given by Tadokoro et al.[31]).

For the homopolymer $(CF_2CF_2CF_2O)_n$ the σ value was calculated from the intrinsic viscosity–molecular weight data measured at 20 °C in the Θ-solvent FC 113 (1,1,2-trichloro-1,2,2-trifluoroethane). The σ values of Fomblin Z and of the $(CF_2CF_2CF_2O)_n$ polymer obtained are 1.64 and 1.69, respectively. As far as poly(tetrafluoroethylene) is concerned, two widely different data values can be found in the literature. The first is the value σ = 3.5, reported by Brandrup and Immergut[25] and obtained from viscosity measurements in perfluorokerosene at 300 °C. From the paper of Chu et al.,[32] who determined the solution characteristics of PTFE in a poor solvent at 340 °C by dynamic light scattering, the value σ = 2.15 can be calculated by assuming for the molecular weight distribution a M_z/M_w ratio of 1.5. The latter appears to be the most reliable, also in view of the fact that Matsuo and Stockmayer calculated rather low characteristic ratios C_∞ for perfluoroalkane chains from experimental dipole moments.[33] The σ values are plotted as a function of the O/C ratio in Figure 7.

Table IV
Glass Transition Temperature, Steric Factor, and Solubility Parameters of Polymers

material	O/C	T_g (K)	σ	δ (J/cm^3)$^{1/2}$
polyethylene	0	190	1.98	17.2
poly(tetramethylene oxide)	0.25	189	1.66	17.3
poly(trimethylene oxide)	0.33	195	1.43	19.2
poly(ethylene oxide)	0.50	206	1.47	20.2
poly(methylene oxide)	1.00	190	1.70	21.7
poly(tetrafluoroethylene)	0	200	2.15	13.2
poly(perfluorotrimethylene oxide)	0.33	172	1.69	11.6
Fomblin Z copolymer	0.71	145	1.64	11.9

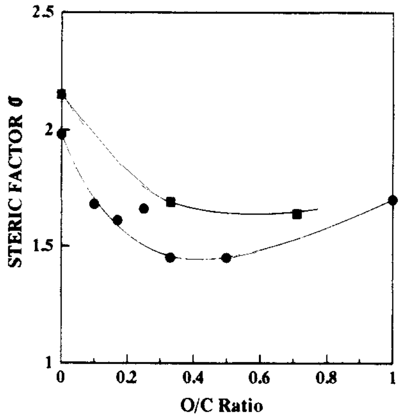

Figure 7. Dependence of the steric factor (σ) on the oxygen to carbon ratio (O/C) for hydrogenated (●) and perfluorinated (■) high molecular weight polymers (see text).

From the figure, it is seen that the introduction of oxygen in a linear paraffin chain brings about only small changes in the steric factor, which seems to reach a minimum at about O/C = 0.33, i.e., for poly(trimethylene oxide).

The same trend, within experimental error, is observed for perfluorinated compounds, which seem to be only moderately stiffer.

From the examination of the data plotted in Figure 7 it appears that a rationalization of the T_g vs O/C results of Figure 1 is not easily reached, however, because the steric hindrance parameter σ is a function of the O/C ratio quite different from the glass transition itself, although several attempts to establish a relationship between the T_gs of the polymers and the respective flexibility have been proposed in the literature.

For example, Elias[34] has correlated satisfactorily the T_gs of about 20 polymers with their σ values. Interestingly, the correlation is a straight line which, extrapolated, indicates a T_g close to 0 K for a polymer of very large flexibility (σ = 1.0).

On the other hand, Aharoni[12] and Privalko[14] have shown that multiple correlations exist between the flexibility and the T_gs; i.e., different polymeric families have different T_g–σ dependences.

According to some authors,[13,35,36] T_g should be a function of the product between a parameter related to the persistence length of the chain (e.g., σ^2 or the characteristic ratio C_∞) and a parameter related to the intermolecular interactions (e.g., the cohesive energy density or the solubility parameter $\delta = (\text{CED})^{1/2}$).

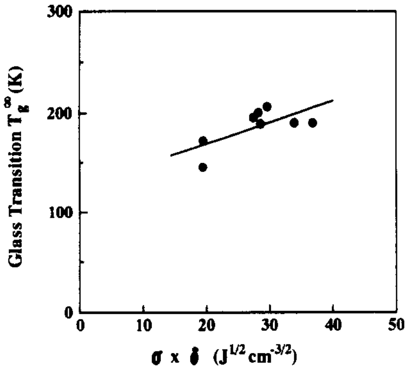

Figure 8. T_g as a function of the $\sigma(\mathrm{CED})^{1/2}$ product.

In Figure 8 the T_g of the two families of hydrogenated and perfluorinated polyethers, taken here as examples of simple linear polymers and whose rather different structural dependence is so clearly indicated by Figure 1, is plotted accordingly, as a function of the product $\sigma(\mathrm{CED})^{1/2}$. The relative poor correlation found is

$$T_g = a + b(\sigma(\mathrm{CED})^{1/2}) \qquad (5)$$

where $a = 126$ K, $b = 2.14\ (\mathrm{cm}^3/\mathrm{J})^{1/2}$, and the correlation coefficient is 0.68.

Further work is needed to extend eq 5 to other polymeric families and to interpret the physical meaning of the a and b parameters.

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