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Thermal stability and bond dissociation energy of fluorinated polymers: A critical evaluation

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Dedicated to Professor Richard D. Chambers on the occasion of his 70th birthday

Abstract

Intrinsic bond dissociation energies (BDEs) of selected fluorinated polymers are critically evaluated. Two distinctive approaches were followed. In the first one, according to Wu and Rodgers [E.-C. Wu, A.S. Rodgers, J. Am. Chem. Soc. 98 (1976) 6112–6115], starting from the gas-phase enthalpy of polymerization we obtained the polymer backbone BDE through appropriate thermodynamic cycles. Revised experimental results indicate that the C–C BDEs of all the polymers taken into account fall within a limited energy interval, comparable to the average experimental uncertainty. Central to the second methodology adopted, is a model compound approach. Thanks to the large number of reliable thermodynamic data available in the scientific literature and to simple end-capping rules, C_2 molecules were chosen as suitable models for infinite linear polymers and alternating copolymers between ethylene and fluorinated olefins. For partially fluorinated polymers, like polyvinylidene fluoride (PVDF), alternating ethylene–tertrafluoroethylene (ETFE) and alternating ethylene–chlorotrifluoroethylene (ECTFE), the weight loss due to HF and HCl evolution during heating experiments was successfully related to the threshold energy $E_o(HX)$ for 1,2-elimination from chemically activated hydrofluoro and hydrofluorochlorocarbons according to the modified Rice–Rampsberger–Kassel (RRKM) unimolecular theory.

Keywords: Fluorinated polymers; Thermal stability; Bond dissociation energy

1. Introduction

Thermal stability of linear vinyl polymers strongly influences their behavior in applications, such as processing and lifetime during cycling at elevated temperatures. Overall, this not a simple issue to address since many different facets must be properly taken into account at the same time. It is well known that the presence along the polymer backbone of traces of contaminants, like metals, and/or constitutional defects (like head to head (h–h) and tail to tail (t–t) sequences), long and short chain-branching (LCB and SCB), polar end-groups, etc., might dramatically alter their ultimate behavior. However, as far as a simple homolitic chain scission is concerned, an important question for understanding thermal stability at a molecular level is the strengths of the various chemical bonds involved. This applies especially to polymers able to withstand temperatures whose associated energy is close enough to the minimum threshold for the bond dissociation of the backbone. When this condition is approached, the thermal stability of a linear vinyl polymer is closely related to its bond dissociation energy (BDE). Fluoropolymers represent the most appropriate example of such a situation. Their thermal endurance is related to the number of fluorine atoms in the repeating unit [1]. Owing to the high strength of the C–F bond, polytetrafluoroethylene (PTFE) is positioned at the top edge of the performances. Its continuous service temperature is 260 °C and, for short periods, the polymer can withstand peak temperatures as high as 450 °C without any appreciable weight loss.

In order to relate the BDE of the polymer to experimental data, like TGA analysis under N_2, two distinctive

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approaches have evolved. Wu and Rodgers [2] estimated BDE of the C–C bond in PFTE from the gas phase heat of polymerization of the monomer, through appropriate thermodynamic cycles. More recently, Dixon et al. [3] tackled the same problem by resorting to model compounds. Heats of formation of closed-shell species and of associated polyatomic radicals were calculated from isodesmic reactions. When compared with polyethylene (PE), PTFE displays a C–C bond strength higher by 30–40 kJ mol^{-1} with both approaches. The difference in energy between C–F and C–H bonds is even larger, accounting thus for the well-known thermal resistance of PTFE versus PE.

Besides PTFE, semi-crystalline fluorinated polymers constitute a broad family of homo and copolymers with interesting properties for a large variety of applications [1]. Among them, partially fluorinated polymers, like polyvinylidene fluoride (PVDF), alternating ethylene–tertrafluoroethylene [4] (ETFE), and alternating ethylene–chlorotrifluoroethylene [5] (ECTFE) copolymers, while displaying lower thermal resistance when compared with PTFE, enjoy better mechanical behavior owing to their much higher cohesive energy density [1]. Accordingly, this class of materials has found a number of interesting applications in those sectors where thermal stability is still demanding, although specifications are not at the extreme level of performance, but where mechanical properties are at a premium. It is therefore interesting to assess clearly the relationships between thermal resistance of these partially fluorinated polymers and their structure.

Years ago, this problem was dealt with by Loginova et al. [6]. The main focus was given to PVDF and ETFE, since these polymers have the same chemical composition but different mutual arrangement of –CF$_2$– and –CH$_2$– units. A large number of thermodynamic data on small fluorinated model compounds and related free radicals has become available. As part of our interest in fluoropolymers [1], we deemed it highly desirable to assess comprehensively the relationships between BDE of VDF, ETFE, and ECTFE and their thermal stability by resorting either to appropriate thermodynamic cycles or to BDE of small model compounds. A secondary focus of this paper is to review old data on BDE of PE and PTFE. This further investigation perfectly complements our main objective, since these two polymers represent the fundamental benchmarks against which any hydrogenated or fluorinated polymer should be compared.

2. Results and discussion

2.1. Background and model approach

The starting point of the approach of Wu and Rodgers [2] was the analysis of the enthalpy of addition of a symmetric molecule X$_2$ to TFE (reaction (1)).

$$\mathrm{X_2 + CF_2{=}CF_2 \rightarrow CF_2XCF_2X} \tag{1}$$

For the gas-phase polymerization, the following identity holds:

$$\Delta H^\circ_\mathrm{p} = \Delta D^\circ_\pi(\mathrm{CF_2{=}CF_2}) - D^\circ[\mathrm{CF_3CF_2{-}(CF_2CF_2)_{\mathit{n}}{-}}] \tag{2}$$

where D°_π is the π BDE of TFE. According to Benson [7] the π bond dissociation energy in a symmetric olefin like TFE is defined as the difference of the BDEs of a given bond in the saturated compound and in the relevant free radical (Eq. (3))

$$D^\circ_\pi(\mathrm{CF_2{=}CF_2}) = D^\circ(\mathrm{CF_3CF_2{-}X}) - D^\circ(^\bullet\mathrm{CF_2CF_2{-}X}) \tag{3}$$

Eq. (3) corresponds to the following reaction:

$$\mathrm{CF_3{-}CF_3 + CF_2{=}CF_2 \rightarrow 2CF_3{-}CF_2^\bullet} \tag{4}$$

With the assumption of an *enthalpy addition rule of chemical groups in a molecule*, Benson's definition has the physical meaning of a double bond singlet–triplet excitation. In the case of an unsymmetrical π bond, such as in vinylidene fluoride (VDF), there are two possible definitions [8]. From the first one (see Eq. (5))

$$D^\circ_\pi(\mathrm{CF_2{=}CH_2}) = D^\circ(\mathrm{CF_3CH_2{-}X}) - D^\circ(^\bullet\mathrm{CF_2CH_2{-}X}) \tag{5}$$

the value of $D^\circ[\mathrm{CF_3CH_2{-}(CF_2CH_2)_{\mathit{n}}{-}}]$ is obtained. Taking into account substitution at the fluorinated end of VDF, one can evaluate also $D^\circ[\mathrm{CH_3CF_2{-}(CH_2CF_2)_{\mathit{n}}{-}}]$.

Despite its ingenuity, this approach fails completely when dealing with alternating copolymers such as ETFE and ECTFE, so that one is forced to resort to a model compound approach. Unfortunately, relatively few thermochemical data are available for fluorinated n-C$_4$ compounds. On the contrary, thanks to the large interest arising from their environmental impact, there is a large number of information on C$_2$ fluorocarbons and their related free radicals [9]. For these reasons, C$_2$ molecules will be our model compounds in this study.

When representing an infinite polymer chain by a small molecule, a general problem is how to end-cap the polymer backbone with appropriate groups or atoms. In the present case, we are dealing with an regular succession of electron attracting –CF$_2$– and –CFCl– units and electron releasing –CH$_2$– groups. Accordingly, C$_2$ fluorocarbon models are chosen so that any –CF$_2$– and –CFCl– unit following or preceding the C atom to be end-capped is substituted by an F atom. Conversely, H atoms simulate the –CH$_2$– group. Following these simple rules, the C–C BDE of PVDF can be simulated unambiguously by one C$_2$ fluorocarbon model. Given the alternated arrangement of monomers, ETFE and ECTFE require three and four model compounds, respectively, as shown in Fig. 1. C$_2$ models for PE and PTFE are ethane and perfluoroethane.

2.2. Polymer chain BDEs

Table 1 lists literature values for enthalpies of formation at 298.15 K (kJ mol^{-1}) for all model molecules, including

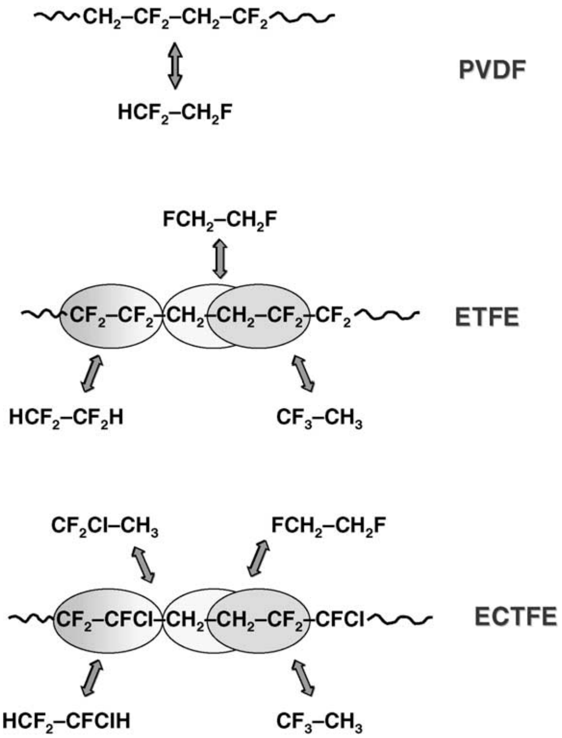

Fig. 1. Model compounds for C–C BDE evaluation in partially fluorinated polymers.

olefins and free radical species, required for BDEs evaluation. In this paper, the overall uncertainty in bond strength is given as the root of the sum of the squares of the uncertainties of the enthalpies of formation of the reactants and products.

From these data, it is possible to evaluate D°_π of the relevant monomers (see Table 2). According to the approach of Wu and Rodgers, these values, coupled to the gas phase heat of polymerization at 298.15 K, allow a first estimation of the C–C polymer backbone BDEs. While ΔH°_p for E [10] (-93.5 kJ mol^{-1}) and TFE [11] (-155 kJ mol^{-1}) have been determined, this value is not directly available for VDF. It is, however, possible to calculate it form the heat of combustion of the solid polymer [12] and the heat of formation of the gaseous monomer [13]. At 298.15 K the gas-phase heat of polymerization of VDF is -105.6 ± 4.1 kJ mol^{-1} [14].

In Table 2 we report also the π bond strength of chlorotrifluoroethylene (CTFE) and the BDE of the related polymer (PCTFE). Since ΔH°_p of CTFE is not available experimentally, this value has been obtained from the heat of combustion of the crystalline polymer [25]. At 298.15 K the heat of formation of the solid polymer is 656.8 kJ mol^{-1}. Accordingly, the gas-crystal enthalpy of polymerization is $\Delta H^\circ_p(\mathrm{g,c}) = -151.3 \pm 4.7$ kJ mol^{-1}. By correcting for the melting enthalpy and the cohesive energy density of the liquid polymer, for PCTFE we finally obtain $\Delta H^\circ_p = 131.6 \pm 4.7$ kJ mol^{-1}.

Following the approach of Wu and Rodgers [2], the C–C BDEs of all the polymers fall within a limited energy interval, comparable to the average experimental uncertainty. The minor exception is due to PCTFE whose BDE is, however, affected by a large uncertainty. The C–C BDE of PE, the benchmark of choice for any polymer, is definitely

Table 1
Literature enthalpies of formation of closed and open shell molecules (kJ mol^{-1})

Species	ΔH_f (298)	Uncertainty	Literature
$CH_2=CH_2$	52.5	0.6	[9]
$CF_2=CH_2$	−336.4	4.0	[9]
$CF_2=CFCl$	−505.5	4.7	[15]
$CF_2=CF_2$	−658.6	2.9	[9]
$CH_3–CH_3$	−84.1	0.4	[16]
$CFH_2–CFH_2$	−433.9	11.8	[9]
$CF_3–CH_3$	−745.6	1.6	[9]
$CF_3–CH_2F$	−895.8	4.2	[9]
$HCF_2–CF_2H$	−894.9	10.0[b]	[17]
$CF_3–CF_2H$	−1104.6	4.6	[9]
$CF_3–CF_2Cl$	−1114.6	10.0	[15]
$CF_3–CFClH$	−925.5	10.0[b]	[18]
$HCF_2–CFClH$	−702.4	10.0[b]	[17]
$CF_2Cl–CH_3$	−536.2	5.2	[17]
$CF_3–CF_3$	−1344.0	4.0	[17]
HF	−273.3	0.7	[22]
HCl	−92.31	0.1	[22]
H_2O	−241.83	0.04	[22]
$CH_3–CH_2^\bullet$	119.0	2.0	[15]
$HCF_2–CF_2^\bullet$	−664.8	18.7	[9]
$CH_3–CF_2^\bullet$	−302.5	8.4	[9]
$CF_3–CH_2^\bullet$	−517.1	4.2	[9]
$CFH_2–CF_2^\bullet$	−449.8	15.0	[9]
$CF_3–CF_2^\bullet$	−892.9	4.0	[19]
$ClCF_2–CF_2^\bullet$	−686.0	17.0	[19]
$CF_3–CFCl^\bullet$	−728.0	10.0	[18]
$ClCF_2–CH_2^\bullet$[a]	−315.2	6.0	[20]
$CH_3^\bullet$	145.7	0.7	[9]
$CH_2F^\bullet$	−32.6	8.4	[9]
$CHF_2^\bullet$	−247.3	8.4	[9]
$CF_3^\bullet$	−467.4	8.4	[9]
$CHClF^\bullet$	−66.1	117	[24]
$CClF_2^\bullet$	−279.1	8.3	[23]
$H^\bullet$	217.998	0.006	[22]
$Cl^\bullet$	121.301	0.008	[22]
$F^\bullet$	79.38	0.3	[22]
$I^\bullet$	106.76	0.04	[22]
$OH^\bullet$	37.196	0.38	[21]

[a] From the isodesmic reaction: $ClCF_2CH_3 + OH^\bullet \rightarrow H_2O + ClCF_2CH_2^\bullet$; $\Delta H^\circ_{298} = -58.0$ kJ mol^{-1}.

[b] Set at the maximum uncertainty value of the referenced databases.

Table 2
Olefin π bond strength (D°_π) and polymer C–C BDE from ΔH°_p (kJ mol^{-1})

Chemical bond	BDE	Uncertainty
$D^\circ_\pi(CH_2=CH_2)$	269.6	4.1
$D^\circ_\pi(CF_2=CH_2)$	265.3	16.6
$D^\circ_\pi(CH_2=CF_2)$	262.4	10.3
$D^\circ_\pi(CF_2=CFCl)$	206.1	22.6
$D^\circ_\pi(CF_2=CF_2)$	216.8	9.4
$D^\circ[CH_3CH_2–(CH_2CH_2)_n–]$	363.1	4.1
$D^\circ[CF_3CH_2–(CF_2CH_2)_n–]$	370.9	17.1
$D^\circ[CH_3CF_2–(CH_2CF_2)_n–]$	368.0	11.1
$D^\circ[CF_3CFCl–(CF_2CFCl)_n–]$	337.7	23.1
$D^\circ[CF_3CF_2–(CF_2CF_2)_n–]$	371.8	9.4

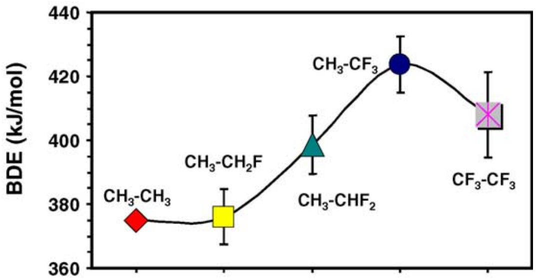

Fig. 2. BDE of fluorinated ethanes: data from Table 1 and [9].

higher than previously reported [2]. The main reason is the value of D°_π. Recent thermodynamic data lead to a π bond strength of E higher by about 23 kJ mol^{-1} than reported in the seminal paper of Benson [7]. Apparently, from the data in Table 2 it turns out that C–C BDEs of linear vinyl polymers having completely different chemical structure like PE, PVDF, PTFE, and PCTFE do not substantially differ from each other. This finding does not agree with the thermal stability data from TGA experiments under N_2 [1]. One reason for this discrepancy may be the different chemical reactions involved. TGA experiments under N_2 refer to a random chain scission of an infinite linear polymer backbone. In contrast, BDE calculated through ΔH°_p more appropriately describes the strength of the pre-terminal C–C bond. Central to the approach of Wu and Rodgers, is an accurate determination of ΔH°_p and D°_π of the associated monomer. However, the gas-phase heat of polymerization is not directly available and consequently there is an inherent degree of arbitrariness. Also Benson's definition of olefin π bond strength implicitly entails a number of approximations. A physically more sound definition of π bond energy would be the energy required to break a π bond by rotation to the diradical transition state for *cis–trans* isomerization [26]. Benson's approach automatically implies a perfect energy addition rule of chemical groups in a molecule. This might be a crude assumption for some open-shell species like the associated free radicals of fluorinated monomers.

In the model compound approach, it is accepted that progressive fluorination is responsible for the increase of the strength of the C–C bond in the series of fluorinated ethanes [1,27] (see Fig. 2). The same trend is observed with the C_2 model compounds reported in Table 3. Accordingly, the C–C bond of perfluoroethane is stronger than the C–C bond in ethane by about 35 kJ mol^{-1}, consistently with the thermal behavior of PTFE versus PE.

Table 3
Bond strength of C_2 fluorocarbon models for fluorinated polymers (kJ mol^{-1})

Chemical bond	BDE	Uncertainty
$D^\circ(CH_3–CH_3)$	375.5	11.9
$D^\circ(FCH_2–CH_2F)$	368.7	16.7
$D^\circ(HCF_2–CH_2F)$	410.1	15.6
$D^\circ(HCF_2–CF_2H)$	400.3	15.5
$D^\circ(CF_3–CH_3)$	423.9	8.6
$D^\circ(CF_2Cl–CH_3)$	402.8	9.8
$D^\circ(HCF_2–CFClH)$	389.0	17.5
$D^\circ(CF_3–CF_2Cl)$	368.1	15.5
$D^\circ(CF_3–CF_3)$	409.2	12.5

Among partially fluorinated polymers, the C–C bond strength of PVDF is unambiguously represented by a single C_2 model compound ($HCF_2–CH_2F$), since all the C–C bonds are energetically equivalent. BDE is 410.1 kJ mol^{-1}, close to 405.5 kJ mol^{-1} reported by Loginova et al. [6]. The group enchainment of ETFE and ECTFE gives rise, respectively, to three and four types of C–C with different bond energies, depending on substituents at the carbon atoms. For ETFE the model compound approach gives the following C–C main chain BDEs: $–CH_2–CH_2– \equiv 368.7$ kJ mol^{-1}; $–CH_2–CF_2– \equiv 423.9$ kJ mol^{-1}; $–CF_2–CF_2– \equiv 400.3$kJ mol^{-1}. For ECTFE two backbone dispositions are the same as in ETFE, while those with the Cl substituent are:$–CF_2–CFCl– \equiv 389.0$ kJ mol^{-1} and $–CH_2–CFCl– \equiv 402.8$ kJ mol^{-1}.

In the paper of Loginova et al. [6], PTFE and PVDF BDEs were used to simulate in ETFE the bond energies of C–C sequences with F atoms substituents. Probably for this reason, we have different results. It is interesting to note, however, that the average bond energy of the two fluorinated sequences in our approach, 412.1 kJ mol^{-1}, is very close to average value (411.8 kJ mol^{-1}) reported by Loginova. The average BDE of the three fluorinated C–C sequences of ECTFE is 405.2 kJ mol^{-1}. Finally, in Table 3 we report also the C_2 model compound for PCTFE ($D^\circ(CF_3–CF_2Cl) = 368.1 \pm 15.5$ kJ mol^{-1}).

As stated above, C_2 model compounds represent the minimum available approach; C_4 and, eventually, higher homologous compounds would more appropriately simulate a random chain scission of a linear vinyl polymer. However, for semi-fluorinated polymers, only data on C_2 models are available. This is not the case for PE and, to a more limited extent, for PTFE. In view of the intrinsic limitations of the Wu and Rodger approach and of the importance of these two

Table 4
Enthalpies of formation of closed and open shell linear alkanes (kJ mol^{-1})

Species	ΔH_f (298)	Uncertainty	Literature
$C_2H_5–C_2H_5$	−127.1	0.7	[15]
$C_3H_7–C_3H_7$	−167.2	0.8	[15]
$C_4H_9–C_4H_9$	−208.4	0.7	[15]
$C_5H_{11}–C_5H_{11}$	−249.7	1.1	[15]
$C_2F_5–C_2F_5$	−2166.1	9.2[a]	[28]
$C_3F_7–C_3F_7$	−2979.2	9.2[a]	[28]
$C_4F_9–C_4F_9$	−3792.3	9.2[a]	[28]
$n\text{-}C_3H_7^\bullet$	100.0	2.0	[15]
$n\text{-}C_4H_9^\bullet$	77.8	5.4	[b]
$n\text{-}C_5H_{11}^\bullet$	57.5	5.4	[c]
$n\text{-}C_3F_7^\bullet$	−1299.4	10.1	[29]
$n\text{-}C_4F_9^\bullet$	−1709.3	10.1	[30]

[a] Arbitrarily set at the standard deviation of the referenced databases.

[b] Calculated from the reaction [31]: $n\text{-}C_4H_9 \rightarrow C_2H_4 + C_2H_5$; $\Delta H_{298} = 93.7$ kJ mol^{-1}.

[c] Calculated from the reaction [31]: $n\text{-}C_5H_{11} \rightarrow C_2H_4 + n\text{-}C_3H_7$; $\Delta H_{298} = 95.0$ kJ mol^{-1}.

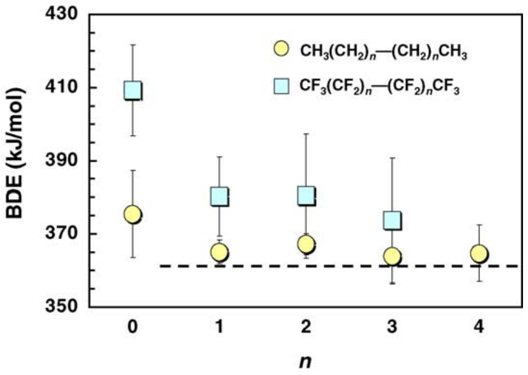

Fig. 3. BDEs of hydrogenated and perfluorinated higher homologous model compounds.

polymers, we deem it worthwhile approaching the main chain C–C bond strength by resorting also to the bond energy of higher homologous model compounds.

For PE it is possible to calculate, from experimental ΔH_f° data, the bond strength of the homologous series $CH_3(CH_2)_n–(CH_2)_nCH_3$, with $n = 0–4$. The scientific literature contains enough information related either to the *n*-alkanes or to the related *n*-alkyl free radicals (see Table 4). Unfortunately, this is not the case of *n*-perfluoroalkanes whose experimental enthalpies of formation have been determined only for a few molecules (perfluoroethane, perfluoropropane, and perfluoroeptane [15]). This situation is even worse for the associated *n*-perfluoroalkyl radicals. However, for *n*-$C_3F_7^\bullet$ and *n*-$C_4F_9^\bullet$ it is possible to estimate ΔH_f° values. Additional data for determining the C–C bond strength in PE and PTFE through the higher homologous approach are reported in Table 4.

Bond strengths of the homologous model compounds $CH_3(CH_2)_n–(CH_2)_nCH_3$ ($n = 0–4$) are reported in Fig. 3. Neglecting the first term of the series, starting from *n*-butane BDE values level off at an average value of 365.3 ± 5.3 kJ mol^{-1}. This figure compares satisfactorily with the BDE reported in Table 2 and obtained from ΔH_p°. For fluorinated compounds of formula $CF_3(CF_2)_n–(CF_2)_nCF_3$, the overall picture is ambiguous, due to the few thermochemical data available for *n*-perfluoroalkanes and related free radicals.

The enthalpy of formation at 298.15 K is available for *n*-C_3F_8 [15] ($\Delta H_f^\circ = -1784.7 \pm 8.8$ kJ mol^{-1}) and *n*-C_7F_{16} [15] only. Accordingly, for estimating heats of formation of relatively large *n*-perfluoroalkanes, we are forced to rely on group contribution methodologies, with Joshi's method being probably the best one available for fluorinated alkanes [28]. Thus, in Table 4 we report the ΔH_f° of *n*-C_4F_{10}, *n*-C_6F_{14}, and *n*-C_8F_{18}. Within the *n*-fluoroalkane series, these molecules are close to *n*-C_3F_8 and *n*-C_7F_{16}, whose enthalpy of formation is accurately predicted by Joshi's method. The enthalpy of formation of *n*-$C_3F_7^\bullet$ and *n*-$C_4F_9^\bullet$ radicals is not experimentally available. There are, however, data concerning BDEs of the related *n*-alkyl iodides [19,32]. For these compounds, ΔH_f° has been evaluated by Joshi's method. Iodide derivatives rather than bromide have been chosen since carbon–iodine bonds are less sensitive to the typical variations of the nature of the carbon atom [33].

For the model compounds of PTFE, starting from *n*-perfluorobutane there are small variations of the C–C bond strength, although data are affected by a large average uncertainty (±11.3 kJ mol^{-1}). From the values reported in Fig. 3, we can estimate a BDE of about 380 kJ mol^{-1} for PTFE. This number is consistently lower than previously reported values quoting for PTFE a BDE higher than that of PE by about 40 kJ mol^{-1}. There is however some internal inconsistency. From experimental ΔH_f° we have $D^\circ(CF_3–C_2F_5) = 424.3 \pm 12.8$ kJ mol^{-1}. Our estimate leads to $D^\circ(C_2F_5–C_2F_5) = 380.3 \pm 10.8$ kJ mol^{-1}, which does not agree with the well known effects brought about by perfluorination [1]. Probably the lack of precise experimental ΔH_f° values on perfluoroalkanes and the related free radicals prevents an unambiguous assessment on the main chain BDE of PTFE. However, this value should be definitely higher than 380 kJ mol^{-1}, as witnessed by thermal stability data of PFTE and PE [1].

2.3. HX elimination from partially fluorinated polymers

Thermal degradation studies at about 550 K of partially fluorinated polymers, like PVDF, ETFE, and ECTFE, reveal substantial amounts of HF and HCl in the volatile products of decomposition [6]. Mechanistically there is a close analogy with the gas-phase 1,2-dehydroalogenation of hydrofluorocarbons and hydrochlorofluorocarbons. This class of reactions has been subjected to intensive investigations [35,36]. The related unimolecular process has been assumed to involve a planar and polar four-centred transition state, and it has been shown [37] that *syn* elimination governs the removal of the hydrogen halide. Common methods for determining experimental reaction rates are to provide the unimolecular reactants with energy in excess of the minimum that leads to HX formation. These include thermal heating, photolytic excitation, and chemical activation. In the last 20 years, this last technique has been applied intensively by Holmes and co-workers [37–44] for determining the rate constants for elimination of HCl and HF from hydrofluorocarbons and hydrochlorofluorocarbons. The resulting experimental data have been matched to rates calculated using the Rice–Rampsberger–Kassel (RRK) unimolecular theory [45] and the modified RRK version (RRKM) [36] to determine E_o(HX), the threshold energy for HF or HCl removal (see Table 5). The data show an increase in the threshold energy for loss of HF, E_o(HF), of 13–30 kJ mol^{-1} for replacement of each H on the α-carbon by a F: $CH_2F–CH_3$, 242.7 kJ mol^{-1} [41]; $CHF_2–CH_3$, 255.2 kJ mol^{-1} [47]; $CF_3–CH_3$, 284.5 kJ mol^{-1} [42]. The α-carbon contains the halogen and the β-carbon the hydrogen that are eliminated. For HF elimination, Cl and F substituents on the α-carbon are equivalent: both of them

Table 5
Threshold energy in kJ mol^{-1} for 1,2-HX elimination from chemically activated hydrofluoro- and hydrochlorofluorocarbons

Molecule	E_o(HX)	Literature
	–CF–CH– → –C=C– + HF	
$CH_2F–CFH_2$	257.3	[45]
$CH_2F–CF_2H$	284.5	[38]
$CHF_2–CF_2H$	311.7	[38]
$CF_3–CH_3$	284.5	[42]
$CClF_2–CH_3$	290.8	[39]
$CH_3–CF_2–CH_3$	225.9	[41]
$CF_3–CH_2–CH_3$	259.4	[42]
$CF_3–CH_2–CF_3$	305.4	[42]
$CF_3–CF_2–CH_3$	286.6	[41]
$CClF_2–CF_2–CH_3$	266.9	[43]
	CCl–CH– → –C=C– + HCl	
$CClF_2–CH_3$	230.1	[39]
$CClF_2–CF_2–CH_3$	231.8[a]	[43]

[a] Threshold energy for 2,3-HCl elimination after 1,2-FCl transfer.

increase E_o. Furthermore, comparing the threshold energies, Table 5 illustrates that replacing the hydrogen of $CF_3–CH_3$ with CH_3 lowers E_o by 25 kJ mol^{-1} and replacing with CF_3 raises E_o by 21 kJ mol^{-1}. For the HCl gas-phase elimination, the 1,2-channel always involves transition states displaying threshold energies consistently lower than for HF removal. The difference of the threshold barriers are related to the nature of the four-centered transition state where the carbon–halogen bond changes from nearly covalent C–Cl bond for HCl loss to a C–F bond that has much pronounced charge separation when HF is released [39].

Given this interesting body of experimental data, it is worth trying to predict, through the usual model compound approach, the weight losses of semi-fluorinated polymers due HX evolution during heating at elevated temperature. Particular attention should be paid to the comparative behavior of PVDF and ETFE, since these two polymers have the same degree of fluorination but opposite mutual arrangement of CH_2 and CF_2 units. Suitable C_2 models for HF elimination are $HCF_2–CH_2F$ for PVDF and $CF_3–CH_3$ for ETFE. Unfortunately, for these two fluorocarbons E_o(HF) is exactly the same: 284.5 kJ mol^{-1}. However, thermal stability data by TGA under N_2, clearly indicate a less pronounced weight loss for ETFE versus PVDF [1]. Moreover, for PVDF Loginova et al. [6] reported an amount of HF evolved during heating experiments at 548 K almost double than for ETFE. C_2 models seem inadequate for predicting the stability of semi-fluorinated polymers versus HF elimination. However, the data of Holmes offer a further possibility since the threshold energies for 1,2-HF elimination are available also for C_3 hydrofluorocarbons. In this connection, $CF_3–CF_2–CH_3$ certainly represents a suitable C_3 model for ETFE. The situation is less clear for PVDF. The nature of the substituents at the α- and β-carbon exerts a strong effect on E_o(HF) [42]. However, since PVDF presents an alternate succession of CH_2 and CF_2 groups, it seems reasonable to assume that the average of the threshold energies of $CF_3–CH_2–CF_3$ and $CH_3–CF_2–CH_3$ (E_o(HF) = 265.7 kJ mol^{-1}) might safely represent the minimum energy required for HF release from the polymer. According to these data, ETFE should have threshold energy for HF loss higher by about 20 kJ mol^{-1} than PVDF. Coupled to the higher main chain BDE, the data of Holmes fit perfectly with the better thermal resistance of ETFE versus PVDF in TGA experiments under N_2 [1,6].

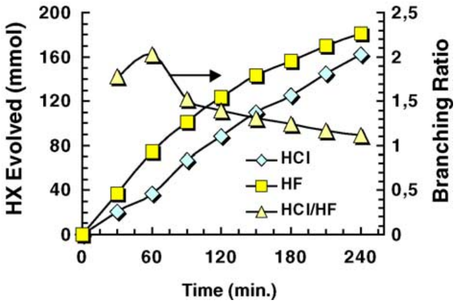

Fig. 4. Amount of HF and HCl evolved vs. heating time at 623 K under N_2 in volatile degradation products of ECTFE (Halar® 5041).

As far as HX elimination is concerned, ECTFE constitutes the most interesting case. Actually, it can be considered as a unimolecular reactant with multiple reactions paths since both HF and HCl are released during heating experiments. To this end, in Fig. 4 we report the time dependence of HF and HCl evolution in the volatile products of degradation of ECTFE [53] during a pyrolysis experiment under N_2 at 623 K. The branching ratio (HCl:HF) is also reported.

It is interesting to compare our data with published pyrolysis studies of unimolecular elimination experiments on chemically activated mixed halogenated species [37–48]. In all these experiments HCl loss was dominant. For $CClF_2–CH_3$ Jones et al. [39] reported a branching ratio of 25:1 whereas, in the low-pressure limit, for $CF_3–CFCl–CH_3$ the reported value was 13.5:1 in favour of HCl [43]. Pyrolysis studies reported branching ratios near 10:1 for $CClF_2–CH_3$. However, at the highest temperatures employed, one study [48] found a branching ratio (HF:HCl) of 2.3:1, very close to our experimental results from ECTFE thermal degradation under N_2.

We note that any successful RRKM model has a transition state with weakly bound hydrogen (C–H bond order near 0.1) and a C–X bond that is slightly distorted (bond order close to 0.9). The main consequence is that the strength of the C–H bond and, to some extent, of the C–X bond might determine in a certain way the value of E_o(HX). The average value of the D°(C–H) for the PVDF model ($CH_2F–CF_2H$) is 430.4 ± 15.6 kJ mol^{-1}, while for ETFE models ($CHF_2–CF_2H$ and $CF_3–CH_3$) we found an average bond strength of 447.3 ± 12.7 kJ mol^{-1} (see Table 6). For the ECTFE model $D^\circ(CF_2ClCH_2–H) = 439.0 \pm 7.5$ kJ mol^{-1}. These data, however, are affected by an uncertainty hampering any clear comparison between C–H bond strengths.

Table 6
BDE of relevant chemical bonds in the four-centered transition state of 1,2-HX unimolecular elimination from PVDF, ETFE, and ECTFE model compounds (kJ mol^{-1})

Chemical bond	BDE	Uncertainty
$D°(H_2CFCF_2–H)$	433.0	15.6
$D°(HCF_2CHF–H)$	426.7	15.6
$D°(HCF_2CF_2–H)$	448.1	21.2
$D°(CF_3CH_2–H)$	446.5	4.3
$D°(CF_2ClCH_2–H)$	439.0	7.5
$D°(H_2CFCHF–F)$	505.7	13.2
$D°(HCF_2CH_2–F)$	458.4	15.6
$D°(HCF_2CHF–F)$	518.2	18.0
$D°(CH_3CF_2–F)$	522.5	8.6
$D°(CH_3CF_2–Cl)$	355.0	8.6

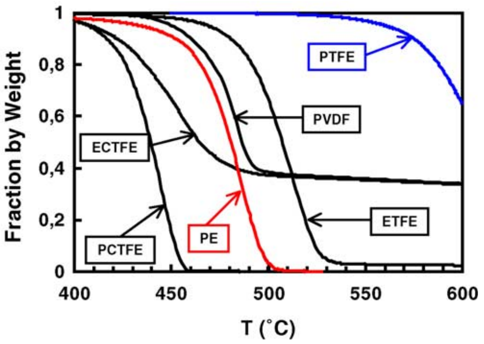

Fig. 5. Thermogravimetric analysis of commercial fluorinated polymers, 10 °C min^{-1} under N_2.

The overall picture becomes clearer when taking into account C–X BDE of the polymer model compounds. We have for ETFE $D°(C–F) = 520.3 \pm 13.3$ kJ mol^{-1} and for PVDF $D°(C–F) = 482.0 \pm 14.4$ kJ mol^{-1}. Conversely, the ECTFE model compound indicates a substantially lower carbon–halogen strength, $D°(C–Cl) = 355.0 \pm 8.6$ kJ mol^{-1}. Within the framework of the RRKM transition-state theory and of the C_2 model compound approach, we can satisfactorily correlate also C–X and, to a lesser extent, C–H BDEs to the HX evolution during thermal degradation of ETFE, PVDF, and ECTFE polymers.

3. Conclusion

As far as weight loss is concerned, the relative thermal resistance is: PTFE > ETFE > PVDF ≈ PE > ECTFE > PCTFE. This however does not tell the whole story, being not fully representative of performances in application. Actually, a careful inspection of Fig. 5 reveals that, in the high temperature range, ETFE from one side, and PVDF and ECTFE from the other, display opposite trends in weight loss. In other words, while a complete depolymerization process is operative for ETFE, thanks to the 1,2-dehydrohalogenation reaction both PVDF and ECTFE behave as char-forming polymers. Even though decreasing the overall thermal resistance, this phenomenon has beneficial effects in some selected applications, like cable sheathing and thin polymer coating protection of metallic parts. This applies especially to ECTFE grades that find use mainly in plenum applications in public buildings and in the chemical protection of apparatus and tanks by electrostatic powder coating or rotomoulding [49]. Actually, HCl loss brings about very efficiently a cross-linking reaction across polymer chains through the newly formed double bonds.

Even for the bond breaking process of the polymer main chain, the situation is not as linear as previously described. Microstructural defects are ubiquitous in macromolecules. In fluoropolymers, they originate from complex radical rearrangements especially related to the strong electrophilic nature imparted to the unpaired carbon species by F atoms substituents [1]. Accordingly, PVDF presents a relatively large content of h–h and t–t sequences that substantially decrease crystallinity. Moreover, backbiting reactions are responsible for SCB [50]. Furthermore, given the high reactivity of the growing radicals, transfer to the polymer is likely to occur leading to LCB defects, as clearly demonstrated for VDF copolymers [51]. Both SCB and LCB entail the presence along the main carbon chain of tertiary hydrogens that affect thermal stability of the produced polymer. For the alternating copolymers between ethylene and fluoro-olefins, monomer sequence distribution has to be taken into account. Notwithstanding the high tendency to alternation, reactivity ratios of ETFE and ECTFE are such that commercial polymers always contain small amounts of $–(CH_2)_n–$ sequences [4,5], with $n = 4–6$. In terms of bond properties, the CH_2 groups in these ‘‘defect’’ domains have lower bond energies as witnessed by the lower CH stretching frequencies than those of the CH_2 in the perfectly alternating chains [52].

Finally, although end groups represent a negligible part of the overall weight of a macromolecule, it is well known that that they might strongly influence the thermal stability of the whole polymer [51]. Real polymers always contain microstructural defects. Since fluoropolymers are at the top edge of the thermal behavior, these defects become increasingly important. A more sound assessment should stem not only from the constitutive bond strengths involved, but also from the overall polymer architecture.

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