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Electron Beam Induced Degradation of Poly(perfluoroethers) and Poly(olefin sulfones)

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G values are reported for a variety of poly(perfluorinated ethers) when exposed in a vacuum system to a 25-kV electron beam. The G values for polymer decomposition ranged from 0.1 to 1.2 depending upon the polymer structure and irradiation temperature and were generally higher for polymers containing perfluoromethylene oxide comonomer units compared to perfluoroethylene oxide and perfluoropropylene oxide units. Activation energies for polymer decomposition were obtained from temperature-dependent electron beam irradiation studies using specular reflectance infrared spectroscopy. Values of about 1 kcal/mol are obtained for the poly(perfluoroethers) and 6.8 kcal/mol for poly(2-methylpentene 1-sulfone), respectively. The β-scissioning reaction in poly(perfluorinated ether) radicals which leads to evolution of COF_2 were investigated using ab initio calculations at the 6-31G* level of theory. The calculations predict a ΔH at room temperature of $\approx$1.2 kcal/mol. Alternative chain scissioning pathways are investigated also.

Introduction

Poly(perfluoroethers) and poly(olefin sulfones) are two polymers used in industry. Poly(perfluoroethers) are widely used in the magnetic recording industry as disk lubricants to achieve the desired tribological characteristics between disk and head. Recently, they have been considered for applications in aerospace engines and satellite instrumentation.[1] Poly(olefin sulfones) are used in the electronics industry as positive-working, high-resolution electron beam, and X-ray resists.[2] Because of their widespread applications, an understanding of their degradation mechanisms, both thermal and high-energy radiation, have been the subject of numerous papers.[3–11] The results of these studies have shown that both classes of polymers primarily undergo radiation-induced main-chain scissioning with gas evolution of small molecules. In poly(perfluoroethers), the main gas-phase products are COF_2 and CF_4, while in poly(olefin sulfones), SO_2, and alkene fragments are produced. For the polymers, evolution of the gases is a result of degradation of the polymer chains, which is a two-step process; the first is main-chain scission induced by the high-energy electron beam and the second is a series of thermally induced β radical scission reactions that initiates at the ends of the fragmented polymer chains. By varying the temperature and measuring the mass loss or film thickness loss, the activation energy for the β radical scissioning reaction may be obtained.

In this report we continue our studies on the mechanism(s) of electron beam induced chain degradation of poly(perfluoroethers) and poly(olefin sulfones). Here, the G value and activation energy for scissioning in a variety of poly(perfluoroethers) and a poly(olefin sulfone) are established from their rate of film thickness or mass loss at different temperatures using infrared spectroscopy. Additionally for poly(perfluoroethers), ab initio computational methods are used to calculate thermodynamic properties for plausible degradation pathways involving cleavage of COF_2 units in order to explore which reactions are reasonable and consistent with the experimental findings.

The structures of the poly(perfluoroethers) used in this study are as follows:

poly(perfluoro-*n*-propylene oxide), PPFNPO

$$-(CF_2CF_2CF_2-O-)_x$$

poly(perfluoropropylene oxide), PPFPO

$$-(CF(CF_3)CF_2-O-)_x$$

poly(perfluoromethyleneethylene oxide), PPFMEO

$$-(CF_2-O-)_x-(CF_2CF_2-O-)_y$$

a PPFMEO copolymer with –OH end groups, poly (perfluoromethyleneethylene oxide), PPFMEO–OH

$$HO-CH_2CF_2-O-(CF_2-O-)_x-(CF_2CF_2-O-)_y-CF_2CH_2-OH$$

poly(perfluoromethylenepropylene oxide), PPFMPO

$$-(CF_2-O-)_x-(CF(CF_3)CF_2-O-)_y$$

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Values for x and y in the chemical structures are provided in the Experimental Section. The structure of poly(2-methyl-1-pentene sulfone) is

$$-(SO_2-C(CH_3)(CH_2CH_2CH_3)-CH_2-)_y$$

Experimental Section

Materials. PPFPO was obtained from E. I. Du Pont De Nemours & Co. under the tradename Krytox 16256; the number average molecular weight, M_n = 8500 and ρ = 1.951 g/cm^3. PPFMPO and PPFMEO were obtained from Montedison USA, Inc., under the trademark Fomblin Fluids, YR (y/x = 25, M_n = 6200, M_w = 8600, ρ = 1.915 g/cm^3) and Z-15 (y/x = 0.7, M_n = 7200, M_w = 13400, ρ = 1.845 g/cm^3), respectively. PPFNPO was obtained from Daikin Inc. (Japan) under the tradename DEMNUM S-100 (M_n = 5600, ρ = 1.878 g/cm^3), and PPFMEO-OH was obtained from Austimont under the tradename ZDOL-2200 (y/x = 0.7, M_w = 2200, ρ = 1.750 g/cm^3). As shown in the chemical structures above, PPFMEO-OH differs from the other perfluorinated ethers by the $-CH_2OH$ end groups. Poly(2-methylpentene 1-sulfone) or PMPS was prepared as described in the literature.[8] The average molecular weight of the polymer (relative to polystyrene standard) was 450 000.

Sample Preparation. Sample substrates used in the infrared reflectivity measurements were prepared by vacuum deposition of ≈150 Å of Cr, followed by ≈2500 Å of gold onto a polished copper disk of 1.5-in. diameter. The chromium served as a layer for good adhesion of the gold. PMPS was then dissolved in Shipley AZ-thinner and spin coated onto the gold substrates. The films were then dried in a vacuum oven at 50 °C for several days to ensure removal of solvent. Film thicknesses were measured on an Alpha Step Profilometer (Tencor Instruments), and film thicknesses were typically 2.0 μm. Poly(perfluoroether) liquids were spin coated onto the gold substrates from Freon TF solutions, and film thicknesses calibrated from infrared and ellipsometry measurements. Film thicknesses ranged from 1 to 2.2 μm, depending upon the sample. All of the film thicknesses in this study never exceeded these values to ensure complete electron penetration into the samples. The penetration depth is readily estimated from the Grün relation:[12]

$$R_g = \frac{0.0459}{\rho} E_0^{1.75} \tag{1}$$

where R_g is the Grün range in micrometers, i.e., the maximum electron beam penetration depth perpendicular to the film, ρ is the density of the film in g/cm^3, and E_0 is the energy in kilovolts incident on the film. For E_0 = 25 kV, as in these studies, R_g = ≈7 μm for poly(perfluoroethers), and R_g = ≈9 μm for PMPS.

Electron Beam Exposure under Vacuum. The apparatus used for 25-kV electron beam exposure of the samples under vacuum, and at low temperatures has previously been described in detail.[6] The electron beam induced changes in the samples were followed as a function of irradiation time, using a constant beam current density of 0.017 83 μA/cm^2. The materials were monitored using infrared specular reflection spectroscopy, using a Perkin-Elmer 580 IR spectrometer equipped with a Model 3600 IR data station. The reflectivity measurements were made in situ by rotation of the sample from the electron beam to the IR beam. All measurements were made with the incident IR beam at 25° from normal to the sample plane.

Electron beam exposures within a vacuum system facilitate the measurement of the current density I (amps/cm^2) of the incident beam. The product of I and time t gives q, the incident charge density (coulombs/cm^2) administered to a sample. Due to the relative ease with which q is measured, many authors report the response of a system as a function of this value. In this report we also use incident charge density, and in addition list the current density. The latter value is given so that our results may be compared with others using a different I to avoid confusion that may arise from a dose rate effect.

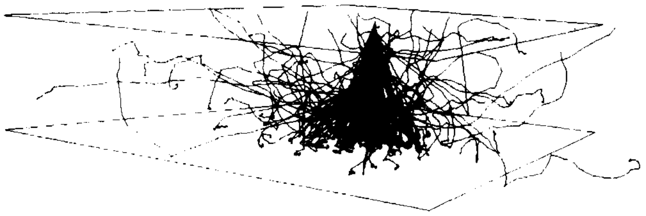

Figure 1. Monte Carlo simulation for the trajectories of 100 electrons, accelerated to 25 kV, penetrating a 2-μm-thick film of PPFPO.

The absorbed dose in units of megarads was determined by use of the following expression:

$$D = E_a/gk \tag{2}$$

where g is the weight of material in grams into which the energy E_a (eV) was deposited, and $k = 6.24 \times 10^{19}$ is the factor used to convert from eV/g to Mrad (1 Mrad = 6.24×10^{19} eV/g). The energy deposited into the films were determined using a Monte Carlo model for electron-solid interactions.[13] For good statistics, 10 000 electron trajectories were used to simulate electron penetration and energy deposition in the films. For the perfluorinated ether film, and film thicknesses studied herein, we have determined that for Q = 1.0 μC/cm^2, $D \approx 2.5$ Mrad. The simulations were performed on an IBM RISC 6000 Model 530 work station. As an illustrative example, the trajectories for 100 electrons in a 2-μm-thick film of PPFPO is presented in Figure 1. For the same data set using 10 000 electrons accelerated at 25 kV, 40.2% of the initial energy is deposited into the 2-μm-thick PPFPO film and the remainder into the substrate, i.e., gold. The total backscattering yield is calculated to be 22%; these are the electrons which are backscattered and exit the top surface of the film.

An important experimental point to consider is how the time dependence of the film thickness or mass loss is obtained. Initially, a number of experiments were conducted to determine whether or not the thickness loss showed a dependence on dose rate. Thus, when the current density was varied from 10^{-10} to 10^{-5} A/cm^2, the thickness loss measurements only depended upon charge density regardless of the value of I and irradiation time t. As a consequence, the film thickness loss rate was obtained by first constructing a plot of film thickness loss against time, the slopes of which gave the rate. To make the results consistent, the same current density was used for all of the samples studied here.

Computational Details

Ab initio calculations were performed using the IBM/AIX G90RevI version of the Gaussian 90 computer code,[14] using IBM RISC 6000 computers. The calculations were performed using restricted Hartree–Fock (RHF for closed shell and ROHF for open shell) wave functions using the 6-31G* basis set.[15] In all cases, the geometry was optimized with no symmetry constraints imposed on the molecules, and direct SCF methods were used. To obtain accurate analytical gradients, a high degree of convergence in the SCF procedure was used, 10^{-9} for the requested convergence on the density matrices, and residual forces of $\leq 3 \times 10^{-4}$ hartree/bohr on the Cartesian components. Hessians were computed for each molecule by differentiation of the energy gradient at the optimized geometries; no

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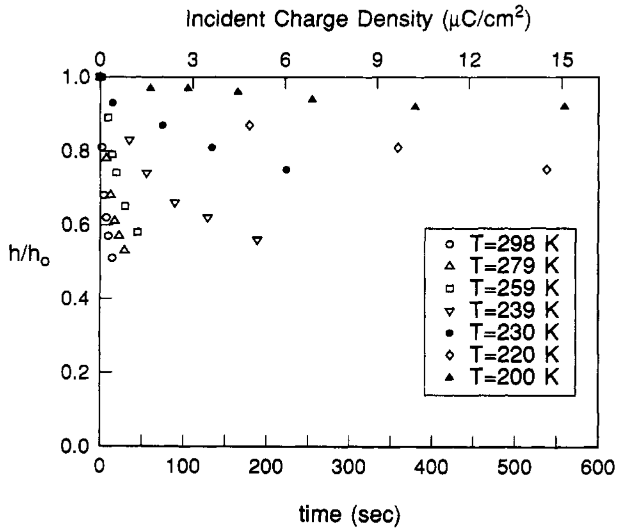

Figure 2. Changes in the normalized film thickness of PMPS as a function of time (and incident charge density) and temperature. Samples were exposed to 25-kV electron beam under vacuum.

imaginary frequencies were obtained. For closed shells, the Hessians are evaluated analytically while for spin restricted open shells, the default is numerical evaluation.[14]

The **z** matrices for many of the model molecules were facilitated by using the Alchemy II molecular modeling software tool,[16] run on an IBM PS/2 Model 80 personal computer. Alchemy II allows an initial minimization of the molecule using a built-in force field, a conjugate gradient procedure that computes all partial first derivatives in order to move all of the atoms simultaneously during each iteration. The minimized geometry is stored on the PS/2 as Cartesian coordinates, which can readily be converted to a **z** matrix file and then transferred to a work station over a LAN (local area network), ready for use in a program application such as Gaussian 90.

Results and Discussion

Electron Beam Degradation of Poly(2-methylpentene 1-sulfone). Poly(2-methylpentene 1-sulfone), or PMPS, was chosen as a calibration for obtaining the activation energy for depolymerization, since a large body of data is available in the literature. Thus thin films of PMPS were exposed to a 25-kV electron beam under vacuum, at $T = 180, 200, 220, 239, 259, 279,$ and 298 K and the film thickness loss as a function of time (and incident charge density) is shown in Figure 2. The changes in the film thickness were obtained by measuring the changes in the percent reflectivity of the characteristic sulfone absorption at 1298 cm^{-1} as a function of time, then relating the percent reflectivity to film thickness using a dispersion analysis previously published for PMPS.[17] These results reveal that the rate of film thickness loss in PMPS decreases with decreasing temperature. These data are consistent with the concept of the ceiling temperature, T_C, for these materials.[2] The ceiling temperature of PMPS has been measured to be ≈240 K.[18,19] From the data presented in Figure 2, it is apparent that film thickness loss from PMPS is relatively rapid above 240 K but begins to slow appreciably below 200 K. This may mean that as the ceiling temperature for PMPS is reached, which is at some value below 240 K, the rate of film thickness loss begins to slow appreciably, or, merely that the monomers are not as volatile below these temperatures. In fact, when PMPS was exposed to an electron beam with the sample at $T = 10$ K, even after very large doses were administered no changes in film thickness were observed. Furthermore, only very small changes were observed in the infrared spectra before and after exposure.

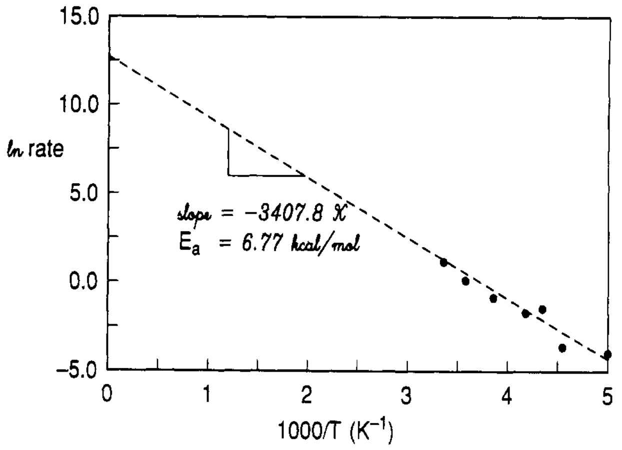

Figure 3. Plot for the rate of film thickness loss versus reciprocal temperature for PMPS exposed to a 25-kV electron beam under vacuum.

The G value for SO_2 evolution was obtained from the decay curves shown in Figure 2, where a polynomial fit to the data points provided the initial slopes. The G value is defined as the number of molecules formed or destroyed per 100 eV of absorbed energy. The G values for formation of SO_2 were 5 (200 K), 7 (220 K), 46 (230 K), 110 (259 K), 280 (279 K), and 800 (298 K). The room-temperature value is consistent with values found in the literature.[9]

A plot of the initial slopes from the normalized film thickness loss data, as a function of reciprocal temperature is shown in Figure 3. The energy of activation for depolymerization may be obtained from Figure 3 and from eq 3:

$$\text{rate} = Ae^{-E_a/RT} \tag{3}$$

where rate is the normalized film thickness loss as a function of time (Figure 2), A is a preexponential constant, E_a is the activation energy for depolymerization, R is the gas constant (1.987 kcal/mol deg), and T is the absolute temperature (kelvin). From the slope in Figure 3, the activation energy, E_a, is equal to 6.77 kcal/mol in the temperature range 180–298 K. Bowden has reported[20] an activation energy for depolymerization of 6.65 kcal/mol for the temperature range between 296 and 413 K. Thus we observe that reliable fits may be obtained using specular reflection infrared spectroscopy as the method of investigation, and we now employ the same methods to obtain data on the poly(perfluoroethers).

Electron Beam Degradation of Poly(perfluoroethers). The electron beam irradiation of poly(perfluorinated ethers) results in main-chain scission leading to mass loss, a decrease in molecular weight, and evolution

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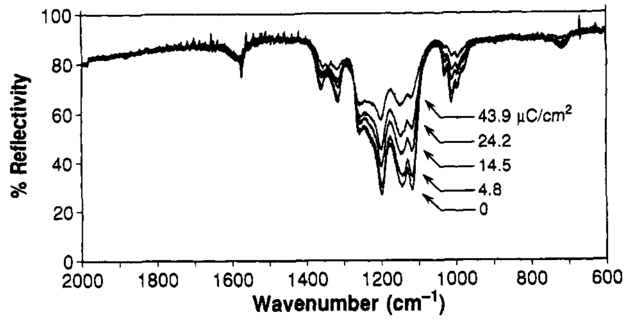

Figure 4. Infrared spectrum of PPFNPO as a function of incident charge density. 25-kV electron beam exposure under vacuum at room temperature. The corresponding changes as a function of exposure time are 0, 4.5, 13.6, 22.6, and 41.0 min for 0, 4.8, 14.5, 24.2, and 43.9 $\mu C/cm^2$, respectively.

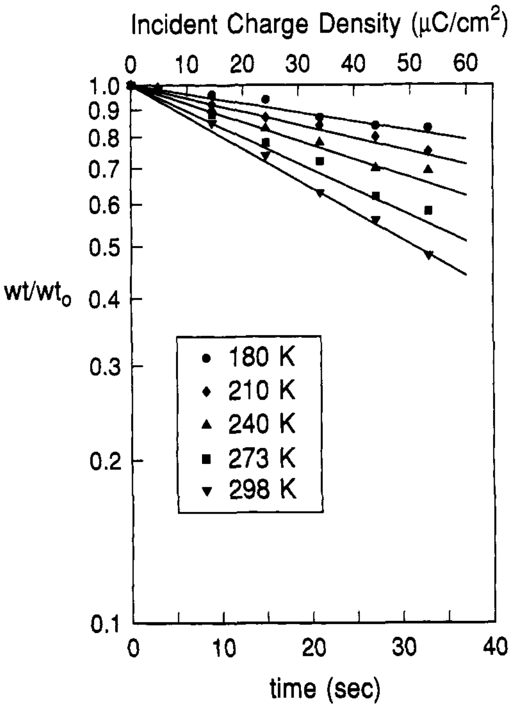

Figure 5. Normalized weight loss versus time (and incident charge density) for PPFNPO exposed to a 25-kV electron beam at various temperatures.

of small gas molecules such as COF_2 and CF_4. G values for monomer units lost and gas products formed, and molecular weight decrement, etc., have been reported at room temperature.[21] Here we report G values and activation energies for decomposition of poly(perfluoroethers) by investigating the rate of weight lost as a function of temperature from 180 to 298 K. As an illustrative example, the changes in the IR specular reflectance spectrum of PPFNPO as a function of incident charge density at 298 K is presented in Figure 4. The effect of the electron beam is to induce main-chain degradation of the polymer, resulting in mass loss (Figure 5). At this temperature, all of the low molecular weight oligomers and small gas molecules like COF_2 formed as a result of the irradiation are pumped away by the vacuum system. To determine the activation energy for monomer unit loss from the poly(perfluoroethers), the mass loss rate was initially determined from IR measurements as a function of time taken at five temperatures, $T = 180, 210, 240, 273,$ and 298 K. The normalized mass loss rate as a function of time (and incident charge density) for PPFNPO is shown in Figure 5 as an illustrative example. To obtain the plots shown in Figure 5, the changes in the percent reflectivity were related to changes in the film thickness via a dispersion analysis[22] and converted to mass lost by multiplication of the film thicknesses by the initial density of the polyperfluoroethers, valid at short irradiation times. All of the other poly(perfluoroethers) exhibited similar behavior, with mass loss rate increasing with increasing temperature. The mass lost by each of the polymers as a function of incident charge density were also converted to monomer units lost per absorbed dose to obtain G values for both polymer and monomer transformation, and these values are summarized in Table I for the poly(perfluoroethers) studied here. The G values for polymer decomposition range from 0.1 to 1.3 and are observed to increase with increasing temperature. The G value for decomposition of monomer units is obtained by multiplying the G value for polymer decomposition by the average degree of polymerization. The G values for loss of monomer units are highest for the unbranched poly(perfluoroethers) like PPFMEO and PPFMEO-OH, 41 and 29, respectively, and lowest for branched structures like PPFPO, where G is 26. The unbranched polymer PPFNPO, with three carbon atoms between each oxygen atom, also has a comparatively lower G value than PPFMEO. These results are consistent with the instability of the $-(CF_2O)-$ homopolymer which will depolymerize to monomeric COF_2; that is, copolymers containing $-(COF_2)-$ units (like PPFMEO) will tend to evolve more gaseous COF_2.

The G values determined here for loss of monomer units vary from 41 to 26, depending upon polymer structure, and are approximately twice as high as the G values determined when the experiments are conducted under atmospheric pressures, where the G values for monomer unit loss ranged from 11 to 22, while the G values for polymer decomposition varied from ≈ 0.2 to 0.8.[22] The higher G values observed here under vacuum is an artifact of the vacuum environment and may be explained via a vapor pressure argument. The operational vacuum pump pressure for our apparatus is 10^{-7}–10^{-8} mmHg; the vapor pressure for PPFPO with a molecular weight of 1500 is $\approx 10^{-5}$ mmHg, while for a molecular weight of 3000 it is $\approx 10^{-6}$ mmHg. Thus it is reasonable to conclude that fragmented polymer chains with molecular weights $\lesssim 1500$ are pumped away in our vacuum system. This effect yields a higher G value for the decomposition of the poly(perfluoroethers) in vacuum.

The energy of activation for monomer molecules transformed may be obtained from eq 3, defined previously. A summary plot for the rate of normalized weight loss versus reciprocal temperature is shown in Figure 6 for all of the poly(perfluoroethers) investigated here. The slopes of the lines from least squares fits yield the activation energies, which are summarized in Table II. The values range from 0.7 to 1.4 kcal/mol, depending upon the poly(perfluoroether). These data indicate that the activation energy for monomer unit loss is lowest for the unbranched poly(perfluoroethers) that contain ≤ 2 carbon atoms between each oxygen atom, while the branched poly(perfluorinated ethers) like PPFPO have the highest. This is consistent with the G value data presented in Table I.

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Table I. *G* Values for Polymer Decomposition and for the Number of Monomer Units Lost (in Parentheses) per 100 eV as a Function of Temperature. *n* Is the Average Degree of Polymerization

		temp, K						
perfluoroether	*n*	180	195	210	220	240	273	298
PPFMEO	83	0.1 (10.7)		0.3 (28.0)		0.4 (30.6)	0.4 (36.4)	0.5 (40.7)
PPFMEO-OH	25	0.4 (10.0)	0.8 (20.3)		1.0 (25.5)			1.2 (29.0)
PPFMPO	38	0.2 (7.5)		0.2 (7.7)		0.4 (15.9)	0.6 (21.2)	0.7 (27.2)
PPFNPO	34	0.3 (9.8)		0.4 (13.6)		0.5 (18.4)	0.7 (23.6)	0.8 (26.0)
PPFPO	51	0.1 (6.6)		0.1 (7.0)		0.3 (14.8)	0.4 (22.5)	0.5 (25.9)

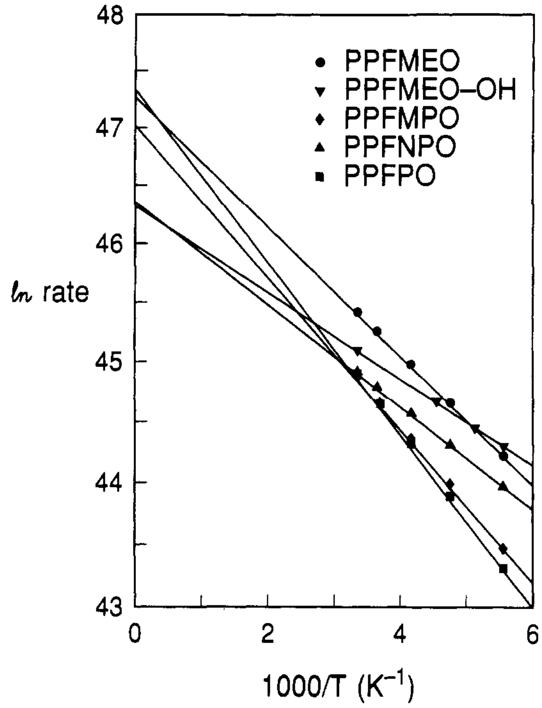

Figure 6. Plot for the rate of normalized weight lost versus reciprocal temperature for some poly(perfluoroethers) exposed to a 25-kV electron beam under vacuum.

Table II. Activation Energy for Monomer Unit Loss

perfluoroether	ΔE (kcal/mol)	perfluoroether	ΔE (kcal/mol)
PPFMEO	1.1	PPFNPO	0.9
PPFMEO-OH	0.7	PPFPO	1.4
PPFMPO	1.3		

A note of caution is stated here for the values obtained for the activation energies. We have discussed the enhancement of the *G* values in a vacuum environment compared to ambient pressure, and as a consequence we are reluctant to state that the process responsible for this activation energy is solely a series of thermal β elimination reactions. The activation energies are indeed small in comparison to the E_a for the poly(sulfone) and certainly suggests that another process, for example, mass removal of radiation-induced fragments by the vacuum system might contribute. For this reason, we decided to explore the possible reactions theoretically to determine the energetics for radical β-elimination reactions. In this report, only the ΔH and ΔG values are determined.

Theoretical Studies on β-Elimination Reactions. The breaking of a bond in the main chain of poly(perfluoroethers), for example, in the simplest case, poly(perfluoromethylene oxide), gives a free radical such as

$$-CF_2OCF_2OCF_2OCF_2OCF_2^{\bullet}$$

Barnaba et al.,[4] in his studies of irradiated poly(tetrafluoroethylene oxide), found two carbon-centered and one oxygen-centered radicals, one of the carbon-centered radicals being most stable. Accordingly, in these studies, we consider primarily carbon-centered radicals as initiating the scissioning sequence. Thus, in the radical structure shown above, a subsequent β scission produces a perfluoromethylene oxide unit, i.e., carbonyl fluoride or COF_2. When branching is introduced into the structure, such as a pendant perfluoromethyl, additional and competitive scissioning processes become possible. In an effort to gain some understanding of the energetics of the bond-scissioning processes possible, we have investigated bond scission reactions from some unbranched model systems for poly(perfluoroethers). Hence, ab initio SCF calculations on a considerable number of model fragments with both closed and open shells were performed. Their total and zero-point energies are summarized in Table III. For each structure, the geometry was optimized, and second derivatives of energy with respect to coordinates were calculated with no imaginary frequencies. The optimized parameters, geometries, population analyses, force constants, and vibrational frequencies are too numerous to list for the purposes of this paper; however, they are available to the interested reader. For the purposes of understanding some of the possible depolymerization reactions, only their energetics are considered here, that is, changes in the internal energies and enthalpies of reactions. The ab initio total energies are representative of a vibrationless molecule in vacuum at 0 K. The internal energy at 298 K (or any temperature) is defined as

$$U = E_{\text{total}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}} \tag{4}$$

where E_{total} is the total energy, E_{vib}, E_{rot}, and E_{trans} are the vibrational, rotational, and translational energies, respectively. The vibrational energy at 298 K is in turn the sum of the zero-point energy and all additional contributions to vibrations from 0 to 298 K:

$$E_{\text{vib}} = E_{\text{zero-point}} + \sum_{\text{vib}} E_{\text{vib}}(0\text{–}298\text{ K}) \tag{5}$$

The enthalpy and Gibbs energies are then described in the usual manner, $H = U + RT$ and $G = H - TS$.

The simplest reaction sequence to model here is the β scission of COF_2 from a polyperfluoromethylene oxide homopolymer radical, and these results are summarized in Table IV. In Figure 7, the optimized geometry for the model "main chain" is shown. There are a variety of conformers that may exist for the main-chain model, but this conformation was chosen to most easily visualize the COF_2 scission reaction. By comparing the optimized geometries shown in Figure 7, it is evident that the backbone of the initial conformer is maintained at all times after COF_2 loss to ensure that the energetics of the β scission reaction is representative of the scissioning of COF_2 itself and excludes additional contributions from conformational changes. The relative energies that are calculated for the β-scission reaction in a given conformer should

Table III. HF/6-31G* Total Energies E_{tot}, Vibrational Energies E_{vib}, Entropy S for Model Poly(perfluoroether) Reactants and Products

perfluoroether	E_{tot} (hartrees)	$E_{zero\text{-}point}$ (kcal/mol)	$E_{vib.}$, 298 K (kcal/mol)	S, 298 K (cal/mol K)
$CF_3OCF_2^\bullet$	−647.753 879	20.640 45	22.973	85.435
$CF_3OCF_2OCF_2^\bullet$	−959.374 516	32.635 13	37.078	104.212
COF_2	−311.615 306	9.907 45	10.130	61.456
CF_3CFO	−548.357 351	18.551 69	20.367	78.558
$CF_3CF_2^\bullet$ (β-CF eclipsed)	−572.877 120	17.242 39	19.143	80.349
$CF_3OCF_2OCF_2OCF_2^\bullet$	−1270.99 490	44.582 54	51.181	123.147
$CF_3CF_2CF_2OCF_2^\bullet$	−1121.23 627	37.849 45	43.563	113.900
$CF_3CF_2CF_2^\bullet$ (β-CC eclipsed)	−809.620 417	25.915 95	29.448	94.392
$CF_3CF_2OCF_2^\bullet$	−884.495 822	29.244 92	33.279	99.629
$CF_3O^\bullet$	−411.009 176	11.435 44	12.192	69.226

Table IV. Reaction Energetics, in kcal/mol, for Some Scissioning Reactions from Perfluoroether Radicals (HF/6-31G*)

reaction	ΔU (T = 0 K)	ΔU (T = 298 K)	ΔH (T = 298 K)	ΔG (T = 298 K)
$CF_3OCF_2OCF_2OCF_2^\bullet \rightarrow CF_3OCF_2OCF_2^\bullet + COF_2$	+1.15	+0.99	+1.58	−11.09
$CF_3OCF_2OCF_2^\bullet \rightarrow CF_3OCF_2^\bullet + COF_2$	+1.25	+1.15	+1.74	−10.98
$CF_3OCF_2OCF_2^\bullet \rightarrow CF_3O^\bullet + CF_3CFO$	+2.37	+2.27	+2.86	−10.12
$CF_3CF_2CF_2OCF_2^\bullet \rightarrow CF_3CF_2CF_2^\bullet + COF_2$	−1.68	−1.86	−1.27	−13.77
$CF_3CF_2CF_2OCF_2^\bullet \rightarrow CF_3CF_2^\bullet + CF_3CFO$	−0.92	−1.15	−0.55	−13.97
$CF_3CF_2OCF_2^\bullet \rightarrow CF_3CF_2^\bullet + COF_2$	+0.04	−0.10	+0.49	−12.08

then be representative of the energetics of COF_2 evolution. Thus the scissioning reaction in a $-(-CF_2O-)_n-$ type of material is modeled using the following sequence of β-scission reactions where carbonyl fluoride is lost:

$$CF_3OCF_2OCF_2OCF_2^\bullet \xrightarrow{-COF_2} CF_3OCF_2OCF_2^\bullet \xrightarrow{-COF_2} CF_3OCF_2^\bullet$$

The β-scission reaction for $CF_3OCF_2OCF_2OCF_2^\bullet$ is summarized in Table IV. Loss of COF_2 from $CF_3OCF_2OCF_2OCF_2^\bullet$ and subsequent loss of COF_2 from $CF_3OCF_2OCF_2^\bullet$ are predicted to proceed at room temperature (298 K) with ΔU values of 0.99 and 1.15 kcal/mol, respectively, while the ΔH values are 1.58 and 1.75 kcal/mol, respectively. These values are consistent with the activation energies determined experimentally for these materials (Table II), but of course the theoretical values reflect the differences between thermodynamic properties, internal energies, and enthalpies between reactant and products. The calculations predict that evolution of COF_2 is endothermic. The negative ΔG values indicate that the scissioning of COF_2 monomer units is a feasible reaction pathway. The ΔG values are dominated by the $T\Delta S$ terms (>10 kcal/mol) compared to the ΔH terms (≈2 kcal/mol).

From $CF_3OCF_2OCF_2^\bullet$, we have also compared the relative energetics for the formation of COF_2 and CF_3CFO. The ΔG values are negative for both of these processes, and thus COF_2 and CF_3CFO may be formed from such a radical precursor. COF_2 evolution requires a β-scission, while CF_3CFO formation requires a scission and subsequent rearrangement. The computed enthalpy for formation of COF_2, ΔH = 1.74 kcal/mol, is considerably less than for formation of CF_3CFO, where ΔH = 2.86 kcal/mol. The G value for evolution of CF_3CFO was experimentally observed to be significantly less than for COF_2 in branched polyperfluoroethers and was not detected in any appreciable quantity from unbranched polyperfluoroethers.[21]

Another important β scission reaction to consider which is pertinent for the scissioning of $-(-CF_2CF_2O-)_n-$ and $-(-CF_2CF_2CF_2O-)_n-$ polymers is the following. In PPFEO, main-chain scission may produce $-CF_2CF_2OCF_2^\bullet$ radicals, while in PPFNPO, $-CF_2CF_2CF_2OCF_2^\bullet$ may be formed. Thus the models used to investigate the evolution of COF_2 from these radicals are

$$CF_3CF_2OCF_2^\bullet \rightarrow CF_3CF_2^\bullet + COF_2$$

$$CF_3CF_2CF_2OCF_2^\bullet \rightarrow CF_3CF_2CF_2^\bullet + COF_2$$

The optimized geometries are shown in Figure 8. The ΔU for the β-scission reactions at T = 298 K are −0.10 and −1.86 kcal/mol, respectively, and the ΔH values are +0.49 and −1.27 kcal/mol, respectively. These values are smaller compared to loss of COF_2 from the perfluoromethylene oxide homopolymer $-(CF_2O-)_n-$ (Table IV). Although at this point in the study we have only examined a few reactions, the results listed in Table IV indicate that β-scission reactions producing a perfluorinated carbon radical is slightly more exothermic (considering the ΔG values) than those where perfluorinated ether radicals are formed.

Another product observed to form upon electron beam irradiation is CF_3CFO. This aldehyde may be formed by the scissioning of a γ C–O bond in $CF_3OCF_2OCF_2^\bullet$ and a γ C–C bond in $CF_3CF_2CF_2OCF_2^\bullet$ and $CF_3CF_2OCF_2^\bullet$ accompanied thereafter by a rearrangement reaction. As compared in Table IV, the energy penalty associated with evolution of CF_3CFO from $CF_3OCF_2OCF_2^\bullet$ as opposed to loss of COF_2 is an additional ≈1.1 kcal/mol, for both ΔU and ΔH. Nevertheless the negative ΔG predicts evolution of CF_3CFO to be a feasible reaction pathway; we have thus far observed experimentally evolution of CF_3CFO from the branched polyperfluoroethers like PPFPO but not from unbranched structures such as PPFMEO.[21]

The formation of COF_2 and CF_3CFO from $CF_3CF_2CF_2OCF_2^\bullet$ is likewise predicted to be feasible, both with negative ΔG values of −13.77 and −13.97 kcal/mol, respectively. However, the enthalpy for formation of COF_2, ΔH = −1.27 kcal/mol, is considerably more negative that for the formation of CF_3CFO, ΔH = −0.55 kcal/mol, thus COF_2 evolution may proceed more readily. Experimentally, the stable gases evolved from PPFNPO are dominated by COF_2.[22]

Conclusions

The activation energies and G values for the depolymerization of poly(2-methyl-1-pentene sulfone) and monomer loss for five poly(perfluoroethers), PPFMEO, PPFMPO, PPFPO, PPFMEO-OH, and PPFNPO, were deter-

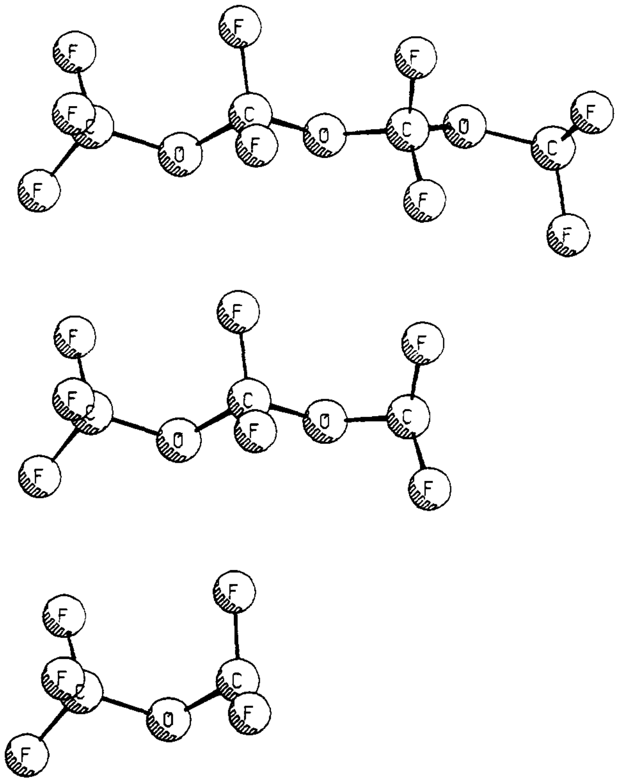

Figure 7. Some optimized geometries of model molecules for the $-(-CF_2O-)_n-$ backbone.

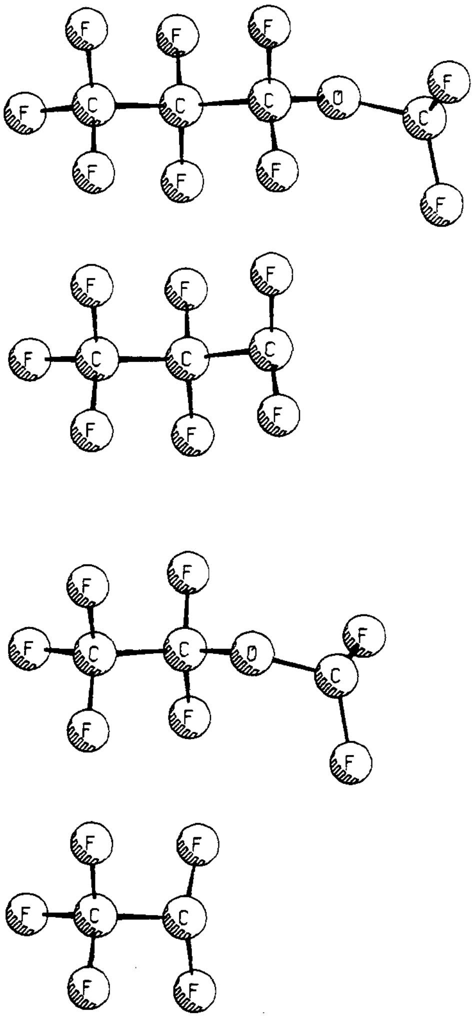

Figure 8. Some optimized geometries used to model the radical scissioning reactions in $CF_3CF_2CF_2OCF_2^{\bullet}$ and $CF_3CF_2OCF_2^{\bullet}$.

mined via infrared studies using electron beam to initiate main chain scissioning. The *G* value for SO_2 evolution from poly(2-methyl-1-pentene sulfone) was 800 at room tempeature, and the activation energy for depolymerization was 6.77 kcal/mol. For poly(perfluorinated ethers), the *G* values for polymer decomposition ranged from 0.1 to 1.2, and the activation energy for monomer unit loss ranged from 0.7 to 1.4 kcal/mol, depending upon structure. Initial results on the poly(perfluoroethers) seemed to indicate that these materials exhibited some unzipping type of depolymerization reactions like polysulfones. While this is most likely for the $-(-CF_2O-)-$ homopolymer, the poly(perfluoroethers) studied here are complicated by C–C–O, C–C–C–O, and C(C)–C–O skeletal units that give rise to evolution of other small fragments as well as larger oligomers from the samples. A better model to pursue to explain the mass loss data is one which contains some unzipping at $-(-CF_2O-)-$ sites (PPFMEO and PPFMPO) accompanied by evolution of other radiation products with high vapor pressures from β-scission reactions. To obtain additional insight, ab initio calculations were performed in parallel with the experiments to investigate radical decomposition mechanisms. These results revealed that the ΔH for formation of COF_2 from poly(perfluoromethylene oxide) radicals was $\approx$1 kcal/mol. Thus the energetics for β-scission reactions are computed to be small and are consistent with the experimental results of high-*G* values and small activation energies.