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Perfluoropolyethers: Intramolecular Disproportionation

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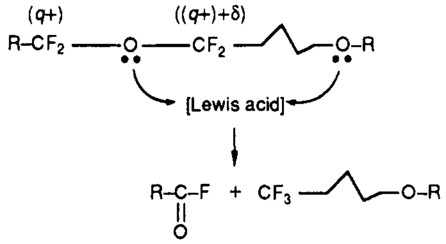
ABSTRACT: Thermal degradation of commercial perfluoropolyethers (Fomblin Z and Y, Krytox, and Demnum) and PFPEO (perfluoropoly(ethylene oxide)) in the presence of Lewis acids (metal oxides and halides) was examined. It is shown that the degradation is dominated by the intramolecular disproportionation process of the following scheme.



The reaction occurs when the two oxygen atoms flanking a monomer unit of polyether chains interact with a Lewis acid site(s). The differential charges induced at the carbons immediately outside and inside the unit cause a fluorine transfer and effect the disproportionation process. It is shown that the susceptibilities of various sectors of perfluoropolyether chains to the postulated process are determined by the disposition of the oxygens flanking the monomer unit of the sector and by the initial net atomic charges of carbons involved in the fluorine transfer. The disproportionation reaction does not occur at internal sectors of Krytox and PFPEO, for example, on account of the "trans" disposition of the successive ether oxygens; the reaction occurs readily and exclusively at chain ends, however.

1. Introduction

Perfluoropolyethers are currently the lubricant of choice for magnetic recording media[1] and are also in use as lubricants in such severe environments as aerospace engines and satellite instruments.[2] Excellent lubricity aside, a wide liquid-phase temperature range, low vapor pressure, small temperature dependency of viscosity, high thermal stability, and low chemical reactivity are the attributes that have led to these high-performance applications. The most often cited, commercially available perfluoropolyethers are Fomblin Z, Fomblin Y, Krytox, and Demnum. Representative structural formulas of these materials are shown in Figure 1. Fomblin Z and Y are prepared by photooxidation of tetrafluoroethylene and hexafluoropropylene, respectively, and are random copolymers of indicated units.[3] Krytox and Demnum are synthesized via base-catalyzed polymerization of perfluoropropylene oxide[4] and trimethylene oxide,[5] respectively. In this report the notations Z-, Y-, K-, and D-lubes shall be used to indicate the respective perfluoropolyethers.

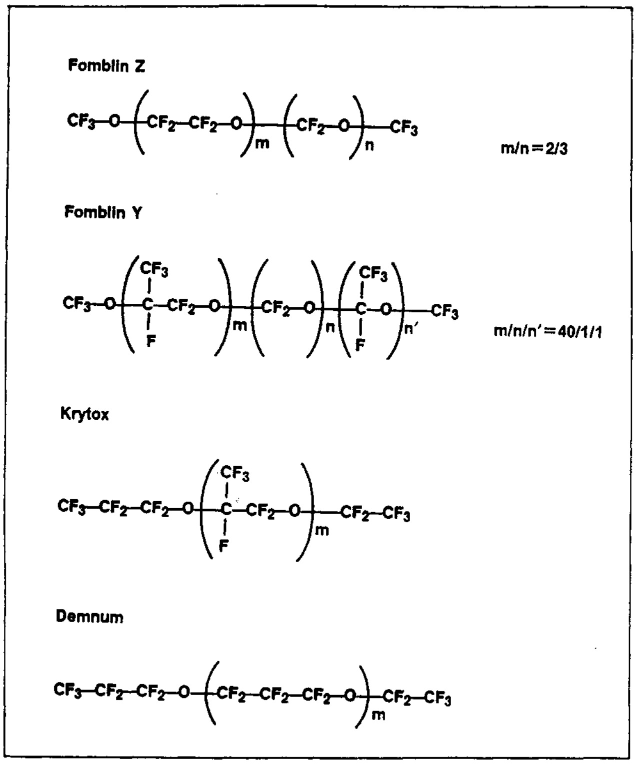


Figure 1. Formulas of commercial perfluoropolyethers, Fomblin Z, Fomblin Y, Krytox, and Demnum.

Because of potential applications at high temperature, the thermal stability and thermal degradation process of these materials have been investigated extensively by many authors.[6–14] Helmick and Jones[14] concluded, on the basis of the result of tensimeter measurements, that the intrinsic decomposition temperature of these material was indeed high (>350 °C) and was insensitive to structural differences such as the presence (or absence) of acetal units, $-O-CF_2-O-$, or of pendant CF_3 side groups. It has been shown repeatedly, however, that their *actual thermal stability* is adversely affected by the presence of a metal surface (e.g. stainless steel); the decrease of stability has been attributed to surface oxide formed under oxidative conditions.[6] Formation of surface halide (FeF_3) under tribological conditions has also been observed for all types, as has subsequent degradation catalyzed by the surface halide in the case of Z-lube.[9,11,12] Zehe and Faut reported complete degradation of Z-lube at 185 °C in the presence of Fe_2O_3.[13] They demonstrated that the process occurred in two stages, the slow first stage during which conversion of surface Fe_2O_3 to FeF_3 occurred and the second stage

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where the degradation proceeded rapidly catalyzed by the surface FeF_3. The corresponding degradation was not observed with K-lube. Severe degradation of Z-lube catalyzed by Lewis acid $AlCl_3$ at temperatures as low as 100 °C has also been reported.[2] The greater vulnerability of Z-lube toward acid attack has been attributed to the presence of acetal units ($-O-CF_2-O-$) in the polymeric chains.[9,12,13] The degradation mechanism most often suggested had been a chain homolysis followed by *unzipping*.

Recently, we conducted a spectroscopic study (^{19}F NMR) of the degradation process of perfluoropolyethers in the presence of Al_2O_3.[15] Al_2O_3 (of the α form) is often used as a structural element in the head-and-disk assembly of magnetic recording media. The study led to a followup investigation of the degradation process in the presence of a stronger Lewis acid, $AlCl_3$.[16] These studies conclusively demonstrated that the degradation process of perfluoropolyethers in the presence of Lewis acid (metal oxides or halides) was dominated by a simple *intramolecular disproportionation reaction* of the following form.

$$R{-}CF_2{-}O{-}CF_2{-}R \rightarrow R{-}C(F){=}O + CF_3{-}R \qquad (1)$$

Reaction 1 occurs most readily at acetal sectors, but with sufficient thermal energy and/or in the presence of a stronger Lewis acid, it occurs at other ether linkages as well.

We have postulated that the envisaged reaction 1 occurs when differential charges are induced on the two carbon atoms of an ether linkage (i.e. $-C^{q+}-O-C^{(q+)+\delta}-$) and that such differential induction occurs when two successive ether oxygens of the polymer chains interact with Lewis acid site(s) on the surface of metal oxide or halide.[16] A larger positive charge is induced on the carbon(s) flanked by the two interacting oxygens. The fluorine transfer of reaction 1 is then from the "outside carbon" (with less induced charge) to the "inside carbon" (with more induced charge). It follows that, when reaction 1 occurs at the terminal ether linkage, the fluorine transfer is from the terminal group into the internal sector, and the fluorocarbonyl end group is generated in the seceding monomer unit. When it occurs in midchain sectors, chain fragmentation occurs and chain segments with a fluorocarbonyl end group are formed. In either situation the process, when continued, leads to complete loss of fluid due to evaporation of successively formed monomer units and/or low molecular weight oligomers.

Most interestingly it has been found that the disproportionation reaction 1 occurs at internal sectors of Z- and D-lubes but exclusively at chain ends in the case of K-lube. We tentatively concluded that the midchain sectors having pendant CF_3 groups were protected from the postulated process. The study also revealed that the alkoxy end groups adjacent to $-CF(CF_3)-$ were also spared from the process.

It would indeed be gratifying if a rationale could be found for the different susceptibilities shown by various sectors of perfluoropolyethers toward the postulated disproportionation process. We report here the result of our further investigation of the process conducted to this end.

We examined the conformation of perfluoropolyethers by molecular mechanics calculations (Allinger's MM2 codes with additional parameters).[17] The calculations showed, not unexpectedly, that the perfluoropolyethers would maintain a zigzag form for the backbone, and the barrier for rotation about any one of the bonds in the backbone would be extremely high ($\gg$ 10 kcal). Hence when there are an odd number of carbons in the backbone sector of a building monomer unit (as in the acetal units in Z- and Y-lubes and the trimethylene units in D-lube), the two oxygens flanking the unit would be exposed on the same side of the chain. When the building unit contains an even number of carbons in its backbone sector (as those in K-lube), two successive oxygens in the chain would be positioned at opposite sides. We also examined perfluoropolyethers by molecular orbital calculations (MNDO).[18] The calculations revealed a surprisingly large variation in the net atomic charges of carbons in the backbone of "free" perfluoropolyethers. The present study revealed that the susceptibility to the disproportionation process (exhibited by various sectors of perfluoropolyethers) was determined by the disposition of the two oxygens flanking the unit, and the net atomic charges of the carbons involved in the fluorine transfer.

2. Experimental Section

As in the earlier studies the degradation process of perfluoropolyethers in the presence of Lewis acids (metal oxides or halides) was examined by placing a given amount (5 g) of lubricant and 1 wt % of the selected Lewis acid in a test tube and immersing the test tube in an oil bath thermostatically maintained at given temperature (200–300 °C).[15,16] For each lubricant, the weight loss was measured after the heat treatment for a given period of time, and the ^{19}F NMR spectrum of the remaining fluid was obtained and analyzed. The fluid remaining in the test tube after a weight loss of 25%, for example, shall be called *25% degraded* lube. $AlCl_3$ is known to sublime at 178 °C. No loss of $AlCl_3$ occurred, however, when immersed in perfluoropolyethers and heated above this temperature (200–250 °C). The reacted $AlCl_3$ powder began to sublime only after complete loss of fluid had occurred.

The efficacy of ^{19}F NMR spectrum in elucidation of structural details of perfluoropolyethers has been well-demonstrated.[3,19] The ^{19}F NMR spectra presented here were obtained with an IBM Instruments AM300 system (^{19}F frequency 282.4 MHz). The chemical shifts were measured in reference to $CFCl_3$, and all the assignments were done on the basis of the extensive data set and empirical formulas given in ref 19.

GPC measurements of starting and degraded lubes were kindly made by Dr. G. Vuren of IBM Almaden Research Center using a Waters system with a refractive index detector.

Z- and Y-lubes used for the study were products of Montedison Co. K- and D-lubes used were products of DuPont Co. and Daikin Industry, respectively. Samples of perfluoropoly(ethylene oxide), PFPEO, were kindly provided by Drs. W. R. Jones, Jr., of NASA Lewis Research Center and T. R. Bierschenk of Exfluor Research Corp. The number-averaged molecular weights of Z-, Y-, K-, and D-lubes were in the range 6000–8000, and those of PFPEO samples were in the range 2000–4000.

Al_2O_3 (powder) and $AlCl_3$ (anhydrous powder) were obtained from Aldrich Chemical Co. TiO_2 was obtained from Alfa Products, and ZrO_2 and ZrF_4 were obtained from AESAR group.

3. Results and Analyses

In order to facilitate the presentation and understanding of the current result, let us briefly recount the degradation processes observed when Z-, Y-, K-, and D-lubes were heated in the presence of Al_2O_3[15] and $AlCl_3$.[16] Parts a–c of Figure 2 show the percent weight losses observed when these lubes were heated in the presence of Al_2O_3 at 200 °C and in the presence of $AlCl_3$ at 200 and 250 °C, respectively. The unique degradation of Z-lube observed in the presence of Al_2O_3 after an induction period (Figure 2a) is attributed to the disproportionation reaction involving the acetal units. We postulated that the reaction was catalyzed by the fluoride surface, as depicted in Figure 3. The process results in (1) chain scission, (2) transformation of the acetal unit into a methoxy end group, and (3) transformation of

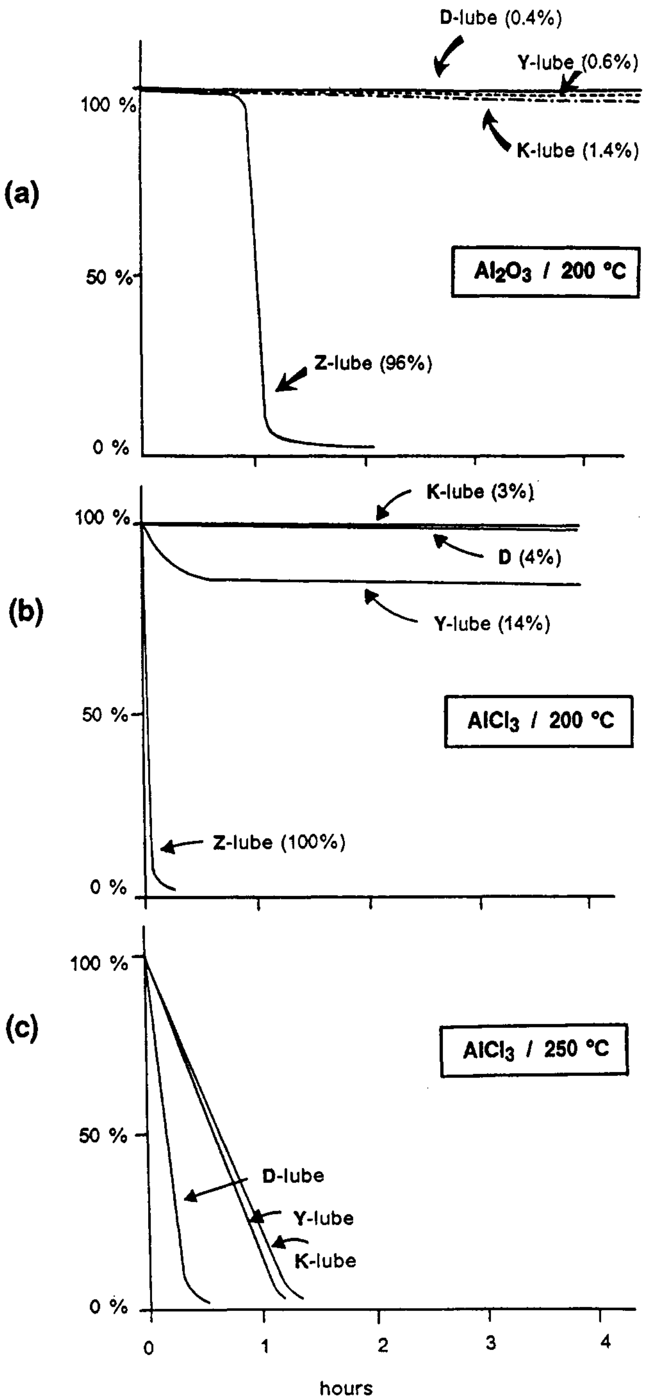


Figure 2. Weight loss observed on perfluoropolyethers (a) when kept in contact with Al_2O_3 (1 wt %) at 200 °C, (b) when kept in contact with $AlCl_3$ at 200 °C, and (c) when kept in contact with $AlCl_3$ at 250 °C. Numbers inside parentheses are the percent weight losses measured after 6 h of treatment.

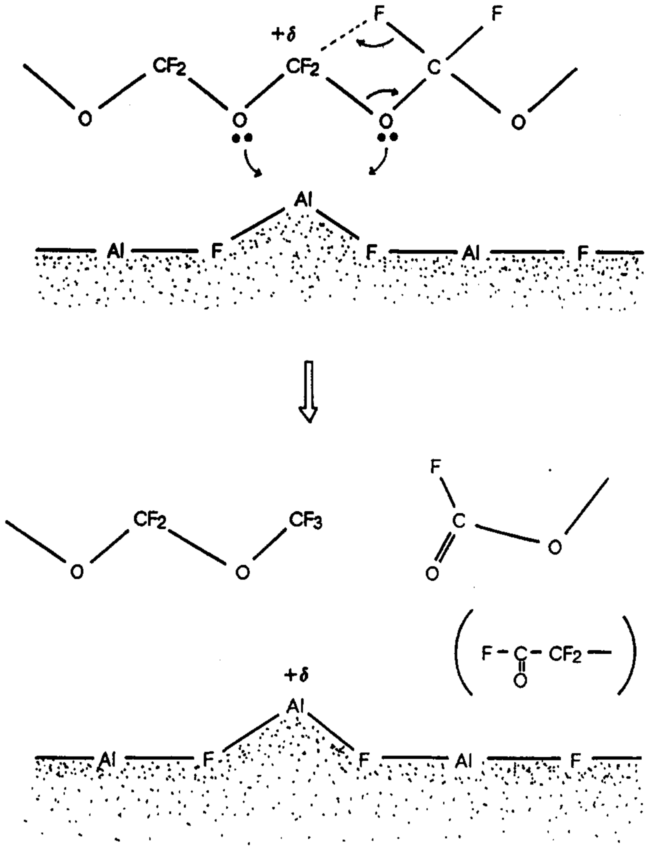


Figure 3. Interaction between a Lewis acid site on AlF_3 and an acetal sector of Z-lube. The partial positive charge developed at the acetal carbon induces a fluorine atom transfer from the adjacent CF_2 unit, leading to chain scission with transformation of the acetal unit into a methoxy end group and the adjacent unit into either a fluoroformate or an acyl fluoride end group.

the adjacent unit into either a fluoroformate end group or an acyl fluoride end group depending upon its original unit. The ^{19}F NMR spectra of partially degraded Z-lubes were in clear accord with the proposed process. The induction period is required for the oxide-to-halide surface conversion. We envisage that the Al_2O_3 surface is sufficiently acidic to induce the disproportionation reaction at sectors where acetal units are consecutively linked. Polymer segments with a fluoroformate end group are formed when the reaction occurs at such sectors. It has been shown that the fluoroformate end group decomposes at 200 °C as follows.[3]

$$R{-}CF_2{-}O{-}COF \rightarrow R{-}COF + F_2CO \qquad (2)$$

The resulting F_2CO could then convert the oxide surface to the halide surface via reaction 3. The AlF_3 surface thus formed commences the vigorous degradation process leading to complete conversion of the fluid into volatile oligomers.

$$Al_2O_3 + 3F_2CO \rightarrow 2AlF_3 + 3CO_2 \qquad (3)$$

The concentration of acetal units in Y-lube is so small that sectors of consecutively linked acetal units are practically nonexistent. This accounts for the stability of Y-lube in the presence of Al_2O_3 at 200 °C.

The result and postulated mechanism presented above predict that the degradation of Z-lube should commence immediately if heated in the presence of AlF_3 of $AlCl_3$ at 200 °C. It also predicts that Y-lube, if treated simiarly, should also degrade to the extent where all its acetal units are removed. The degradation modes observed for Z- and Y-lubes when heated at 200 °C in the presence of $AlCl_3$ (Figure 2b) are in total accord with these predictions. The concentration of acetal units, $-O-CF_2-O-$ and $-O-CF(CF_3)-O-$, in Y-lube is 1-2 units per chain. The partial degradation of ~14 wt % reached in the early stage of treatment for Y-lube reflects the probability of the minor segments generated by the disproportionation reaction at acetal units to be short enough to evaporate at 200 °C. Again, the proposed processes were strongly substantiated by the ^{19}F NMR spectra of partially degraded lubes.

The complete loss of fluid observed for Y-, K-, and D-lubes when heated at 250 °C in the presence of $AlCl_3$ (Figure 2c) is intriguing. It is easily seen that Y-lube becomes, after complete removal of acetal units by the disproportionation process, a homopolymer of perfluoropropylene oxide (as in K-lube) with either the methoxy or ethoxy groups terminating the chain. Here the ethoxy end groups are formed from branched acetal units, $-O-CF(CF_3)-O-$, by the disproportionation process. The NMR analyses revealed that the mass loss observed at 250 °C for K and Y (after conversion to the homopolymer form) was entirely due to the disproportionation process occurring at the alkoxy end groups adjacent to $-CF_2-$, with the fluorine transfer consistently from the end group into the internal sector. The degradation sequence in the case of K-lube is thus as follows.

$$\begin{gathered}
CF_3-CF_2-CF_2-O-[-CF(CF_3)-CF_2-O-]_{m}-CF_2-CF_3 \\
\downarrow \\
CF_3-CF_2-CF_2-O-[-CF(CF_3)-CF_2-O-]_{m-1}-CF(CF_3)_2 \quad + \quad FCO\text{-}CF_3 \\
\downarrow \\
CF_3-CF_2-CF_2-O-[-CF(CF_3)-CF_2-O-]_{m-2}-CF(CF_3)_2 \quad + \quad (CF_3)_2C=O \\
\downarrow \\
\text{etc.}
\end{gathered} \tag{4}$$

In complete contrast the degradation of D-lube was found to proceed via the disproportionation process occurring throughout the chains.

$$\begin{gathered}
R-O-CF_2-CF_2-CF_2-O-CF_2-CF_2-CF_2-O-R \\
\downarrow \\
R-O-CF_2-CF_2-CFO \quad + \quad CF_3-CF_2-CF_2-O-R
\end{gathered} \tag{5}$$

In order to account for these results, we thence postulated the disproportionation process involving two successive ether oxygens as discussed earlier. Though it was extremely enticing to attribute the stability of the midchain sectors with pendant CF_3 groups (K-lube) and the alkoxy end groups adjacent to $-CF(CF_3)-$ against the postulated disproportionation process to a steric factor, it seemed to contradict the fact that the isoproxy end groups generated in Y- and K-lubes readily underwent the process as given in (4). If the process entails interaction of two successive ether oxygens with Lewis acid site(s) on a solid surface, the disposition of the successive oxygens along the polyether chain ought to play a critical role. Examination of the "two carbon system" without a pendant CF_3 group, PFPEO, should hence be most revealing. The need to demonstrate that the postulated disproportionation process was not limited to the aluminum system appeared also crucial.

3.1. Disproportionation by Other Metal Oxides and Halides. Catalytic degradation of Y-lube in the presence of variety of metal oxides (including Al_2O_3) had been reported by Sianesi et al.[6] They attributed the process to Lewis acid sites on the oxide surface, but suggested a mechanism initiated by a C–O bond homolysis followed by unzipping.

We heated Y-, K-, and D-lubes (5 g) in the presence of TiO_2, ZrO_2, and ZrF_4 (1 wt %). Complete loss of fluid occurred at 250 °C in the case of ZrF_4 and at 300 °C for TiO_2 and ZrO_2. The ^{19}F NMR spectra of partially degraded lubes obtained here were exactly the same as those obtained earlier using $AlCl_3$.[16] The prevalence of the disproportionation process independent of the exact chemical identity of metal oxide (or halide) is thus demonstrated. The thermal barrier and/or the rate of the process is clearly dependent on the strength of Lewis acids present on the oxide (or halide) surface.

3.2. Degradation of PFPEO. The ^{19}F NMR spectrum of the particular PFPEO used for the degradation study is shown in Figure 4a. The major peak, that of ethylene oxide units, $-O-CF_2-CF_2-O$, is recognized at −88.5 ppm. The end groups are mostly the methoxy form (86%); a minor amount (14%) of the ethoxy end groups are also present, as indicated. When this PFPEO was heated at 200 °C in the presence of $AlCl_3$, gentle bubbling commenced immediately and continued steadily until complete loss of fluid occurred 90 min later.

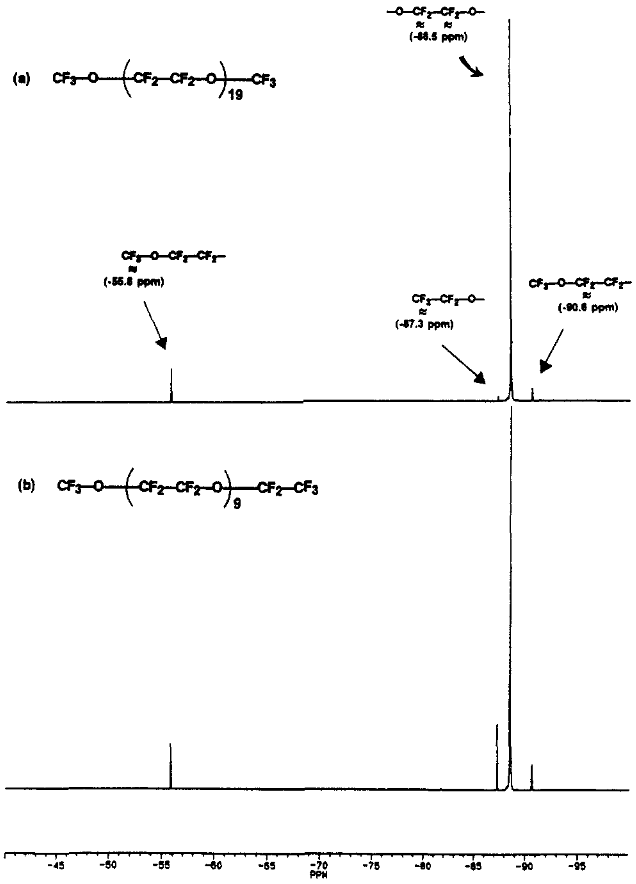


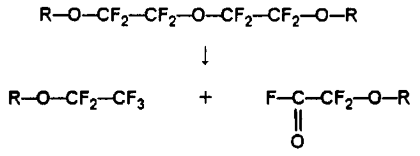
Figure 4. ^{19}F NMR spectra of PFPEO (perfluoropoly(ethylene oxide)): (a) starting sample; (b) 60% degraded sample. The peaks were assigned as indicated, and the "average" formulas were determined as shown.

Let us assume PFPEO chains capped totally with the methoxy end groups. If the disproportionation occurs exclusively at chain ends, the degradation sequence would be as follows.

$$\begin{gathered}
CF_3-O-[-CF_2-CF_2-O-]_{m}-CF_3 \\
\downarrow \\
CF_3-O-[-CF_2-CF_2-O-]_{m-1}-CF_2-CF_3 \quad + \quad F_2CO \\
\downarrow \\
CF_3-CF_2-O-[-CF_2-CF_2-O-]_{m-2}-CF_2-CF_3 \quad + \quad F_2CO \\
\downarrow \\
CF_3-CF_2-O-[-CF_2-CF_2-O-]_{m-3}-CF_2-CF_3 \quad + \quad CF_3-COF \\
\downarrow \\
\text{etc.}
\end{gathered} \tag{6}$$

Note that once the original methoxy end group has been converted to the ethoxy end group, the subsequent disproportionation process regenerates the ethoxy end group and secedes perfluroacetyl fluoride at each occurrence.

If, on the other hand, the disproportionation process occurs at midchain sectors, the reaction would be as follows.



$$\mathrm{R{-}O{-}CF_2{-}CF_2{-}O{-}CF_2{-}CF_2{-}O{-}R} \longrightarrow \mathrm{R{-}O{-}CF_2{-}CF_3} + \mathrm{F{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}CF_2{-}O{-}R} \qquad (7)$$

Here, as the degradation proceeds, polyether chains with the ethoxy end groups and the acyl fluoride end groups in equimolar proportion are produced. The chemical shift values of the resultant acyl fluoride end group are known from the spectrum of partially degraded Z-lube as follows.[15]

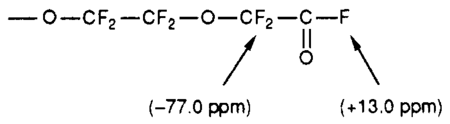


Figure 4b shows the ^{19}F NMR spectrum of 60% degraded PFPEO. The growth of the ethoxy peak as the result of the disproportionation process is conspicuously revealed. No new signals, especially those of the acyl fluoride end group at +13.0 and −77.0 ppm, were observed! We then trapped the effluent vapor from the degradation process in perfluorobenzene kept at 0 °C. The ^{19}F NMR spectrum of the resulting solution consisted of the signals due to ethylene oxide oligomers (mostly $CF_3{-}O{-}CF_2{-}CF_2{-}O{-}CF_2{-}CF_3$) and a strong singlet due to $CF_3{-}COOH$ at −76.5 ppm. It is thus shown that the observed, continuous mass loss of PFPEO is due entirely to the disproportionation reaction at the chain ends. Furthermore, as evidenced in Figure 4b, the amount of the methoxy end groups remaining in the 60% degraded PFPEO is comparable to that of the ethoxy end groups. It is hence concluded that, once a certain amount of ethoxy end groups is generated, most of the degradation of PFPEO occurs at the ethoxy end groups (see reaction 6).

3.3. Conformations of Perfluoropolyethers and Net Atomic Charges. No experimental results have been reported regarding the conformation of perfluoropolyethers. Recently Pacansky et al. examined the structures of simple perfluoroethers (e.g. $CF_3{-}O{-}CF_3$) and diethers (e.g. $CF_3{-}O{-}CF_2{-}CF_2{-}O{-}CF_3$) by ab initio calculations and the structures of perfluoropolyether chains by the molecular mechanics method.[20] They noted that the chains would attain a helical form through accumulative rotations about the successive C–O bonds. The calculated structures of $CF_3{-}O{-}CF_2{-}CF_2{-}O{-}CF_3$ and $CF_3{-}O{-}CF(CF_3){-}CF_2{-}O{-}CF_3$, model units for PFPEO and K-lube, showed that the O–C–C–O skeletal segment would retain a roughly planar, trans form in both cases. The structure of D-lube was not examined.

We also examined, by the molecular mechanics method,[17] the conformations of "short" Z-lubes, PFPEO, and K- and D-lubes. Figures 5 and 6 show the "space-filled" renderings of the computed forms. The proximity and exposure of the two oxygens of an acetal unit in Z-lube are conspicuous (Figure 5a). The two oxygens flanking each monomer unit in D-lube are also positioned on the same side (Figure 5b). In PFPEO and K-lube, the two oxygens flanking each monomer unit are positioned on opposite sides of the chain (Figure 6a,b). We suggest that the disproportionation reaction does not occur in the midchain sectors of PFPEO and K-lube on account of this "trans" disposition of the successive oxygens. The reaction occurs at chain ends due to a much lower barrier for reorientation, permitting interaction of two successive ether oxygens with the solid surface.

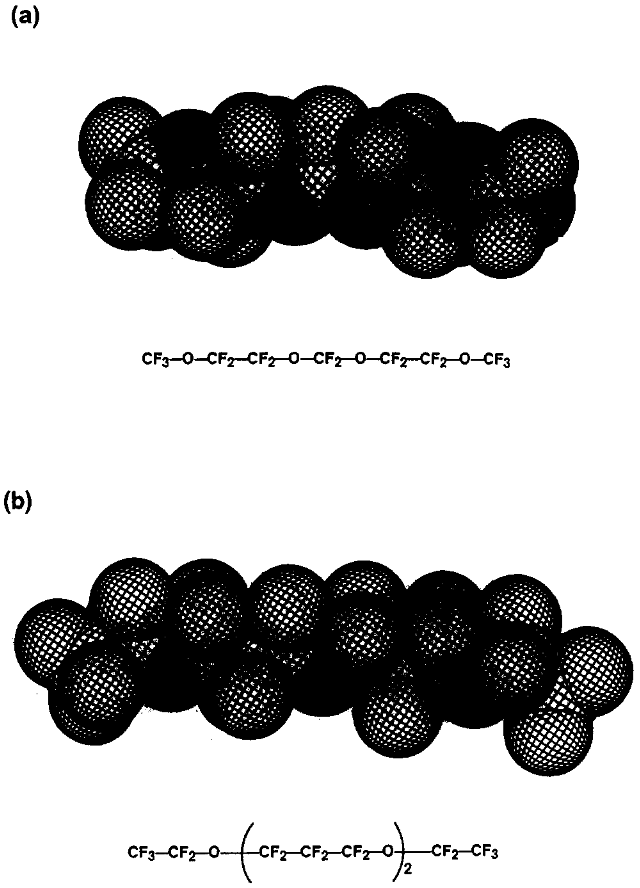


Figure 5. Conformations obtained by the molecular mechanics method: (a) short Z-lube; (b) short D-lube.

The much higher reactivity of the ethoxy end group in comparison to that of the methoxy end group revealed in the degradation of PFPEO was at first surprising. Shown schematically in Figure 7a are the net atomic charges of carbons in a model PFPEO unit computed by the geometry-optimized MNDO method.[18] There apparently exists a large variation in the net atomic charges of carbons of the polymer (without interaction with Lewis acids). The calculated charges on the fluorine atoms are all −0.19 ± 0.01, and those on the oxygen atoms are all −0.41 ± 0.02. Most interestingly, the methoxy carbon has a much larger charge, +0.79, in comparison to +0.56 of the ethoxy carbon (the carbon adjacent to oxygen in the ethoxy end group). A much higher reactivity of the ethoxy end group is attributed to its smaller net atomic charge. In the disproportionation process postulated at chain ends, the alkoxy end-group is formally oxidized, while the fluorine-receiving internal sector is reduced. It follows that an alkoxy end group with a smaller net positive charge would be more receptive to the oxidative process.

Shown in Figure 7b are the net atomic charges of carbons computed for a model acetal unit. A large positive charge of the acetal carbon (+0.76), combined with the ideal disposition of the oxygens, accounts for its particular vulnerability to the reductive end of the disproportionation process.

Figure 8 shows the net atomic charges of carbons computed for model units related to K-lube and Y-lube (after conversion to the homopolymer form). We note that the tertiary carbon in the internal sector has an extremely small charge of +0.38. It offers an explanation why the alkoxy end groups adjacent to $-CF(CF_3)-$ are spared from the disproportionation process. The tertiary carbon, due to its small charge, would be most resistive to the reductive end of the disproportionation process. Also revealed here is that the isopropoxy carbon has a charge

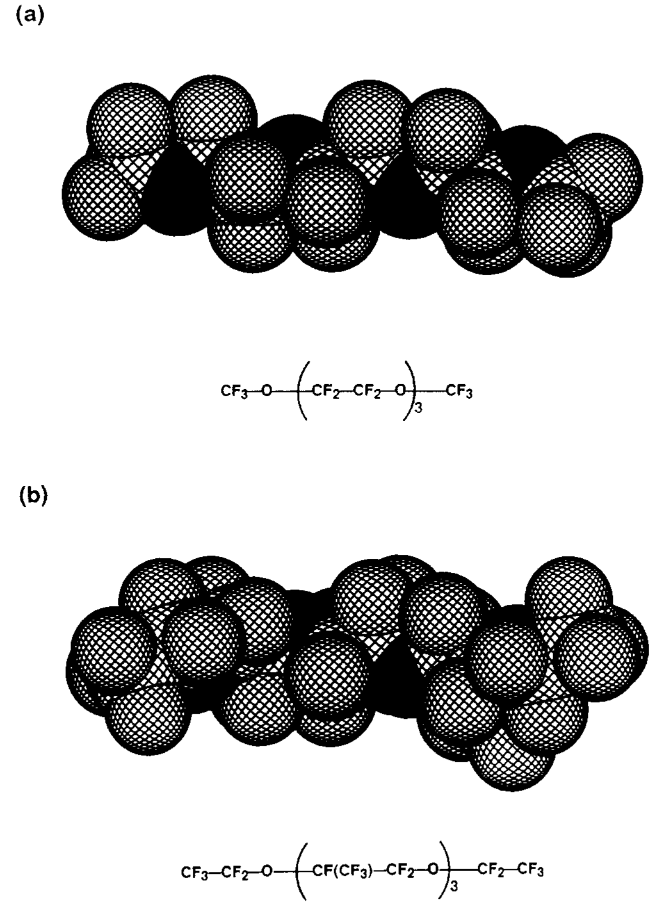


Figure 6. Conformations obtained by the molecular mechanics method: (a) short PFPEO chain; (b) short K-lube.

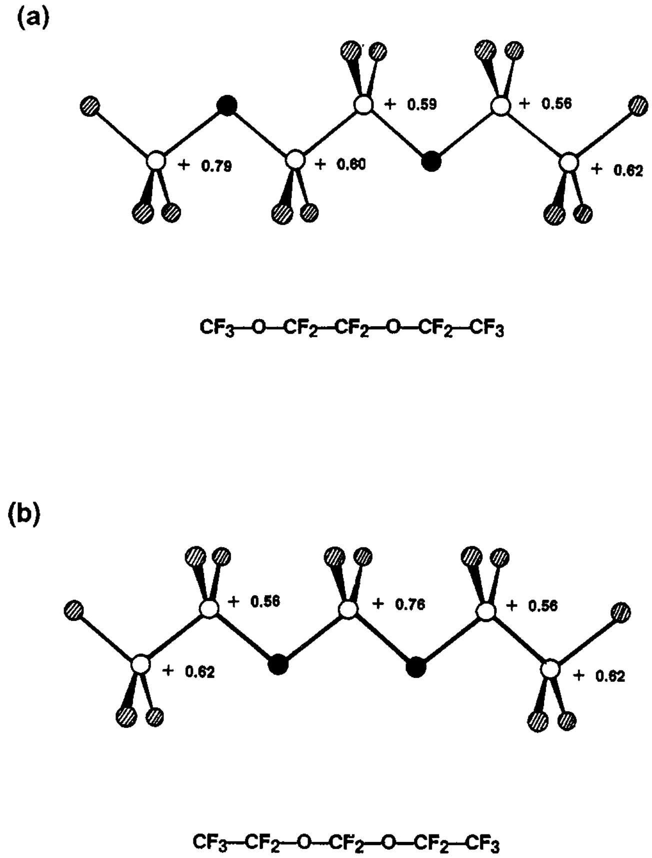


Figure 7. Net atomic charges of carbons computed by the MNDO method: (a) model PFPEO unit; (b) model acetal unit. The charges on the fluorine atoms are all −0.19 ± 0.01, and those of the oxygen atoms are all −0.41 ± 0.02.

of +0.34 much smaller than 0.56 of the ethoxy carbon. It is then predicted that, in the degradation of K-lube, the disproportionation process occurs much more readily at the newly evolved and self-regenerating isopropoxy end groups than at the original or remaining ethoxy end groups.

3.4. GPC Study. As stated already, the disproportionation process occurs throughout the internal sectors of D-lube, while, for K-lube, the process occurs exclusively at chain ends, seceding one monomer unit at a time. The number-averaged molecular weight of D-lube should then decrease precipitously in the early stage of degradation, while that of K-lube is expected to decrease linearly with its mass loss. These predictions have been verified by the number-averaged molecular weights determined from the ^{19}F NMR spectra.[16] The GPC chromatograms of starting and partially degraded perfluoropolyethers, delineating the weight-averaged moleculer weight distribution should be even more elucidating.

The weight-averaged molecular weight distribution of D-lube should rapidly approach a Gaussian distribution, encompassing the shortest possible chains as the disproportionation recurs. The weight-averaged molecular weight distribution of K-lube and PFPEO should shift downward proportionately with the mass loss; the actual distribution curves, however, might appear askew, reflecting the higher reactivities of the newly evolved and regenerating end groups in comparison with the activities of the starting end groups.

Shown in Figures 9a, 10a, and 11a are the GPC chromatograms of starting and 50–60% degraded D- and K-lubes and PFPEO. The patterns represent the weight-averaged distribution since a differential refractometer was used as the detector. In each figure the patterns were normalized to represent the same total mass. The distribution pattern of the partially degraded D-lube is indeed Gaussian; several peaks resolved at the lowest molecular weight end are due to oligomers (of vapor phase at 250 °C, but remained captured through the refluxing process). The gradual downward shift of the distribution pattern predicted for partially degraded K-lube and PFPEO can be witnessed in the higher molecular weight halves of each curves; they are parallel to the corresponding segments of the starting materials. The askewness of these patterns in the lower molecular weight side is attributed to the accelerated reaction rates of the polymer chains with the newly evolved end groups.

We decided to examine how well one could simulate the observed degradation patterns based on the postulated, simple disproportionation scheme. The results are shown in Figures 9b, 10b, and 11b. In each case, starting with a set of chains, the weight-averaged distribution of which was adjusted to match the actual distribution in the starting samples, the degradation process was simulated as follows.

For D-lube: (1) Fragmentation occurs randomly throughout the chains. (2) The probability for the disproportionation to occur is proportional to the chain length, the longest chain in the starting set given a unit probability. (3) For the result in Figure 9b, the process was repeated for three cycles.

For K-lube: (1) The disproportionation reaction occurs only at the ethoxy end groups adjacent to $-CF_2-$ and at the isopropoxy end groups generated therefrom. (2) At each occurrence of the disproportionation, the chain length is decremented by the unit size, and the seceded monomer is "lost" from the fluid. (3) The isopropoxy end group is

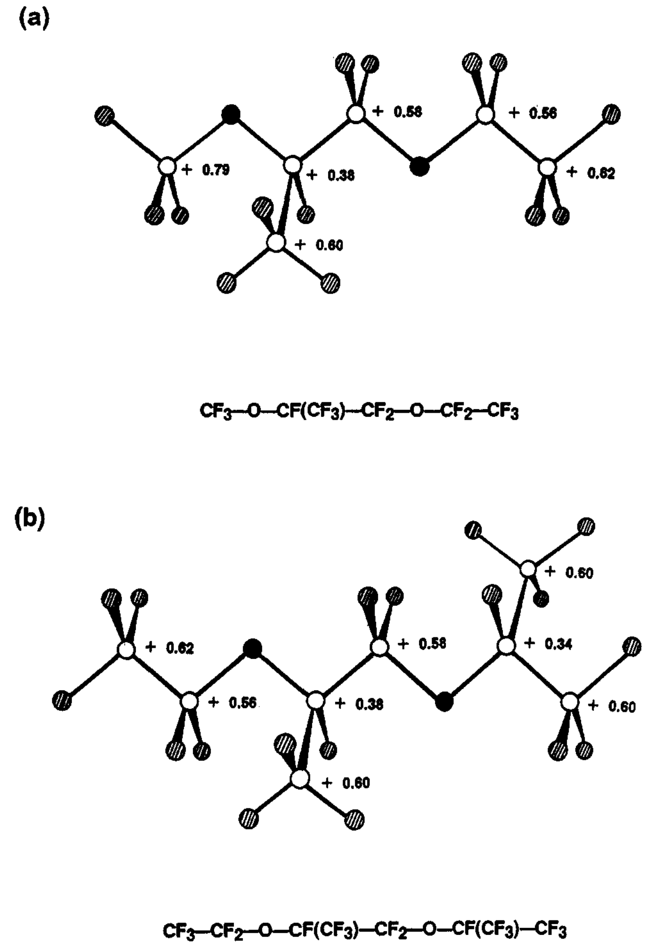


Figure 8. Net atomic charges of carbons computed by the MNDO method: (a) model K (or Y) unit with *n*-alkoxy end groups; (b) model K (or Y) unit with an isopropoxy end group. The charges on the fluorine atoms are all −0.19 ± 0.01, and those of the oxygen atoms are all −.041 ± 0.02.

30 times more reactive than the ethoxy end group. (4) The process was repeated until 50–60% of the original mass was lost.

For PFPEO: (1) The disproportionation reaction occurs at the methoxy end groups in the starting material and at the ethoxy end groups generated therefrom. (2) At each occurrence of the disproportionation, the chain length is decremented by the unit size, and the seceded monomer is "lost" from the fluid. (3) The ethoxy end group is 20 times more reactive than the methoxy end group. (4) The process was repeated until 50–60% of the original mass was lost.

Thus, in contrast to K-lube, the degradation of PFPEO occurs at both ends. In Figure 11b, the fraction indicated by E-M, for example, represents the chains with an ethoxy end group at one end and a methoxy end group at the other. The small "hump" seen toward the lowest molecular end of the observed curve of degraded PFPEO is thus attributed to the most rapidly shrinking chains with ethoxy end groups at both ends.

In view of the simple scheme assumed, the agreements attained above between the observed and simulated chromatograms are gratifying and add further credence to the postulated disproportionation mechanism.

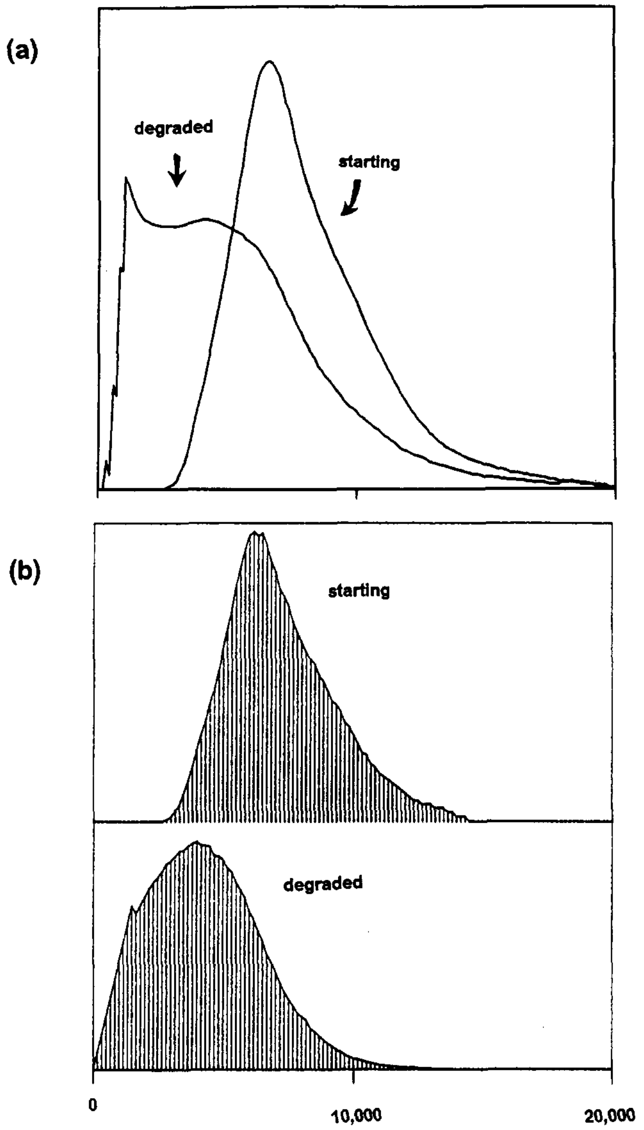
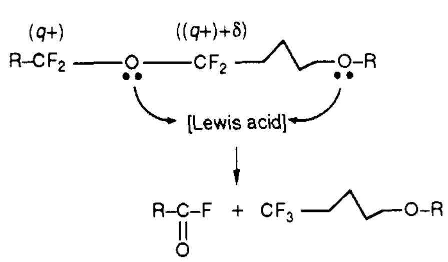


Figure 9. GPC chromatograms of starting and degraded D-lubes: (a) observed; (b) simulated. Successive bars represent groups of chains differing by one monomer molecular weight.

4. Summary and Discussions

The results obtained in the present and earlier studies[15,16] have shown that the thermal degradation of perfluoropolyethers in the presence of Lewis acids is singularly dominated by the intramolecular disproportionation process of the following scheme.



The reaction occurs when the two oxygen atoms flanking a monomer unit of polyether chains interact with Lewis acid site(s). The differential charges induced at the carbon immediately outside the unit and the carbon inside the unit lead to a fluorine transfer from the outside carbon to the inner carbon and effect the disproportionation process as shown. The susceptibilities of various sectors of perfluoropolyether chains to the postulated process are thus strongly dependent upon the disposition of the two oxygens flanking the monomer unit of the sector and also on the initial net atomic charges of carbons involved in the fluorine transfer.

The disproportionation reaction hence does not occur at internal sectors of PFPEO and K-lube on account of

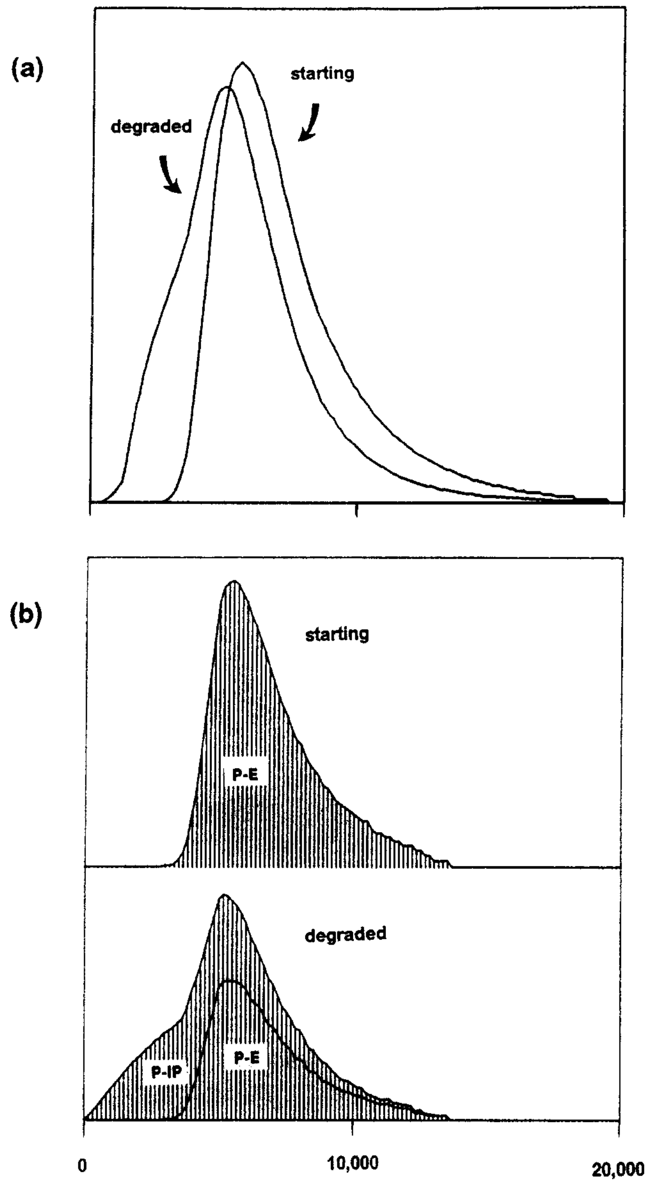


Figure 10. GPC chromatograms of starting and degraded K-lubes: (a) observed, (b) simulated. Successive bars represent groups of chains differing by one monomer molecular weight. The notation P-IP, for example, indicates the polyether chains with a *n*-propoxy end group adjacent to $-CF(CF_3)-$ and an isopropoxy end group adjacent to $-CF_2-$.

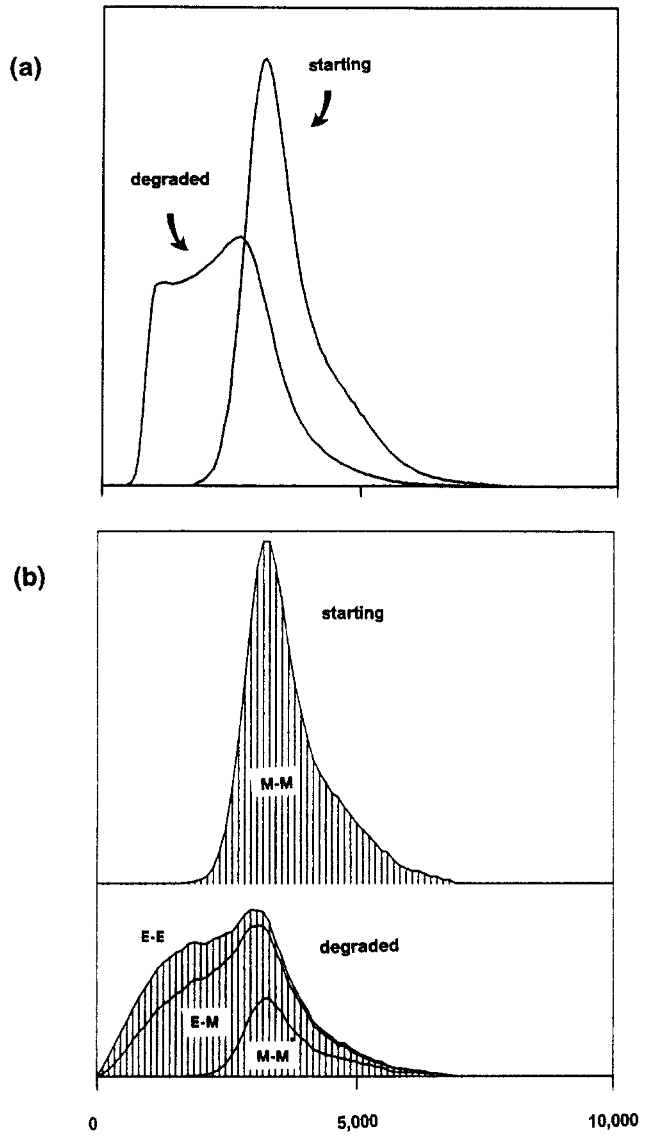


Figure 11. GPC chromatograms of starting and degraded PFPEO samples: (a) observed; (b) simulated. Successive bars represent groups of chains differing by one monomer molecular weight. The notation E-M, for example, indicates the polyether chains with an ethoxy end group at one end and a methoxy end groups at the other.

the "trans" disposition of the successive ether oxygens; the reaction occurs readily and exclusively at chain ends, however, where the energy barrier for reorientation is low. The reactivities of the alkoxy end groups are found to increase in the order CF_3-O-, CF_3-CF_2-O-, and $(CF_3)_2CF-O-$; they are inversely related to the initial net positive charges born by the respective alkoxy carbons. The reaction does not occur at alkoxy end groups adjacent to $-CF(CF_3)-$, however; this is ascribed to the extremely small initial positive charge borne by the tertiary carbon of the $-CF(CF_3)-$ group. The chain-end reaction of PFPEO occurs at 200 °C in the presence of $AlCl_3$, while the corresponding reaction of K-lube requires a higher temperature (250 °C). This may be ascribed to a steric effect of the pendant CF_3 units of the isoproxy end group and the internal propylene unit of K-lube.

The disproportionation process occurs throughout the internal sectors of D-lube and at acetal sectors of Z- and Y-lubes; here two successive ether oxygens are positioned on the same side of the chain. The extreme vulnerability of acetal units is due to the ideal disposition of the oxygen atoms and the large initial positive charge of the acetal carbon, favoring the reductive end of the disproportionation process. In the case of D-lube, the amount of the original ethoxy end groups remained essentially unaltered, when compared to that of the internal sectors, during the initial half of the degradation process. Thus when all other factors (the disposition of the oxygens and the initial atomic charges of carbons involved) are favorable and similar, the reaction does not occur preferentially at chain ends.

In many tribological and wear studies reported earlier, it was concluded that branched perfluoropolyethers were more stable than linear ones. The perceived stability was attributed to a steric effect of the pendant CF_3 groups. However, the "branched" polyether examined in these studies was always K-lube, and linear polyethers examined were Z- and/or D-lubes. The observed extra stability of K-lube is more aptly attributed to the "difference in damage", as the disproportionation process is limited to chain ends for K-lube whereas, for Z- and D-lubes, the process occurs at internal sectors, causing fragmentation.

References and Notes

(1) Moulder, J. F.; Hammond, J. S.; Smith, K. L. *Appl. Surf. Sci.* **1986**, *25*, 446.

(2) Bierschenk, T. R.; Kawa, H.; Juhlke, T. J.; Lagow, R. J. *NASA Contract. Rep.* **1988**, No. 182155.

(3) Sianesi, D.; Pasetti, A.; Fontanelli, R.; Bernardi, G. C.; Caporiccio, G. *Chim. Ind. (Milan)* **1973**, *55*, 208.

(4) Gumprecht, W. H. *ASLE Trans.* **1966**, *9*, 24.

(5) Ohsaka, Y. *Petrotech (Tokyo)* **1985**, *8*, 840.

(6) Sianesi, D.; Zamboni, V.; Fontanelli, R.; Binaghi, M. *Wear* **1971**, *18*, 85.

(7) Snyder, C. E., Jr.; Gschwender, L. J.; Tamborski, C. *Lubr. Eng.* **1981**, *27*, 344.

(8) Jones, W. R., Jr. *NASA Tech. Memo.* **1982**, No. 82834.

(9) Jones, W. R.; Paciorek, K. J. L.; Ito, T. I.; Kratzer, R. H. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 166.

(10) Carré, D. J.; Markowitz, J. A. *ASLE Trans.* **1985**, *28*, 40.

(11) Carré, D. J. *ASLE Trans.* **1986**, *29*, 121.

(12) Mori, S.; Morales, W. *Wear* **1989**, *132*, 111.

(13) Zehe, M. J.; Faut, O. D. *NASA Tech. Memo.* **1989**, No. 101962.

(14) Helmick, L. S.; Jones, W. R., Jr. *NASA Tech. Memo.* **1990**, No. 102493.

(15) Kasai, P. H.; Tang, W. T.; Wheeler, P. *Appl. Surf. Sci.* **1991**, *51*, 201.

(16) Kasai, P. H., Wheeler, P. *Appl. Surf. Sci.* **1991**, *52*, 91.

(17) For the MM2 calculation, PCMODEL (V. 5.0) of Serena Software was used.

(18) For the MNDO calculation, MOPAC (V.5) by J. P. Stewart of Frank J. Seiler Research Laboratory (U.S. Air Force Academy, Colorado Springs, CO) was used.

(19) Ciampelli, F.; Venturi, M. T.; Sianesi, D. *Org. Magn. Reson.* **1969**, *1*, 281.

(20) Pacansky, J.; Miller, M.; Hatton, W.; Liu, B.; Scheiner, A. *J. Am. Chem. Soc.* **1991**, *113*, 329.

Registry No. PFPEO, 67584-22-9; Fomblin Z, 64772-82-3; Fomblin Y, 62168-88-1; Krytox, 52700-35-3; Demnum, 105060-59-1; $AlCl_3$, 7446-70-0; Al_2O_3, 1344-28-1; AlF_3, 7784-18-1.