Perfluoropolyethers with Acid End Groups: Amphiphilicity and Emulsification

PAUL H. KASAI

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099
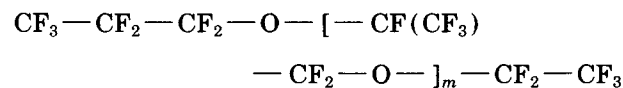
SYNOPSIS

Interactions of PFPE-acids (perfluoropolyethers with carboxylic end groups) with a metal oxide surface and with aqueous systems were examined. The study revealed that (1) PFPE-acids are preferentially adsorbed on metal oxide (ZrO_2) surfaces over PFPE of nonfunctionalized form, (2) PFPE-acids of shorter chain length are preferentially adsorbed over PFPE-acids of longer dimension, and (3) the low molecular weight fraction (MW = 1300) of Demnum-SH is abundant in molecular chains terminated with the acid end group at both ends. The study also revealed that PFPE-acids, if agitated with aqueous solution of electrolyte, form an extremely stable macroemulsion of the water-in-oil type. The emulsion is extremely viscoelastic and may contain 50% by weight (hence, 65% by volume) of water. Water is occluded as droplets of diameter of 1–100 microns. A mechanism exists whereby aqueous protons are transported between droplets with the transfer rate $\geq$ 50 Hz at room temperature. Relevance of these observations in the lubricant application of PFPEs in magnetic recording media is discussed. © 1995 John Wiley & Sons, Inc.
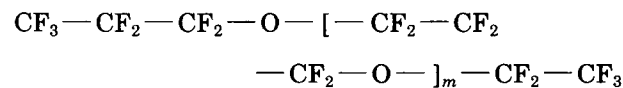
INTRODUCTION

Perfluoropolyethers (PFPEs) 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] PFPEs are commercially available in several distinct structural forms. Representative formulas of such PFPEs known by the brand names Krytox, Demnum, and Fomblin Z, respectively, are as follows:
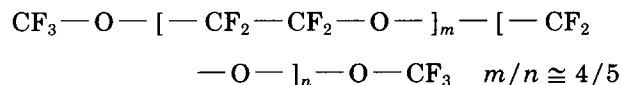
Krytox

$$CF_3 - CF_2 - CF_2 - O - [- CF(CF_3)$$
$$- CF_2 - O -]_m - CF_2 - CF_3$$

Demnum

$$CF_3 - CF_2 - CF_2 - O - [- CF_2 - CF_2$$
$$- CF_2 - O -]_m - CF_2 - CF_3$$

Fomblin-Z

$$CF_3 - O - [- CF_2 - CF_2 - O -]_m - [- CF_2$$
$$- O -]_n - O - CF_3 \quad m/n \cong 4/5$$

Krytox is made by base-catalyzed polymerization of hexafluoropropylene oxide. The pertinent synthetic steps involved are shown schematically in Figure 1.[3] Demnum is made similarly but starting with 2,2,3,3-tetrafluorooxetane. The hydrogen atoms in the resulting polymers are replaced by fluorine by subsequent contact with F_2 in solution.[4]

The propagation sequence in Figure 1 is terminated with elimination of F^-, and a polymeric chain with an acylfluoride end group is formed. Both Krytox and Demnum are also available in the acid form: Krytox-H and Demnum-SH. In accord with the polymerization sequence, the acid end group is present only at the propagation end of the chain.

Fomblin Z is synthesized by photooxidation of tetrafluoroethylene and is a linear, random copolymer of ethylene oxide units and methylene oxide units as indicated.[5] It is also available in the acid form: Fomblin Z-DIAC. Unlike Krytox-H or Demnum-SH, Z-DIAC has acid end groups at both ends.

Base Catalyzed Polymerization

$$R-CF_2-O-CF_2-R' \rightarrow$$

$$R-\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}-F + CF_3-R' \quad (1)$$

Base-catalyzed polymerization scheme (left figure):

(F^-)

$R-O^-$ + $\underset{\displaystyle \diagdown O \diagup}{CF_3-C-CF_2}$ → **polymerization**

$$R-O-\underset{\displaystyle F}{\overset{\displaystyle CF_3}{\underset{\displaystyle |}{\overset{\displaystyle |}{C}}}}-CF_2-O^-$$

↓ **termination**

$$R-O-\underset{\displaystyle F}{\overset{\displaystyle CF_3}{\underset{\displaystyle |}{\overset{\displaystyle |}{C}}}}-\underset{\displaystyle O}{\overset{\displaystyle }{\underset{\displaystyle \|}{C}}}-F \quad + \quad F^-$$

↓ $+ H_2O$

$$R-O-\underset{\displaystyle F}{\overset{\displaystyle CF_3}{\underset{\displaystyle |}{\overset{\displaystyle |}{C}}}}-\underset{\displaystyle O}{\overset{\displaystyle }{\underset{\displaystyle \|}{C}}}-OH \quad + \quad HF$$

↓ $+ F_2$

$$R-O-\underset{\displaystyle F}{\overset{\displaystyle CF_3}{\underset{\displaystyle |}{\overset{\displaystyle |}{C}}}}-\underset{\displaystyle O}{\overset{\displaystyle }{\underset{\displaystyle \|}{C}}}-OF \quad + \quad HF$$
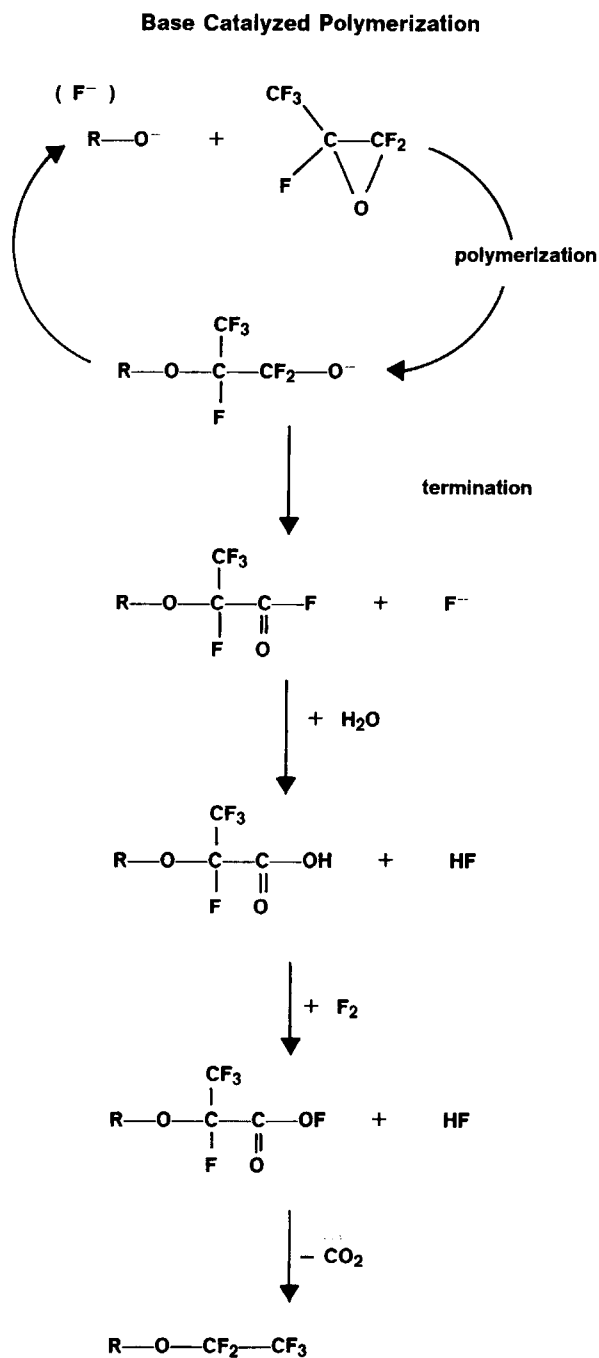
↓ $- CO_2$

$$R-O-CF_2-CF_3$$

Figure 1 Base-catalyzed polymerization of hexafluoropropylene oxide. The termination step generates the acylfluoride end group.

Hereinafter, for the sake of brevity, we shall use the notation PFPE-acids to represent generically these PFPEs with carboxylic end groups.

Recently, it was shown that PFPEs have a propensity to undergo the intramolecular disproportionation of the following scheme[6]:
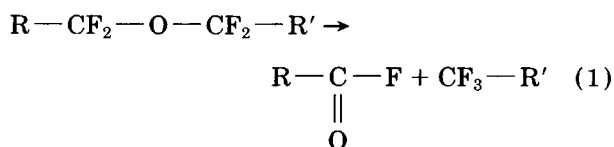
The process occurs when PFPEs are heated (200–300°C) in the presence of Lewis acid (metal oxides or halides). For PFPE chains having building monomer units such that the number of the backbone carbons between a pair of successive ether oxygens is odd, e.g., Fomblin-Z or Demnum, reaction (1) occurs at any such ether linkage. For PFPE chains with an even number of backbone carbons between successive ether oxygens throughout the chain, e.g., Krytox or perfluoro[poly(ethylene oxide)], reaction (1) occurs exclusively at the terminal ether oxygen. The fluorine transfer is then always from the end group to the internal segment, and the fluorocarbonyl group is formed in the leaving monomer unit.

The immediate "physical consequence" of reaction (1) is the shortening of the chain length. The drop in the average chain length would be precipitous for PFPE of the odd-number-carbon type. In contrast, for PFPE of the even-number-carbon type, the chain length decrement is by one monomer unit per each reaction. The "chemical consequence" of reaction (1) is such that, for Fomblin Z or Demnum, even when one starts out with the normal nonfunctionalized form, short PFPE-acid molecules would be produced.

The surfactant nature of short PFPE-acids was examined extensively by Chittofrati and others.[7-11] The system typically examined by these authors was a water/oil/surfactant ternary system where the oil phase is nonfunctionalized PFPE (of Krytox-like structure with the molecular weight of ~ 800) and the surfactant is the same PFPE with the carboxylic end group: $-O-CF_2-COONH_4$. It has been shown that, in such a PFPE oil/surfactant system, water of up to 20% by weight can be solubilized in the form of microemulsion where water is contained in droplets of diameter of 2–8 nm.

In a lubricant application of PFPE, the substrate–PFPE interfacial interaction is expected to alter greatly if PFPE of nonfunctionalized form changes to PFPE-acid. Also, in a thin-layer application such as that realized in the head–disk interface of recent magnetic recording files, the interaction between short PFPE-acids and water molecules of ambient environment may become comparable to or surpass the substrate–PFPE interaction, thus adversely affecting the lubricant performance.

Presented in this report are results of our examination of (1) the presence and the extent of preferential adsorption of PFPE-acids (over non-functionalized PFPE) by a metal oxide surface, (2) the preferential adsorption of shorter PFPE-acids by a metal oxide surface, and (3) the interaction of PFPE-acids with water.

The study revealed, not unexpectedly, that PFPE-acids are preferentially adsorbed by metal oxide and that, among PFPE-acids of varying dimensions, shorter molecules are adsorbed more strongly than are those of longer dimension. The study also revealed, unexpectedly, the presence of a significant amount of short bifunctional chains in Demnum-SH. The study then revealed that PFPE-acids form extremely stable macroemulsions of the water-in-oil type if agitated with water with dissolved electrolytes (e.g., NaCl). The emulsion thus produced may contain 50% by weight—hence, 64% (!) by volume—of water and be extremely viscoelastic. Water is occluded here as droplets of diameter of 1–100 microns.

EXPERIMENTAL

The presence and extent of preferential adsorption of PFPE-acids by metal oxide were determined by preparing slurry mixtures of PFPE samples and ZrO_2 powder (a model metal oxide), separating the adsorbed and nonadsorbed fractions of PFPE and performing ^{19}F-NMR analyses of the fractions thus obtained. The efficacy of the ^{19}F-NMR spectra in the elucidation of structural details of PFPE has been well demonstrated.[5,12] The ^{19}F-NMR spectra presented here were obtained with an IBM Instruments AM300 system (^{19}F frequency 282.4 MHz). The ^{19}F-chemical shifts were measured in reference to $CFCl_3$, and the assignments were done based on published data bases.[12] The proton NMR spectra were obtained with an IBM Instruments AM250 system.

PFPE samples, Krytox-H, Demnum-SH, and Fomblin Z-DIAC, were obtained from DuPont Co., Daikin Industries, and Montefluos S.p.A., respectively. The ^{19}F-NMR analyses yielded the number-average molecular weight of ~ 5000 for Krytox-H, ~ 3000 for Demnum-SH, and ~ 2000 for Z-DIAC. ZrO_2 of finely powdered form (mesh-325) was obtained from Johnson Matthey. A chlorine-free fluorocarbon solvent FC72 (of 3M Corp.) was used for preparation of slurry mixtures, for removing physisorbed PFPE from the ZrO_2 surface, and also for general rinsing purposes throughout the experiment.

RESULTS AND DISCUSSION

Functionality Selective Adsorption

To determine and demonstrate that PFPE-acids are preferentially adsorbed over PFPE of nonfunctionalized form by the metal oxide surface, the following experiment was performed: Two grams each of Demnum-SH ($M_n = 3000$) and Demnum-S20 (nonfunctionalized Demnum of $M_n = 3000$) were mixed and dissolved in FC72 (100 mL). Fifty grams of ZrO_2 (mesh-325) was added to the solution, and the resulting slurry was stirred overnight at room temperature. The slurry was then placed in a fritted funnel (porosity F) and filtered with vacuum suction. The fluid filtrate thus collected was essentially all PFPE as FC72 was removed by vacuum suction.

Figure 2(a) shows the ^{19}F-NMR spectrum of the initial mixture. The assignments of individual peaks and their positions (in ppm) are also shown. Thus, peak 2, e.g., belongs to the propoxy end group, while peak 8 belongs to the carboxylic end group and peak 9 belongs to the ethoxy end group. Consistently with its 1 : 1 composition of Demnum and Demnum-SH, the area integration of peaks revealed a 1/1 ratio for peaks 9 and 8 and a 2/1 ratio for peaks 2 and 8. Figure 2(b) shows the spectrum of the filtrate. The spectrum is essentially that of Demnum (of nonfunctionalized form). Several weak signals observed in Figure 2(b) but not in Figure 2(a) are attributed to contaminants originating from the solvent. It is thus clearly shown that PFPE-acids are preferentially adsorbed by the metal oxide surface over PFPE of nonfunctionalized form.

Size-Selective Adsorption of PFPE-acids

PFPEs, in general, have little compatibility with either aqueous or hydrocarbon-based solvents. They are soluble only in highly fluorinated solvents. We surmised that whether or not a given PFPE-acid molecule was adsorbed on a metal oxide surface would be determined by the relative strength of the heat of adsorption of the carboxylic end at the adsorption site vs. the heat of solvation of the whole molecule in the solvent phase. It follows that if the metal oxide surface is exposed to PFPE-acids with a molecular weight distribution of some dispersity PFPE-acid molecules of shorter dimension would be preferentially adsorbed.

We then performed the following experiment: Twenty grams of Demnum-SH was dissolved in 100 mL of FC72. Fifty grams of ZrO_2 was added to the resulting solution, and the slurry was stirred
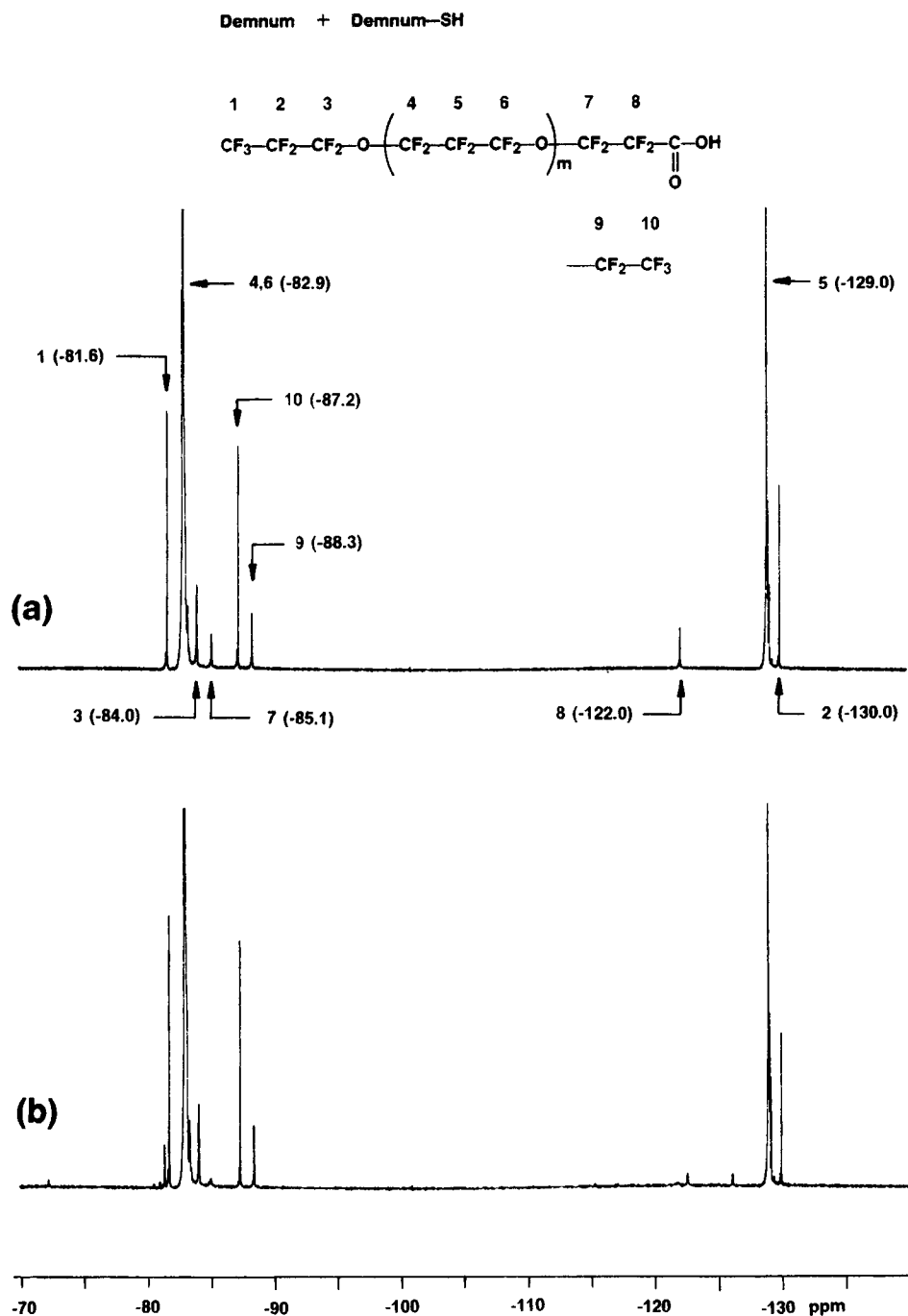
Demnum + Demnum—SH

Figure 2   (a) ^{19}F-NMR spectrum of 1 : 1 mixture of Demnum (M_n = 3000) and Demnum-SH (M_n = 3000). (b) Spectrum of the mixture after it had been in contact with ZrO_2. See text for details.

overnight at room temperature. The slurry mixture was then filtered (as before), and the ZrO_2 cake in the funnel was broken and rinsed twice with additional FC72 (25 mL each). From the entire filtrate, upon removal of the solvent, 18 g of PFPE was recovered. The ZrO_2 cake was then re-moved from the funnel, broken and soaked in CF_3CH_2OH (100 mL), and filtered. From the final filtrate, upon removal of the solvent, the balance (2 g) of PFPE was recovered. The first, major fraction that was not adsorbed onto ZrO_2 from the FC72 solution shall be called the FC72 fraction.

The second fraction that was adsorbed onto ZrO_2 from the FC72 solution, but was removed by CF_3CH_2OH, shall be called the ZrO_2 fraction.

Figure 3(a) and (b) show the ^{19}F-NMR spectra of the FC72 fraction and the ZrO_2 fraction of Demnum-SH thus produced. It is immediately evident that the intensities of peaks associated with the end groups (e.g., peaks 2 and 8) relative to those asso-

ciated with the internal segments (peaks 4, 5, 6) are much stronger in the spectrum of the ZrO_2 fraction. It is thus shown that Demnum-SH molecular chains of shorter dimension are indeed preferentially adsorbed. It should be mentioned that peak 8 has shifted from -122.0 ppm for the FC72 fraction to -121.5 ppm for the ZrO_2 fraction. The shift is attributed to the exchange of the acidic protons with
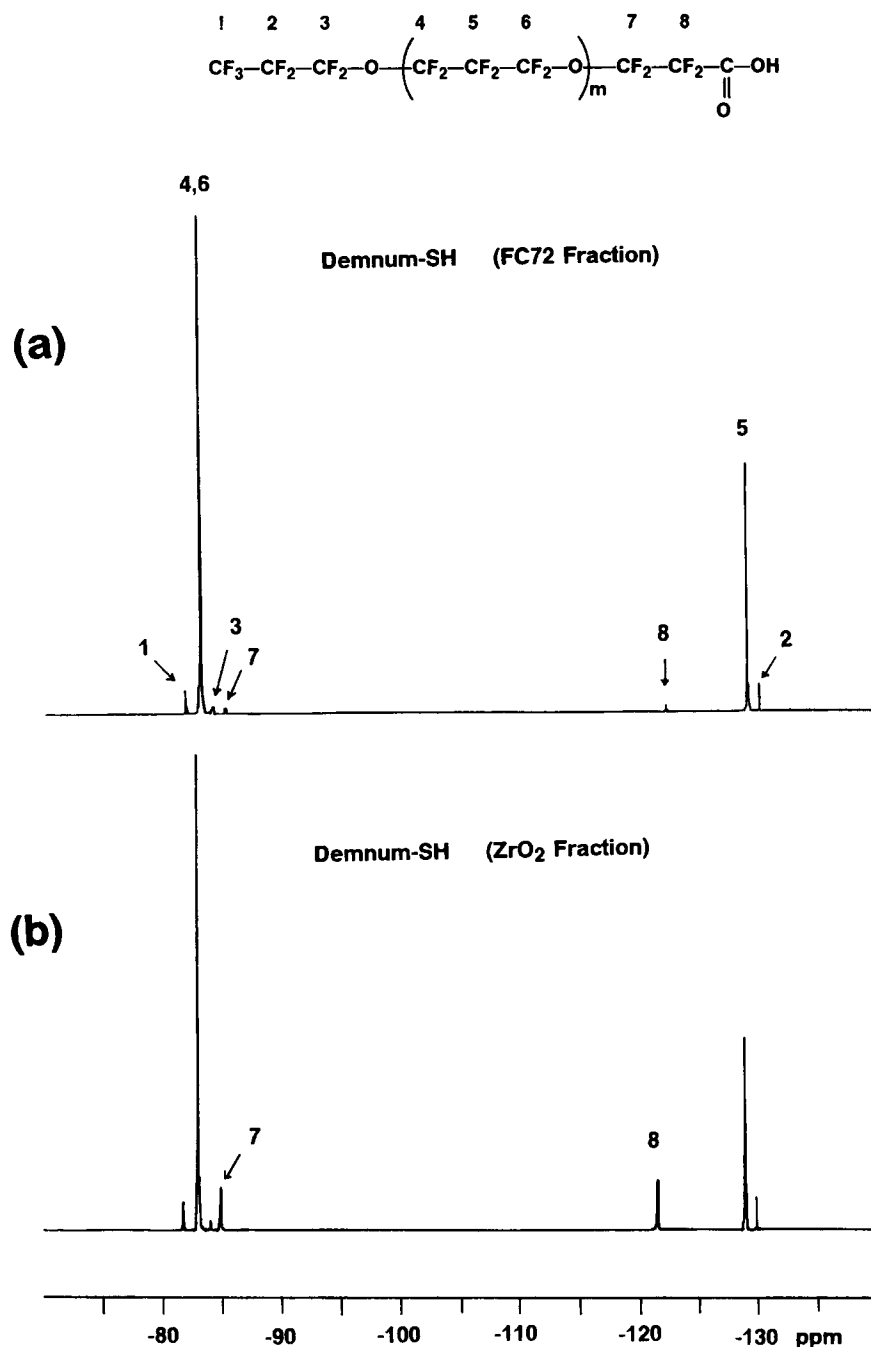

Figure 3 ^{19}F-NMR spectra of Demnum-SH: (a) the FC72 fraction; (b) the ZrO_2 fraction. See text for details.

ubiquitous impurity cations on the metal oxide surface.

Most interestingly, the NMR spectra also revealed the following: The intensity ratio [peak 8/ peak 2], determined by area integration, for the FC72 fraction [Fig. 3(a)] is 0.9/1.0. This ratio is consistent with the fact that Demnum-SH should be functionalized only at the propagation end of the polymerization sequence (Fig. 1), and Demnum-SH of this particular lot contained $\sim$ 10% nonfunctionalized Demnum. The intensity ratio [peak 8/ peak 2] for the ZrO_2 fraction is 5/1. No peaks attributable to end groups other than those already identified were observed. It is thus concluded that, in the ZrO_2 fraction, two-thirds of polymer chains are terminated with the carboxylic end group at both ends. The number-average molecular weights were determined as 3000 for the FC72 fraction and 1300 for the ZrO_2 fraction.

It is intriguing to speculate on the origin of "bifunctional Demnum-SH" found in the ZrO_2 fraction. The possibility that the extra carboxylic end groups were formed by the disproportionation process (1) catalyzed by ZrO_2 was ruled out immediately. No degradation occurred when nonfunctional Demnum was stirred with ZrO_2 at room temperature overnight. Degradation, hence, the formation of carboxylic group, was observed only when the mixture was heated above 250°C. We suggest that short, "bifunctional Demnum-SH" chains are present in the original sample and that they have been produced by the disproportionation reaction (1) occurring during the manufacturing processes. The disproportionation reaction (1) should also produce short Demnum chains terminated with the propoxy end group at both ends. They are readily fractionated from the bulk fluid because of higher vapor pressure. The vapor pressure of bifunctional Demnum-SH should be extra low because of its extra polarity and propensity of carboxylic groups to dimerize.*

The reaction mechanism detailed earlier for the intramolecular disproportionation process then predicts that bifunctional chains should not exist at all in Krytox-H. The same sequence of experiment for the size-selective adsorption was performed for Krytox-H. The ^{19}F-NMR spectrum of the FC72 fraction of Krytox-H thus obtained is shown in Figure 4(a). The assignments of individual peaks and their positions are also shown. The propoxy end

group is thus represented by peaks 1 and 2, and the carboxylic group is represented by peaks 7 and 8. The section encompassing peaks 2, 6, and 8 is shown expanded in Figure 4(b). The area integration revealed that the intensity ratio [peak 8/peak 2] is exactly 1/2. The NMR spectrum (of the same region) observed from the ZrO_2 fraction of Krytox-H is shown in Figure 4(c). The carboxylic peak 8 has shifted to -126.2 ppm due to cation exchange. Much larger intensities of peaks 2 and 8 relative to peak 6 in Figure 4(c) clearly shows that Krytox-H chains of shorter dimension are preferentially adsorbed. The intensity ratio [peak 8/peak 2] in Figure 4(c), however, remained exactly at 1/2. The absence of bifunctional chains in the shorter fraction of Krytox-H is thus strongly substantiated. The number-average molecular weights of Krytox-H determined from the NMR spectra are 5000 for the FC72 fraction and 1300 for the ZrO_2 fraction.

The size-selective adsorption experiment was also performed on Z-DIAC. The ^{19}F-NMR spectra of the FC72 fraction and the ZrO_2 fraction of Z-DIAC thus obtained are shown, respectively, in Figure 5(a) and (b). Here, peak 3_{EM}, e.g., indicates peak 3 of methylene oxide unit flanked by an ethylene oxide unit and a methylene oxide unit, and peak 1_E indicates a carboxylic end group adjacent to an ethylene oxide unit. Peaks almost in contact with peaks 3_{EE} and 2_E are due to methylene and ethylene oxide units immediately following the carboxylic end groups. Their intensities are, hence, equal to 1_M and 1_E, respectively. It is clearly shown that Z-DIAC of shorter dimensions are preferentially adsorbed on the ZrO_2 surface. The number-average molecular weights are 2000 for the FC72 fraction and 850 for the ZrO_2 fraction.

Emulsion of PFPE-acids: Formation and Visual Observation

As stated earlier, the surfactant nature of short PFPE-acids has been extensively examined by Chittofrati and others.[7-11] The system typically examined by these authors has been a water/oil/surfactant ternary system where the oil phase is nonfunctionalized PFPE (of Krytox-like structure with molecular weight of $\sim$ 800) and the surfactant is the same PFPE with the carboxylic end group: $-O-CF_2-COONH_4$. It has been shown that, in such a PFPE-oil/surfactant system, water of up to 20% by weight can be solubilized in the form of microemulsion where water is contained in droplets of diameter of 2–8 nm.

---

* The IR spectrum of Demnum-SH, e.g., shows a broad OH band extending from 2500 to 3200 cm^{-1} expected for the hydrogen-bonded dimer of carboxylic acid; its envelop is essentially identical to that given by trifluoroacetic acid.
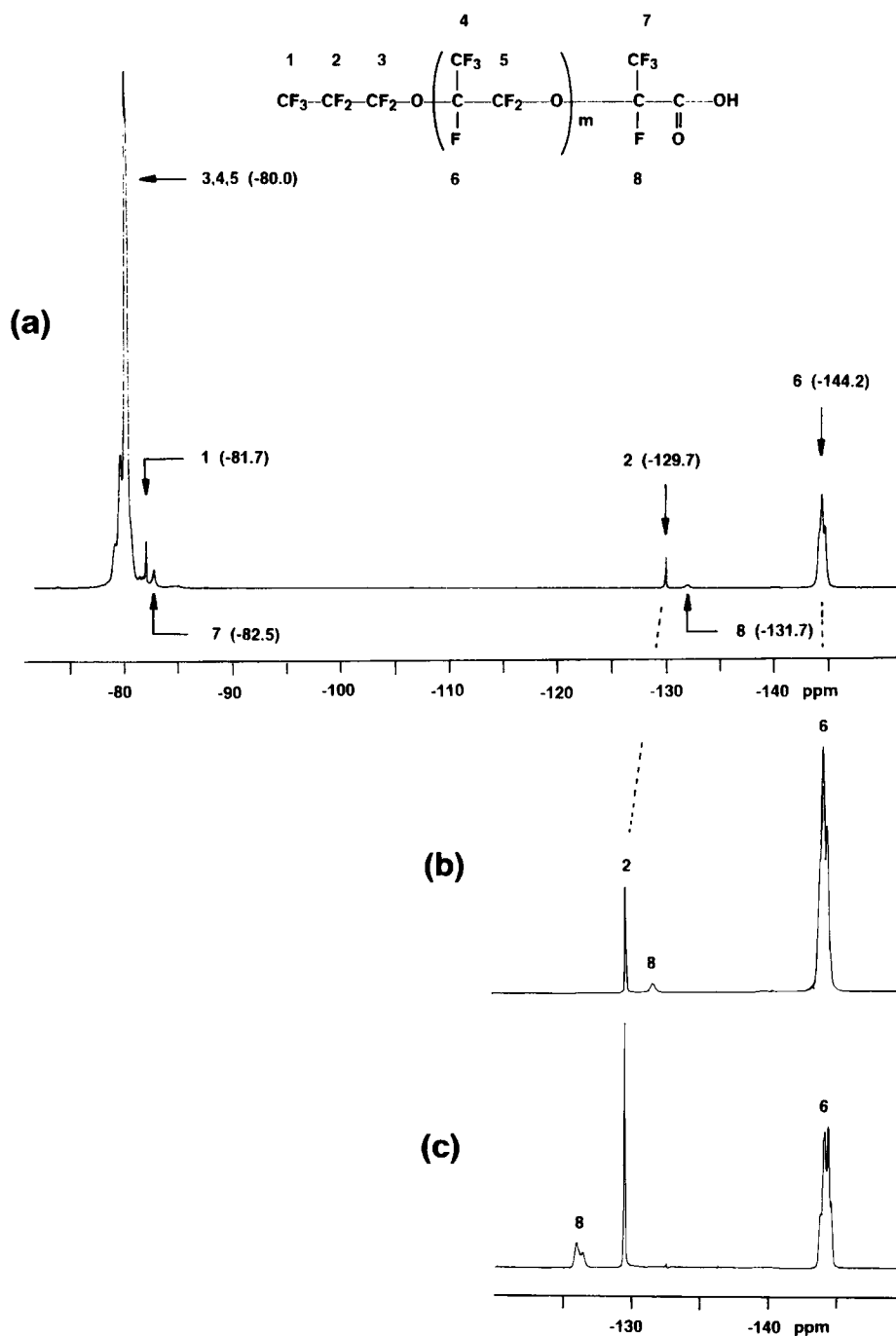
CF_3—CF_2—CF_2—O—$\left(\begin{array}{c}CF_3 \\ | \\ C \\ | \\ F\end{array}\!-\!CF_2\!-\!O\right)_m$—$\begin{array}{c}CF_3 \\ | \\ C \\ | \\ F\end{array}$—$\begin{array}{c}C \\ \| \\ O\end{array}$—OH

1 2 3   4 (CF$_3$) 5   7 (CF$_3$)
                     6   8

(a)

3,4,5 (-80.0)

6 (-144.2)

1 (-81.7)

2 (-129.7)

7 (-82.5)

8 (-131.7)

-80   -90   -100   -110   -120   -130   -140 ppm

(b)

6

2

8

(c)

6

8

-130   -140 ppm

Figure 4 ^{19}F-NMR spectra of Krytox-H: (a, b) the FC72 fraction; (c) the ZrO$_2$ fraction. See text for details.

PFPEs, in general, have little compatibility with aqueous systems. PFPE-acid and water (deionized), when agitated together, quickly separate into two layers of the original volume proportion. However, we found that complete emulsification (with homogeneous consistency) occurs when PFPEs having carboxylic end groups are shaken with water with dissolved electrolytes. Gelation was observed with Demnum-SH, Krytox-H, and Z-DIAC. It was not observed with PFPE of nonfunctionalized form, nor with PFPE possessing hydroxy end groups (i.e., Demnum-SA and Z-DOL). Electrolytes tested were NaCl, CuSO$_4$, ZnCl$_2$, ZnSO$_4$, HCl, and NaOH. The consistency of the gel varied from "mayonnaiselike"
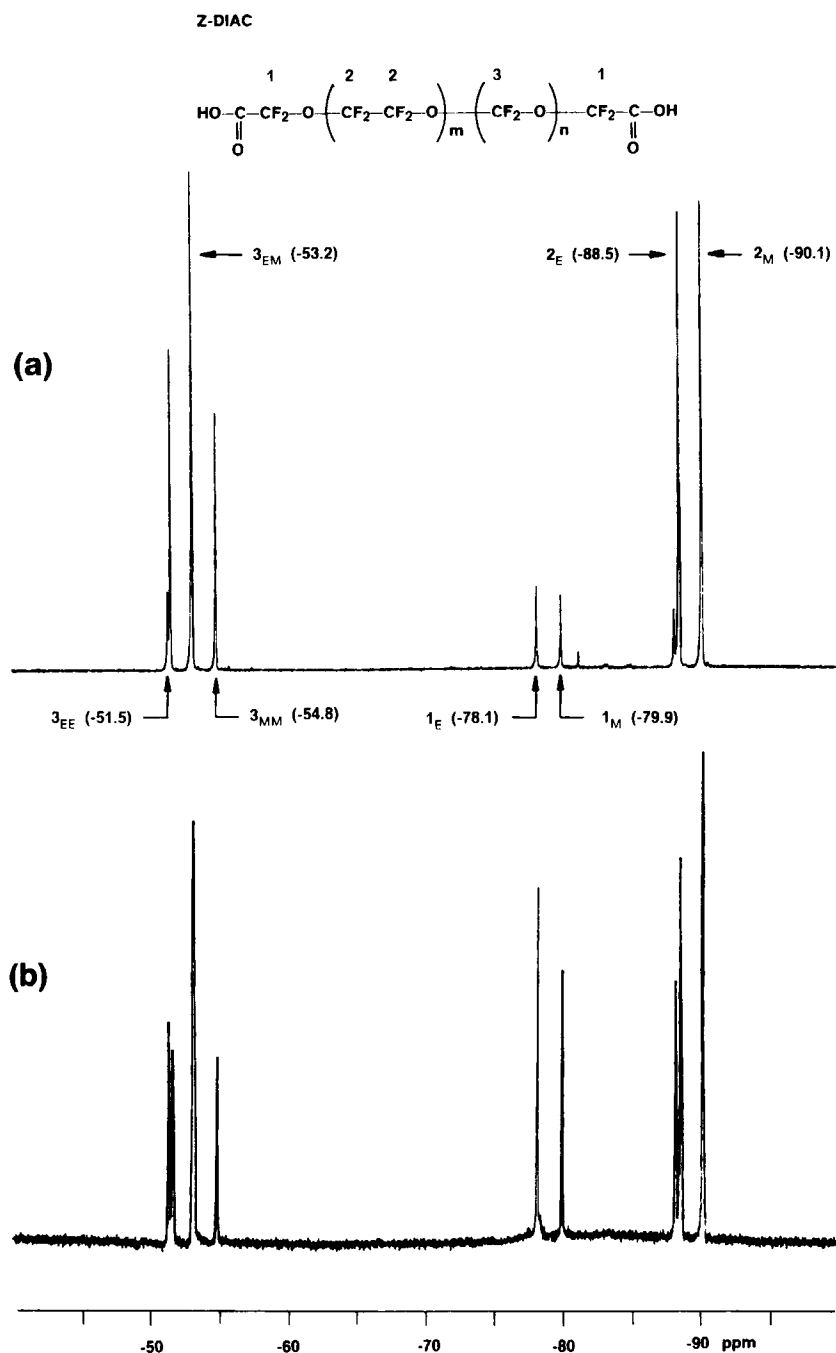
Figure 5 ^{19}F-NMR spectra of Z-DIAC: (a) the FC72 fraction; (b) the ZrO$_2$ fraction.

to "butterlike" depending on the PFPE-acid/electrolyte combination and the concentration of the electrolyte solution.

When 1 g of Demnum-SH (0.53 cc) was shaken with 1 g of 1M NaCl solution (1 cc), e.g., the entire volume changed into a homogeneous gel of milk color with a mayonnaiselike consistency in a few minutes. When 1 g of Krytox-H was shaken with 2 cc of 1M NaCl solution, gelation occurred between Krytox-

H and ~ 1 cc of the electrolyte solution, and the excess electrolyte solution formed a clear layer atop the resulting gel. The following further general observations were made regarding the gels formed by PFPE-acids/water (electrolyte) systems:

1. Rapidity with which the gelation proceeds to completion varies greatly depending upon the electrolyte used. It took ~ 10 min of shaking
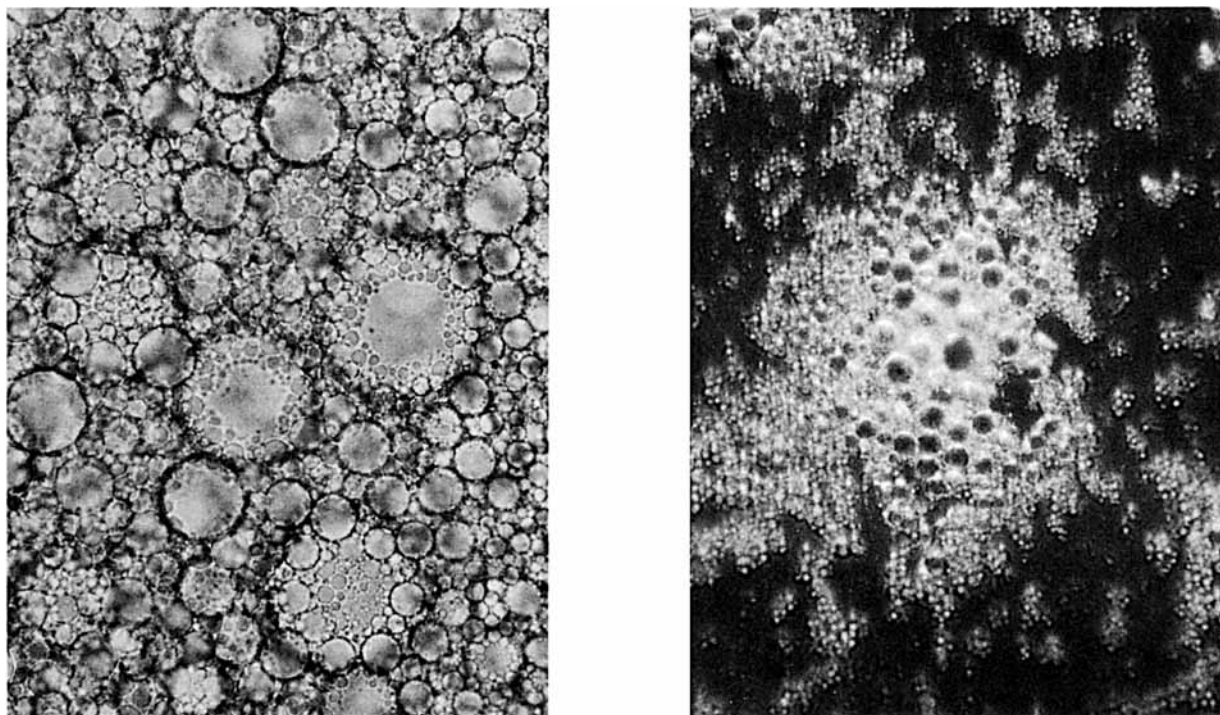
(a)   **(b)**

Figure 6   Microscope images of Krytox–H/ZnSO$_4$ (1M) emulsion: (a) ×200 (transmission); (b) ×100 (reflection).

for 1 g each of Krytox-H and 4M HCl solution, but only several seconds for 1 g each of Krytox-H and 1M ZnSO$_4$ solution. The gelation proceeded faster with a polyvalent electrolyte, and the resulting gel was harder with such an electrolyte.

2. The consistency (viscosity) of the gel increases for several days, just on standing, after the initial formation/shaking.

3. The resulting gels are hydrophobic. The gels, once formed, do not disperse when placed in water (with or without an electrolyte).

4. The gels disperse readily in additional PFPE (with or without the carboxylic end groups).

5. The gels show no (ionic) conductivity.

6. The gels are "stable." Typically, no change was observed after standing at room temperature for several weeks; for some PFPE-acid/ electrolyte combination, a clear layer of PFPE-acid (representing a fraction of the original PFPE-acid) appeared at the bottom.

No flocculation occurred when heated at 80°C for 2 h.

The gels formed between PFPE-acids and water (containing electrolyte) are thus concluded to be emulsion of the water-in-oil type. The maximum volume fraction of water (the inner phase) appears to be ~ $\frac{2}{3}$. It is intriguingly close to the theoretical maximum, 0.74, for the closest packing of hard spheres of identical size. Figure 6 shows microscope images of gel obtained from Krytox-H and 1M ZnSO$_4$ solution. It is revealed that the gel is composed of spherical droplets of diameters of 1–100 microns.

Stable emulsification of one liquid in another generally requires the presence of an amphiphilic surfactant component which forms the interfacial layer.[13] It is surmised that the water droplets in PFPE-acid/water (electrolyte) emulsions are formed and stabilized by a surrounding layer of PFPE-acid molecules of shorter dimension acting

as surfactant molecules. PFPE-acid molecules of longer dimension (most probably in the dimeric form*) constitute the continuous phase of the emulsion. The role of electrolyte is to strengthen the interfacial film by interacting with the carboxylic sector of the surfactant molecules. The situation is depicted schematically in Figure 7.

Emulsion of PFPE-acids: NMR Study

The ^{19}F-NMR spectrum of Demnum-SH/ZnCl$_2$ ($1M$) gel was examined. Each fluorine peak appeared slightly broader (δW_{fwhm} = 0.5 ppm vs. 0.1 ppm for neat Demnum-SH). The increased line

---

* See the footnote on page 802.

width is attributed to the increased viscosity of the gel system. The peaks due to CF$_2$'s α and β to the carboxylic group (peaks 7 and 8 in Fig. 3) showed a downfield shift of $\sim$ 1 ppm due, presumably, to the interfacial interaction of the carboxylic end groups. The chemical shift values of all other peaks remained unaltered.

The proton NMR spectra of the gels were most revealing. Figure 8(a) shows the proton spectra of (1) Krytox–H/HCl ($4N$) gel (dotted line showing peak A' at 5.6 ppm), (2) Krytox–H/NaCl ($1M$) gel (dotted line showing peak B' at 4.2 ppm), and (3) a 50 : 50 mixture of the two preceding gels (solid line). The spectra of individual gels (1) and (2) are identical to those of the corresponding aqueous solutions. The signal observed from the HCl gel (peak
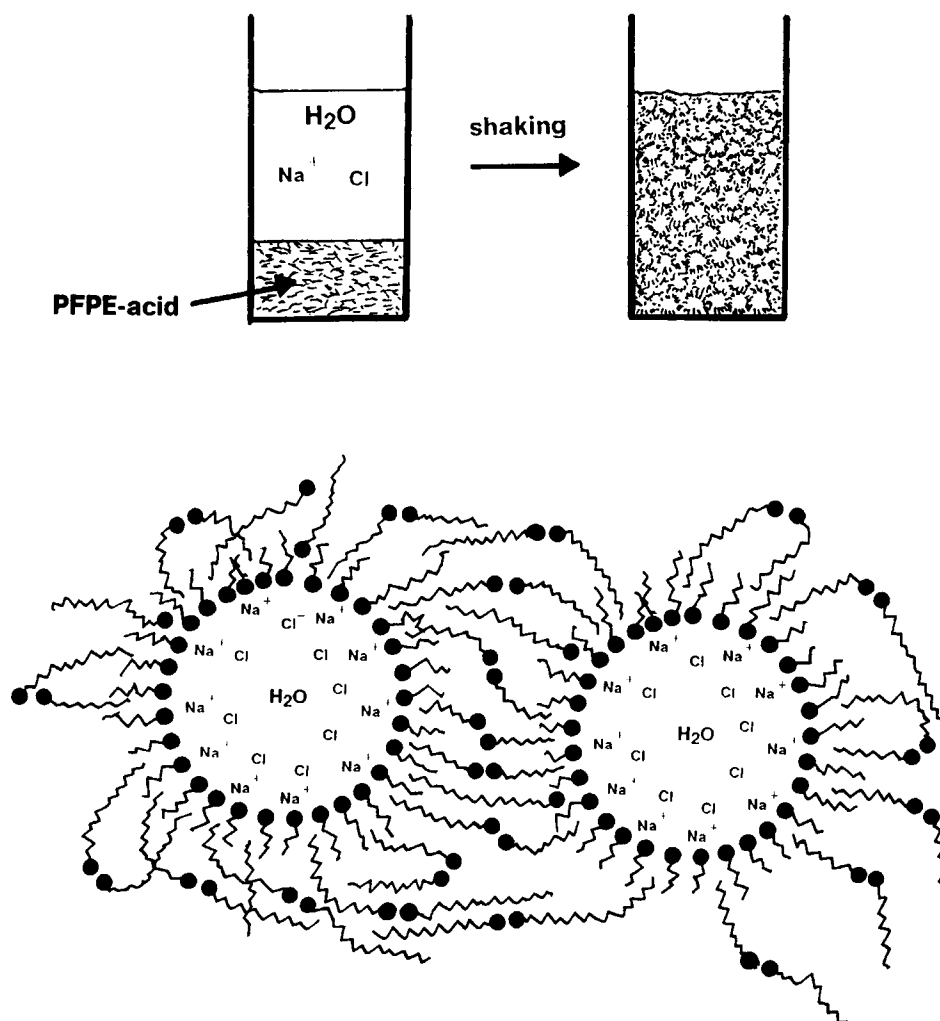

Figure 7 Water droplets in PFPE-acid/water (electrolyte) emulsions are stabilized by a surrounding layer of PFPE-acid molecules of short dimension acting as a surfactant. Electrolytes strengthen the interfacial film by interacting with the carboxylic sectors of surfactant molecules.
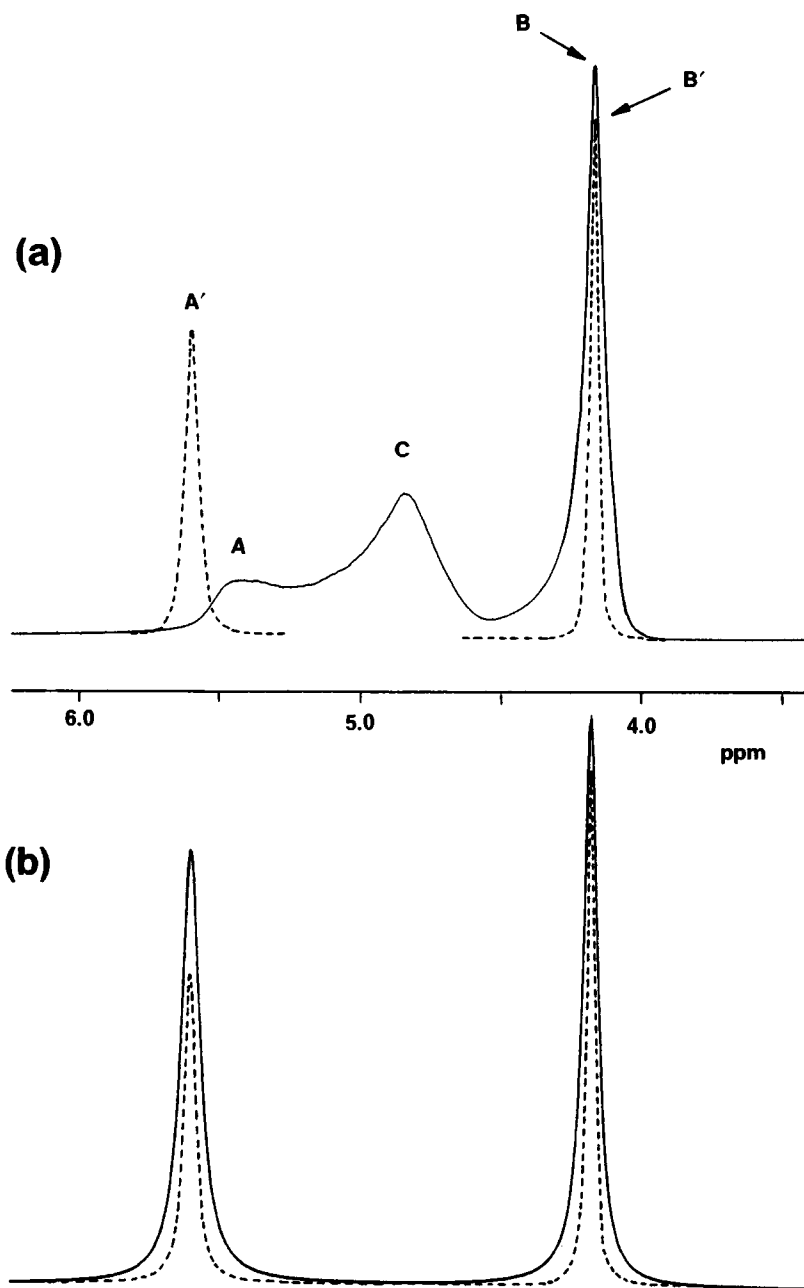
Figure 8   (a) The proton NMR spectra of Krytox-H/HCl ($4N$) gel (dotted line with peak A' at 5.6 ppm), Krytox-H/NaCl ($1M$) gel (dotted line with peak B' at 4.2 ppm), and a 50 : 50 mixture of the two gels (solid line). (b) Computed spectra of the mixed gel assuming no coalescence of the droplets and no exchange (of the protons) between droplets (dotted line) and a steady-state exchange at 50 Hz (solid line). See text for details.

A') represents the exchange-coalesced signals of the hydronium ions and water (hence, the broader line width and a higher chemical shift compared to the signal of the NaCl gel, peak B').

The spectrum of the mixed gel comprises three peaks: A, B, and C. Coalescence of droplets occurs inevitably during mixing of gels and insertion of the

mixture into an NMR tube. Peak C of the mixed gel is attributed to droplets resulting from such coalescence. The NaCl gel is much more viscous than is the HCl gel. The sharpness of peak B and its coincidence with peak B' of the NaCl gel attest to the presence of "NaCl droplets" maintaining the original integrity. A closer inspection reveals, however, that
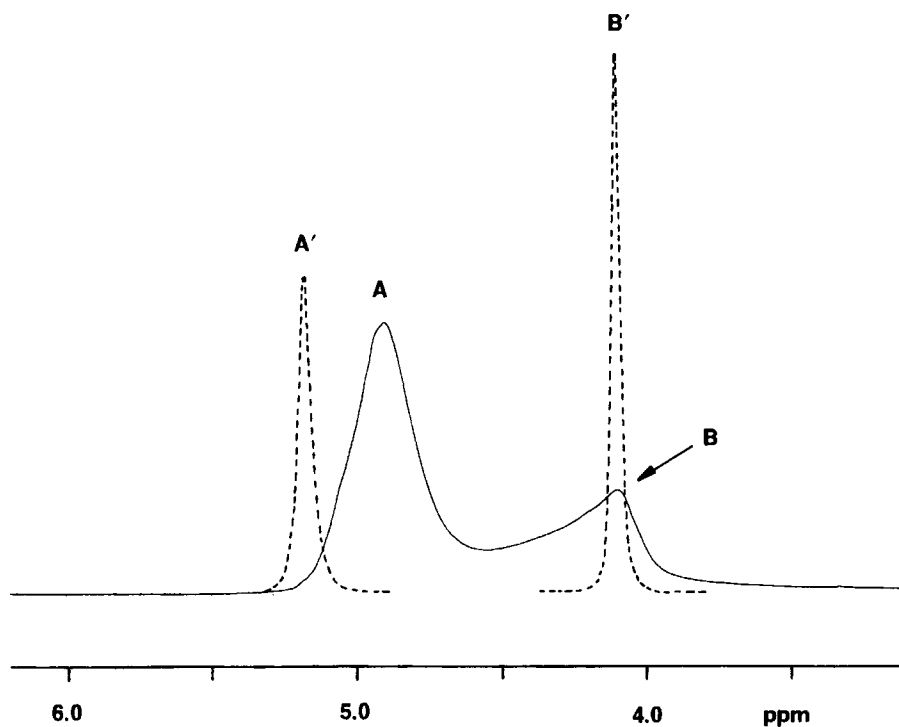
Figure 9 The proton NMR spectrum of 1 : 1 mixture of Krytox–H/HCl (2N) gel and Krytox–H/NaCl (1M in D₂O) (solid line). The spectra of Krytox–H/HCl (2N) gel (dotted line with peak A' at 5.2 ppm) and that of Krytox–H/NaCl (1M in H₂O) gel (dotted line with peak B' at 4.2 ppm) are shown for comparison.

the line width of peak B (which may be accurately assessed on the high-field half) is significantly broader than that of peak B'. The increased line width indicates the presence of a mechanism whereby protons are exchanged between droplets. The HCl gel is soft; the exchange process at HCl droplets is, hence, expected to be faster. The much wider line width and the high-field shift of peak A are attributed to the faster exchange process and partial coalescence. The spectrum of the mixed gel in Figure 8 was obtained 30 min after the mixing. The coalescence progressed spontaneously; the spectrum of the mixed gel changed, on standing at room temperature for several days, to a broad singlet at the peak C position.

The NMR spectrum of protons distributed between two sites and jumping between the two sites at a steady-state rate can be computed by the method of modified Bloch equation.[14] We, hence, computed the spectra of a fictitious mixture of the HCl gel and the NaCl gel wherein no coalescence of droplets occurs and protons are exchanged between droplets at a "steady-state" rate. We aimed to determine the rate at which the high-field half of the computed peak B matches the corresponding sector of the observed spectrum. The result is shown in Figure 8(b).

The dotted line is the spectrum computed for a zero exchange rate; the solid line is that computed for the exchange rate of 50 Hz. The latter figure should represent the rate of proton exchange occurring involving NaCl droplets.

We also made Krytox–H/HCl (2N) gel and Krytox–H/NaCl (1M in D₂O) gel. Figure 9 shows the proton spectrum of a 50 : 50 mixture of these gels (solid line). The spectrum observed from the HCl (2N) gel and that of the NaCl (1M, H₂O) gel are also shown (dotted lines). The spectrum of the mixed gel was obtained ~ 30 min after the mixing. Here, all the proton signals must be due to (1) those residing in the HCl droplets, (2) those in the droplets resulting from coalescence of HCl and NaCl droplets, and (3) those protons that have migrated into NaCl (1M, D₂O) droplets through an exchange process. A well-defined peak B in the observed spectrum is a clear substantiation for the presence of a mechanism whereby protons are exchanged between droplets. The presence of ~ 1 wt % water in short PFPE-acid (MW = 723) was reported by Monduzzi, et al.[10] It corresponds to one water molecule per two carboxylic groups. It cannot be concluded, at present, whether the protons are being exchanged between droplets

as H^+ ions of carboxylic groups or as H_2O of hydration.

CONCLUDING REMARKS

The present study thus has shown that PFPE-acid molecular chains are adsorbed on the polar substrate surface in preference to nonfunctionalized PFPE chains and that PFPE-acids of shorter dimension are adsorbed preferentially over those of longer dimension. Preferential adsorption of polymeric species driven by size and/or functional group differentiation is a well-known process. Experimental demonstration of such processes for PFPEs, however, has not been reported previously. In magnetic recording disk manufacture, PFPE lubricants are applied onto the disk surface by dipping disks into a dilute solution of PFPE in freon or fluorinated hydrocarbon solvent. Preferential adsorption of PFPEs (originating from size and/or the end-group differentiation) during the dipping process and its consequence on lubricant performance have not been addressed explicitly.

Fragmentation of PFPE molecular chains and formation and accumulation of organic debris containing carboxylic groups at the head–disk interface of magnetic recording systems have been reported by several authors.[15,16] The present study suggests a plausible sequence of events whereby catalytic degradation of PFPE is followed by fractionation of degradation products by size and end-group functionality, accumulation of short PFPE-acids, and, eventually, gelation as the acid molecules come in contact with ambient water and ubiquitous inorganic electrolytic contaminants.

REFERENCES

1. J. F. Moulder, J. S. Hammond, and K. L. Smith, *Appl. Surf. Sci.*, **25**, 446 (1986).
2. C. E. Snyder, L. J. Gschwender, and W. B. Campbell, *Lubr. Eng.*, **38**, 41 (1988).
3. W. H. Gumprecht, *ASLE Trans.*, **9**, 24 (1966).
4. Y. Ohsaka, *Petrotech (Tokyo)*, **8**, 840 (1985).
5. D. Sianesi, A. Pasetti, R. Fontanelli, G. C. Bernardi, and G. Caporiccio, *Chim. Indust.*, **55**, 208 (1973).
6. P. H. Kasai, *Macromolecules*, **25**, 6791 (1992).
7. A. Chittofrati, D. Lenti, A. Sanguineti, M. Visca, C. Gambi, D. Senatra, and Z. Zhen, *Colloids Surf.*, **41**, 45 (1989).
8. A. Chittofrati, D. Lenti, A. Sanguineti, C. Gambi, D. Senatra, and Z. Hou, *Prog. Colloid Polym. Sci.*, **79**, 218 (1989).
9. A. Chittofrati, A. Sanguineti, M. Visca, and N. Kallay, *Colloids Surf.*, **63**, 219 (1992).
10. M. Monduzzi, A. Chittofrati, and M. Visca, *Langmuir*, **8**, 1278 (1992).
11. A. Chittofrati, M. Visca, and N. Kallay, *Colloids Surf.*, **74**, 251 (1993).
12. F. Ciampelli, M. T. Venturi, and D. Sianesi, *Org. Magn. Reson.*, **1**, 281 (1969).
13. See, e.g., D. Myers, *Surfactant Science and Technology*, VCH, New York, 1988, pp. 209–253.
14. See, M. L. Martin, G. J. Martin, and J. Delpuech, *Practical NMR Spectroscopy*, Heyden, London, 1980, pp. 293–311.
15. V. J. Novotny, N. W. Karis, and N. W. Johnson, *J. Tribol.*, **114**, 61 (1992).
16. J. Xuan, G. Chen, and J. Chao, *IEEE Trans. Magnet.*, **29**, 3948 (1993).