

Thermogravimetric Behavior of Perfluoropolyether

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SYNOPSIS

In this article, two kinds of perfluoropolyether (PFPE) with different terminal groups were investigated using thermogravimetric analysis (TGA), infrared (IR) spectroscopy, gel permeation chromatography (GPC), and gas chromatography/gas mass spectrum (GC/MS) analysis. PFPEs with a hydroxyl or carboxylic acid terminal group were more heat stable than was PFPE with carboxylic methyl ester. Perfluoropropylene oxide-type PFPE with a perfluoroethyl terminal group at one end tends to lose weight more rapidly than does copolymer-type PFPE with dihydroxyl or dicarboxyl methyl ester terminal groups at both ends. The residual weight fraction of PFPE with a perfluoroethyl terminal group was dependent on the average molecular weight. The number-average molecular weight of PFPE can be calculated from the peak intensity ratio between the polar group and C—F stretching by measuring the IR spectrum of PFPE. The number-average molecular weight of PFPE increased because of the evaporation loss of its low molecular weight fraction and the crosslinking reaction of PFPE with increase in temperature. GC/MS analysis showed that the main product of the pyrolysis of PFPE was hexafluoropropylene. We speculated on the PFPE degradation mechanism and the optimum PFPE chemical structure in terms of heat stability. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that perfluoropolyether (PFPE), which consists principally of fluorine, oxygen, and carbon, has the unique characteristics of low vapor pressure, low surface tension, high specific gravity, solubility in highly fluorinated solvents only, and nonflammability and possesses additional advantages of chemical inertness, high lubricity, low toxicity, and high environmental stability.^{1,2} PFPE oils are commercially produced, e.g., as Krytox by E. I. du Pont de Nemours & Co.³ and Fomblin by Montedison Co.⁴ PFPE oil is used as a lubricant on the surface of hard magnetic disks⁵ and in the aerospace industry, because of its fluidity over a very wide temperature range. Its high thermal stability has enormous technological importance. Gas chromatography/gas mass spectrum (GC/MS) analysis of

the heat decomposition of PFPE indicated the formation of $\text{CF}_2=\text{CF}-\text{CF}_3$ as the main product and other gaseous low molecular weight products. However, little has been published on its thermal stability. This study clarifies the thermal behavior of PFPE by using the thermogravimetric analysis (TGA) technique and subsequent infrared (IR) measurement. The average molecular weight change of PFPE was measured by gel permeation chromatography (GPC). Low molecular weight substances produced by the pyrolysis of PFPE were identified from their chemical structure using GC/MS. The PFPE samples used here have a carboxylic acid, carboxyl methyl ester, or hydroxyl group at each end of one PFPE molecule. We observed that the PFPE weight reduction with carboxyl ester terminal groups was larger than that with hydroxyl terminal groups. The decrease in the absorbance ratio of the PFPE functional groups to the C—F band with increase in temperature is thought to be due to the evaporation of the low molecular weight fraction and crosslinking reactions.

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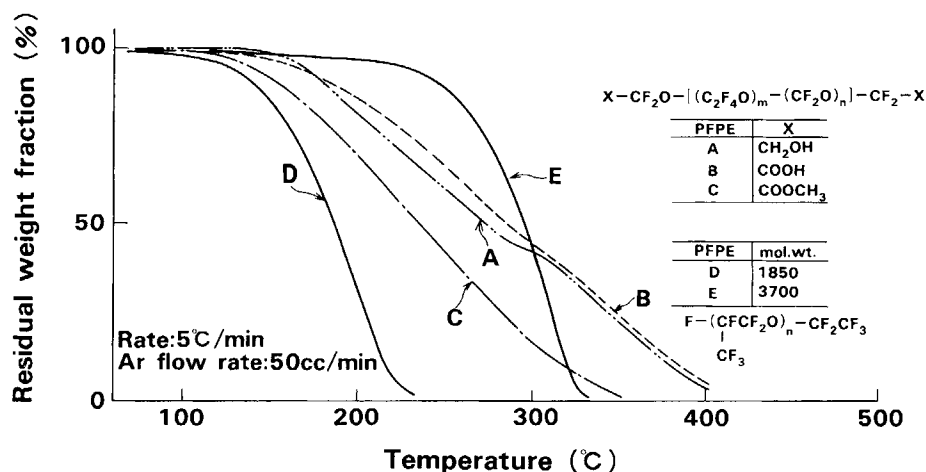


Figure 1 TGA of two kinds of PFPE in an Ar atmosphere.

EXPERIMENTAL

TGA was conducted using the Thermoplus F (Rigaku Denki Co.). For TGA, we used perfluoropolyether specimens 5–10 mg in weight which were weighed in an aluminum pan. TGA was performed at a heating rate of 5°C/min and an argon flow rate of 50 cc/min. The residual weight fraction was recorded in an argon atmosphere at a rate of temperature increase of 15°C/min up to about 400°C. TGA was conducted first, and, subsequently, the IR spectra of the PFPE oils were measured with a Nippon Denshi Model A-3 recording spectrophotometer. The specimen was coated on KRS-5 cells. The hydroxyl or the carboxyl content in the PFPE samples was calculated from the absorbance intensity of these functional groups in the IR spectra. Two kinds of PFPE oils were used for this study: One was copolymer-type PFPE which consisted of the sequential bonding of a perfluoroethylene oxide unit and a perfluoroformaldehyde unit. It was prepared by the UV-induced polymerization of perfluoropropylene mixed with oxygen gas. The other was perfluoropropylene oxide-type PFPE which was synthesized by the anionic polymerization of perfluoropropylene oxide at low temperature. We used three kinds of copolymer-type PFPE with average molecular weights of about 2000. They had a hydroxyl, carboxylic acid, or carboxyl methyl ester terminal group at each molecular end. We had also two perfluoropropylene oxide-type PFPEs with average molecular weights of 1850 and 3700, respectively, which had carboxyl methyl ester terminal groups. The GPC measurement conditions were as follows: A GPC-2014D apparatus (Waters Co.) was used. The GPC column was Zorbax PSM Binodal S (DuPont). The solvent was 1,1,2-trichloro-1,2,2-trifluoroethane and

its flow rate was 1.0 mL/min. The measurement temperature was 23°C and the sample concentration was 0.5–2.0 (wt/vol) %. The sample solution was filtered using a 0.5 μm pore diameter Shodex DT ED-13CR before injection. The amount of the sample injected was 100–200 μL. The GPC detector was a differential refractive index-type sensor R-401 (Waters Co.). The calibration curve was formed by using a series of 10 kinds of standard monodispersed polystyrene solved in a mixture of 1,1,2-trichloro-1,2,2-trifluoroethane and chloroform (the volume fraction ratio of the mixed solvent was 10/7) because standard polystyrene is insoluble in only 1,1,2-trichloro-1,2,2-trifluoroethane. GC/MS analysis of PFPE was performed under pyrolysis conditions of 200°C for 10 min with a Shimadzu temperature increasing gas chromatograph, Type GC-6AM, and a Shimadzu heat-decomposition apparatus, Type PYR-2A.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

Figure 1 shows TGA curves for two kinds of PFPE with different terminal groups (Fomblin series) and with different molecular weights of 3700 and 1850 (Krytox series) in an argon gas atmosphere at 5°C/min. The TGA measurement was performed in an inert gas atmosphere which simplified the thermal degradation mechanism of PFPE. The oxidation reaction in the thermal degradation was completely eliminated in the argon atmosphere. TGA curves can be roughly divided into two types: one for groups A, B, and C and one for groups D and E. The main difference between the two types was that the co-

polymer PFPE exhibited a gradual weight decrease compared to perfluoropropylene oxide PFPE. It seems that this gradual decrease in the TGA curves was caused by an irregularity in the main chain of the copolymer-type PFPE. There was also an irregularity in the chemical structure of the PFPE which inevitably formed in the polymer chain of the copolymer-type PFPE during the UV-induced polymerization of the perfluoroethylene and oxygen gas mixture. Two kinds of PFPE with hydroxyl or carboxyl terminal groups were more heat stable than was PFPE with a carboxyl methyl ester terminal group. This may be because of the hydrogen-bonding ability. PFPE with a stronger hydrogen-bonding ability seems to be more thermally stable than is PFPE with a weaker ability. On the other hand, perfluoropropylene oxide-type PFPE D and E have the same hydrogen-bonding ability. The PFPE of D showed that the weight loss was initiated at a lower temperature than that of E. This result can be explained by the fact that D has a lower average molecular weight than that of E. As shown in Figure 9, the PFPEs with perfluoroalkyl groups like CF_3 — or C_2F_5 — at both ends did not change their average molecular weight by heat treatment up to 300°C . This indicates that the decreases in the residual weight fractions of D and E in Figure 1 do not mean a degradation of PFPE from the chain ends but simply the evaporation of the PFPEs.

Figure 2 shows TGA curves of copolymer-type PFPE (Fomblin series) in an argon atmosphere. The terminal groups of these copolymer-type PFPEs were perfluoromethyl at both molecular ends of the polymer chain. The magnitude of kinetic viscosity is proportional to the average molecular weight of

the PFPE. The initiation temperature of the weight decrease was in proportion to the kinetic viscosity of the PFPE. The curve of the residual weight fraction showed that the PFPE becomes more thermally stable as its average molecular weight increases. TGA also revealed that a PFPE with a higher kinetic viscosity (255 cSt) exhibited a more rapid weight loss than did one with lower viscosity (30 cSt). This may also be affected by the molecular weight distribution, i.e., PFPE with 255 cSt may have a narrower molecular weight distribution than one with a lower kinetic viscosity.

A PFPE with a lower kinetic viscosity which contains a lower average molecular weight portion may have a wider molecular weight distribution. It can be speculated that the slow weight loss is caused by the simple evaporation of the PFPE with the wider molecular weight distribution. The temperatures at a residual weight fraction of 30% for these three kinds of PFPE almost coincided at about 380°C . For the other types of PFPE, the temperature at a residual weight fraction of 30% did not coincide at the same temperature but varied in proportion to the average molecular weight of the PFPE used.

Figure 3 shows the relation between holding time and residual weight fraction at different constant temperatures held for 60 min with carboxyl methyl ester or hydroxyl terminal groups. As shown in Figure 3, a large portion of the weight decrease occurred in the period during which the temperature rose to its constant value. The residual weight fraction of PFPE with hydroxyl terminal groups was larger than that of PFPE with carboxyl methyl ester terminal groups at each temperature. This suggests that the difference in weight reduction may be caused mainly

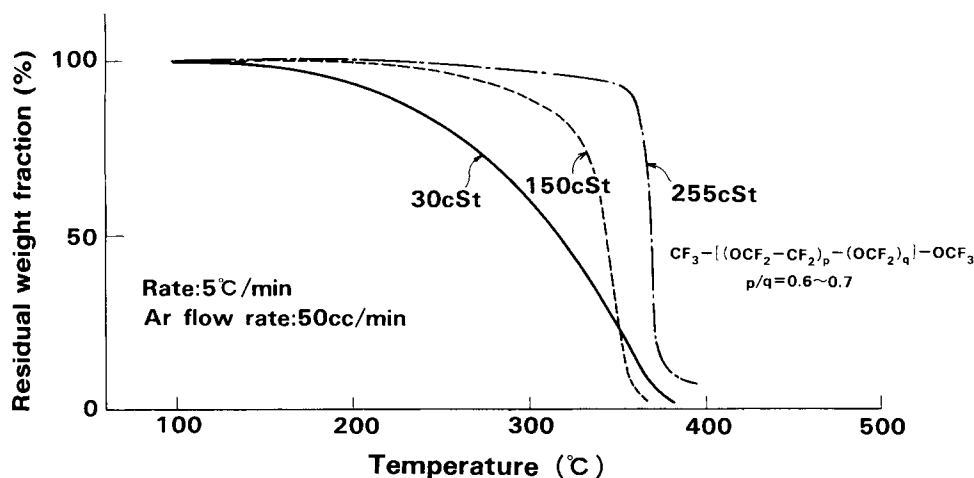


Figure 2 TGA of copolymer-type PFPE composed of ethylene oxide and perfluoroformaldehyde chain units in an Ar atmosphere.

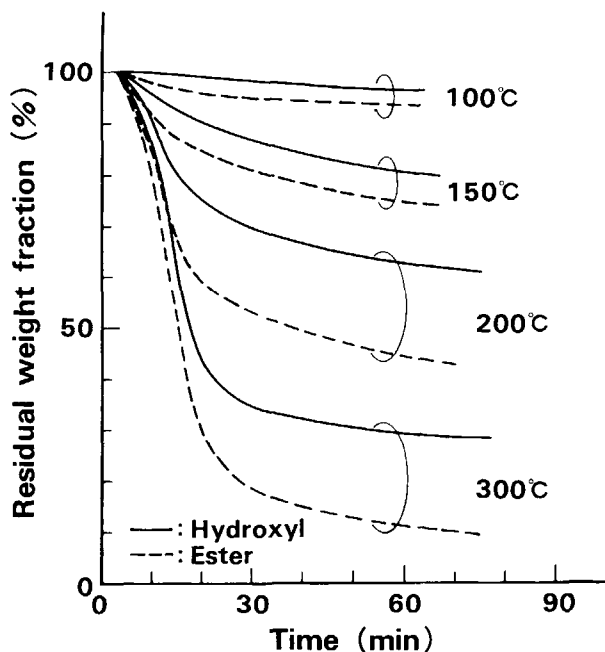


Figure 3 Relation between holding time and residual weight fraction of PFPE with carboxyl methyl ester and hydroxyl terminal groups at different constant temperatures held for 60 min after reaching a constant value.

by the different hydrogen-bonding abilities of these two terminal groups. Figure 4 shows the relation between weight loss rate and temperature at 10 and 50 min from the start of heating. The rate at 10 min was very much larger than that at 50 min. The weight loss in the initial period of heating was much faster than that at 50 min, because of the large amount of energy which flowed from the furnace to the PFPE specimen in the aluminum pan. The PFPE weight loss rate increased with increases in temperature. The difference in weight loss rate between PFPEs with carboxyl methyl ester or hydroxyl terminal groups could not be detected during the initial period of heating. The rates at 50 min after initiation were almost the same for these two kinds of PFPE. The effects of the two terminal groups on thermal degradation may be almost the same as those shown in Figure 4.

Figure 5 shows the relation between temperature and the residual weight fraction of PFPE after heating for 60 min. The residual weight fraction of PFPE with hydroxyl terminal groups decreased linearly with temperature between 100 and 300°C. For PFPE with carboxyl methyl ester terminal groups, the residual weight fractions almost coincided with that of PFPE with hydroxyl terminal groups up to 150°C, but in the 150–300°C temperature range, the residual weight fractions of PFPE with hydroxyl terminal

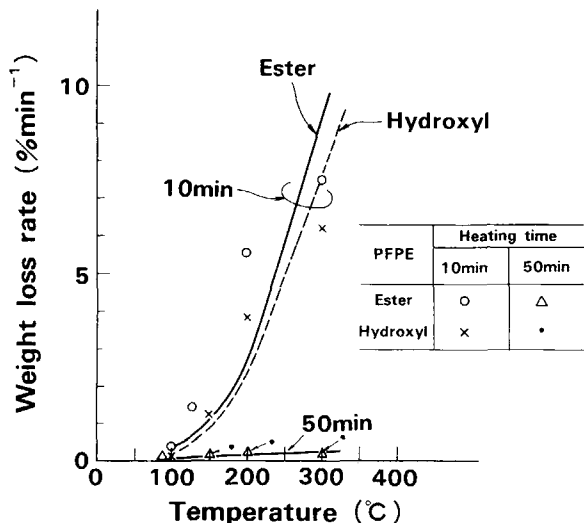


Figure 4 Relation between weight loss rate and temperature at 10 and 50 min from the start of heating.

groups were 15–20% larger than that of PFPE with carboxyl methyl ester terminal groups. The reason for this phenomenon is that the hydrogen bonds in the PFPE molecules dissociate to the same degree at temperatures up to 150°C but the dissociation energy of the hydrogen bonding between carboxyl methyl ester terminal groups may diminish easily as the temperature increases from 150 to 300°C.

Figure 6 shows IR spectra of copolymer-type PFPE with dicarboxyl methyl ester terminal groups after heat treatment at 150, 200, and 300°C for 60 min. These IR spectra were characterized by the absorption peaks of carbonyl (C=O) in carboxyl methyl ester at about 1800 cm^{-1} and the stretching vibration peaks of C—F bonds and of ether bonds (C—O—C) at 1300–1150 cm^{-1} . The peak inten-

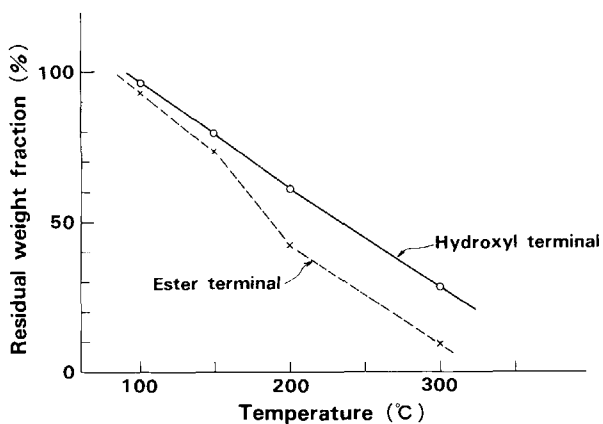


Figure 5 Relation between temperature and residual weight fraction after heating for 60 min at each constant temperature.

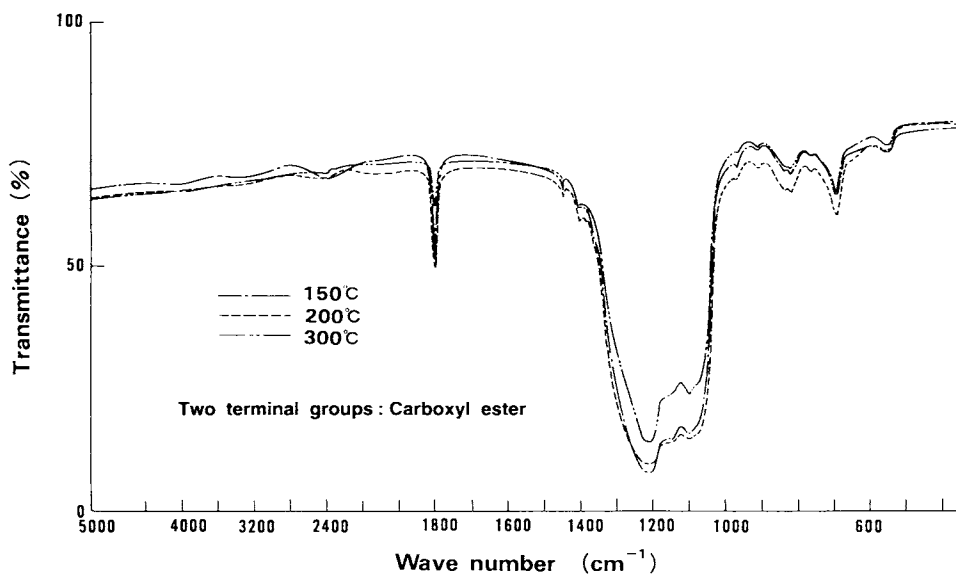


Figure 6 IR spectra of copolymer-type PFPE with dicarboxyl methyl ester terminal groups after heat treatment at 150, 200, and 300°C for 60 min.

sities at about 1800 cm^{-1} became weaker with increases in temperature. This peak showed a large blue shift characteristic of a perfluorinated compound. The peak intensities at 1200 cm^{-1} remained constant because of the stability of the C—F bonding, whereas the peak intensities of the stretching vibration of carbonyl groups decreased rapidly compared with the intensity of the C—F stretching vibration. The broadening of the absorbance at about 1300 cm^{-1} increased with increases in temperature. This phenomenon may be attributed to the cross-

linking between PFPE polymer chains during the thermal degradation.

Figure 7 shows IR spectra of copolymer-type PFPE with dihydroxyl terminal groups after holding it at each temperature for 60 min. The peak intensities about 3400 cm^{-1} , which was the characteristic band of the hydroxyl stretching vibration, decreased with increases in temperature. The peak intensities changed less than those of the absorption assigned to carboxyl methyl ester. This seems to show that the hydroxyl termination groups are more heat sta-

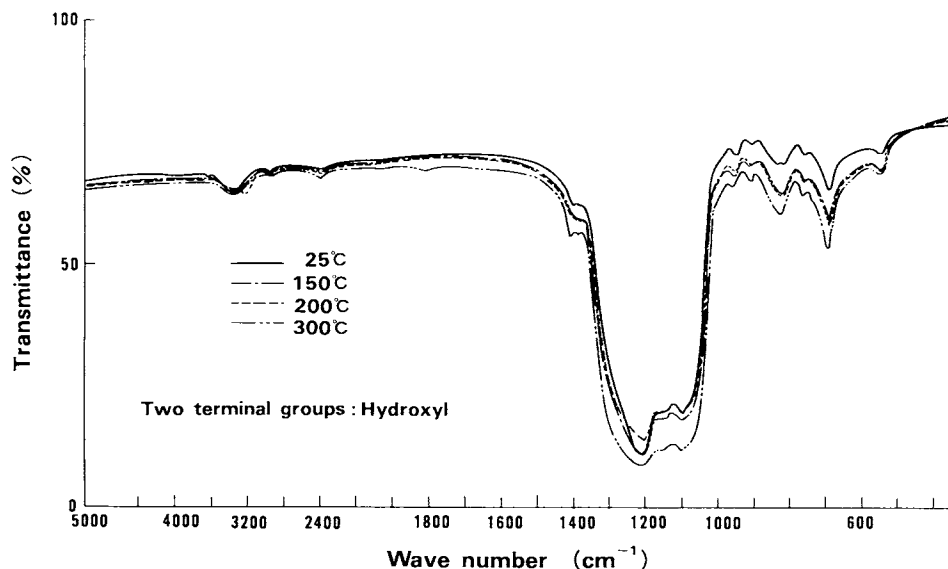


Figure 7 IR spectra of copolymer-type PFPE with dihydroxyl terminal groups after holding it at a certain temperature for 60 min.

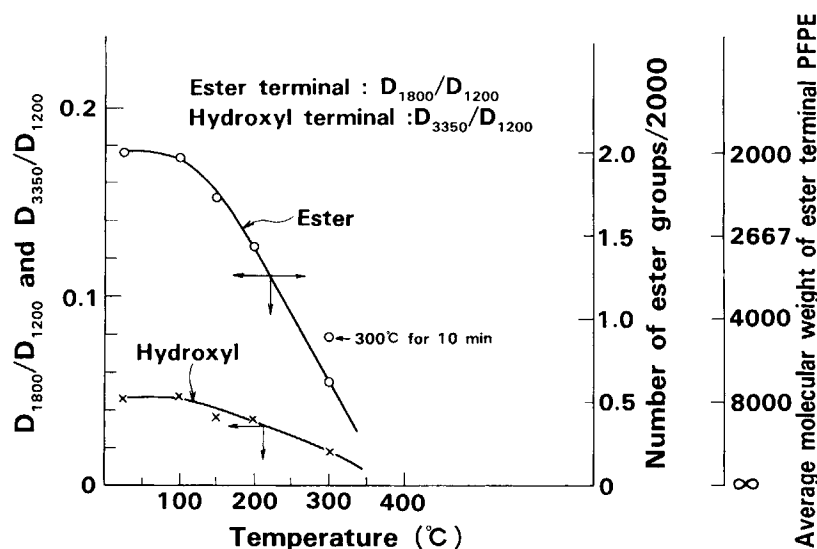


Figure 8 Relation between holding temperature and absorbance ratio of 1800–1200 cm^{-1} for dimethyl ester terminal groups and those of 3350–1200 cm^{-1} for dihydroxyl terminal groups.

ble than are the methyl ester terminal groups in PFPE chains. The broadening of the absorption peak in the 1050–1300 cm^{-1} range is believed to be caused by the crosslinking reactions in the same way as PFPE with dimethyl ester terminal groups. As with PFPE with dicarboxyl methyl ester, the absorption intensity ratio of 3400 cm^{-1} to about 1200 cm^{-1} of PFPE with dihydroxyl terminal groups decreased with increases in temperature. This phenomenon seems to be caused by random crosslinking reactions between the PFPE chains.

Figure 8 shows the relation between the holding temperature and absorbance ratio of 1800–1200 cm^{-1} for dimethyl ester terminal groups and those of 3350–1200 cm^{-1} for dihydroxyl terminal groups. The absorbance peak at 1200 cm^{-1} , which is the characteristic band for the C—F stretching vibration, was adopted as the standard absorption because of its constant intensity. The absorbance ratio of PFPE with ester terminals and hydroxyl terminals were almost constant up to 100°C. The ratio decreased with increases in temperature above 100°C. The absorbance ratio of PFPE with diester terminal groups decreased more steeply than that of PFPE with dihydroxyl terminal groups. The number of carboxyl methyl ester groups per 2000 carbons was calculated assuming that the molecular absorption coefficient of ester carbonyl in PFPE is 700 mol/cm . The average molecular weight of PFPE with carboxyl methyl ester terminal groups was also calculated up to 300°C on the assumption that every PFPE molecule has two terminal groups. The increase in the

molecular weight of PFPE was confirmed by GPC measurement. The data showed that the number-average molecular weight increased above 250°C.

Figure 9 shows the relation between heat-treatment temperature and number-average molecular weight of the perfluoropropylene oxide-type PFPE by means of GPC. Under 150°C, the number-average molecular weight is almost constant. This means that a large amount of PFPE with a low molecular weight evaporates at 150°C and a small amount of

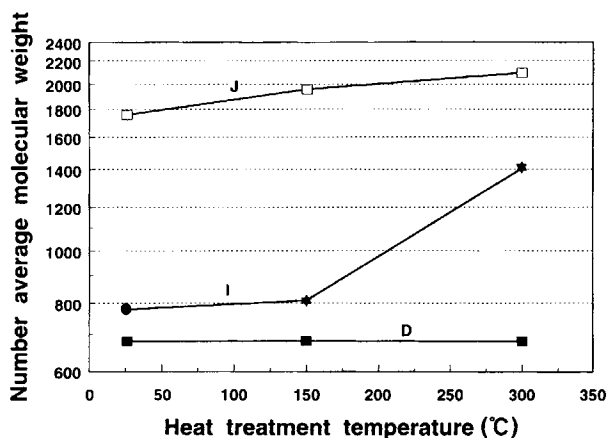


Figure 9 Relation between heat-treatment temperature and the number-average molecular weight of the perfluoropropylene oxide-type PFPE obtained by gel permeation chromatography. PFPE: perfluoropropylene oxide type. Heat treatment time: 2 h. Terminal groups: D, perfluoroethyl; I, carbonyl; J, carboxyl.

recombination reaction occurs between the PFPE chains.

Figure 10 shows the relation between heat-treatment temperature and number-average molecular weight of untreated copolymer-type PFPE and those treated at 150 and 300°C for 2 h. A new PFPE fraction with a higher molecular weight than that of the untreated PFPE was generated at 300°C. This may be due to the occurrence of a PFPE radical recombination reaction during heat treatment. The PFPE radicals seem to be generated by the scission of the covalent bond in the chemical structure of PFPE, especially in relation to the terminal groups.

Table I shows the identification of the gaseous products of perfluoropropylene oxide-type PFPE with one carboxylic acid terminal group. No high molecular weight substances with mass numbers between 500 and 800 were detected in the pyrolysis experiments. The main gaseous product of peak number 2 had a retention time of 6.4 min. The mass spectrum was identified with the reference chemical substance, $\text{CF}_3-\text{CF}=\text{CF}_2$. The other three peaks were also identified with standard substances as shown in Table I.

Summarizing some results of this study, mainly derived from Figures 1-3 for the residual weight fraction and Figures 9 and 10 for the relation between number-average molecular weight and heat-treatment temperature, we can speculate on a desirable chemical structure for a heat-stable PFPE. Perfluoropropylene oxide-type PFPEs with functional groups, i.e., hydroxyl, carboxyl, or carboxyl methyl ester groups at both ends, have less heat stability than that of PFPEs with no functional groups at the ends. The PFPEs with no functional groups have perfluoromethyl groups, i.e., CF_3- at both ends. This is indicated in Figure 9, where the number-average molecular weight of PFPE with no functional groups maintained its room temperature

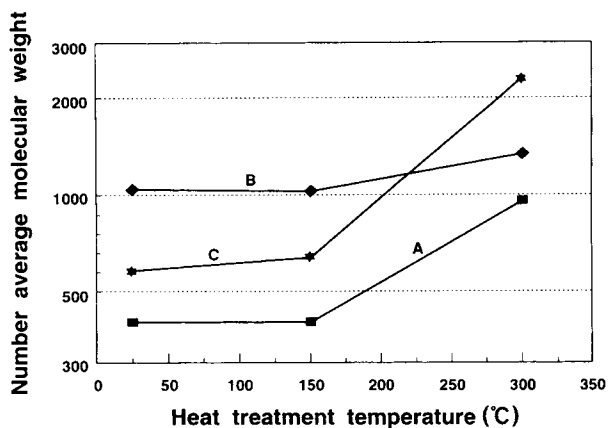


Figure 10 Relation between heat-treatment temperature and the number-average molecular weight of untreated copolymer-type PFPE and those treated at 150 and 300°C for 2 h. PFPE: copolymer type. Terminal groups: A, hydroxyl; B, carboxyl; C, carboxyl methyl ester.

value up to 300°C. This is because the binding energies of $\text{C}-\text{H}$, $\text{C}-\text{O}$, and $\text{C}=\text{O}$ bonds are smaller than that of the $\text{C}-\text{F}$ bond of which PFPE is composed. This may also be applicable to the heat resistivity of copolymer-type PFPE. PFPE becomes more heat stable as its average molecular weight increases. Comparing copolymer and perfluoropropylene oxide-type PFPEs, we may conclude that the copolymer type is more heat stable than is the perfluoropropylene oxide type. This is because trifluoromethyl groups in perfluoropropylene oxide units are more likely to be eliminated by heat treatment than are difluoromethylene units, i.e., $-\text{CF}_2-$ or its irregular sequences of monomer units. The residual weight fraction of a thin film of copolymer-type PFPE on the surface of an acidic substrate may be larger than that of perfluoropropylene oxide-type PFPE, because of its flexible molecular chain and also its hydrogen bonds based on the basicity of

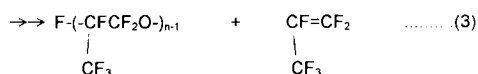
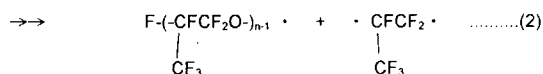
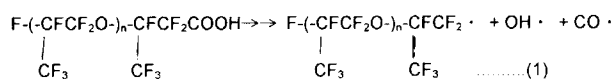
Table I Identification of Gaseous Products of PFPE with One Carboxyl Terminal Group

Peak No.	Retention Time (min)	Identified Substance	Amount (ppm)
1	2.5	CHF_3	1
2	6.4	$\text{CF}_3-\text{CF}=\text{CF}_2$	26
3	12.7	$\text{CF}_3-\text{CH}_2-\text{CF}_3$ or $\text{CF}_3-\text{CHFCHF}_2$	1
4	22.2	$\text{FCH}=\text{CH}-\text{CH}_2\text{F}$ or $\text{CH}_2=\text{CF}-\text{CH}_2\text{F}$	3

Pyrolysis condition: 200°C 10 min. PFPE: perfluoropropylene oxide type. PFPE: \bar{M}_n 6000. Terminal group of PEPF: one carboxylic acid group.

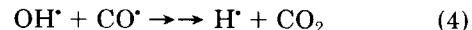
PFPE chains to an acidic substrate such as metal oxide or silicon dioxide.

We can speculate on the PFPE degradation mechanism by integrating some of our results. The initiation reaction of the PFPE degradation caused by heat treatment begins at the molecular chain ends. The degradation reaction proceeds toward the middle of the PFPE polymer chain accompanied by intramolecular rearrangement or develops into an interreaction between different PFPE chains resulting in a crosslinked polymer. If no radicals are generated at the end groups in PFPE molecular chains by heat treatment, the molecules can maintain their original molecular configuration at room temperature up to about 400°C. Once a radical is formed at the end groups, radical groups can easily react with intra- or interneighboring atoms in PFPE chains because of the high reactivity of the radical species. As the degradation reaction proceeds, PFPE polymer molecules change their chemical configuration, conformation, average molecular weight, and molecular weight distribution in the process of molecular rearrangement which is caused mainly by substitution, scission, subtraction, and additional reactions. So, the chemical structure of PFPE with no functional groups at either end is the most heat stable up to high temperature. From Table I, the degradation reaction of perfluoropropylene oxide-type PFPE is considered to start at end groups during radical scission. The sequential radical degradation reactions can be estimated as follows based on the fact that the main gaseous species generated by the heat treatment of perfluoropropylene oxide-type PFPE was $\text{CF}_3\text{—CF=CF}_2$. The initiation reaction generates some radicals and the following reaction generates $\text{CF}_3\text{—CF=CF}_2$:



Hydroxyl radicals and carbon monoxide radicals were not detected in this study. From the result of the formation of propylene derivatives composed of both hydrogen and fluorine atoms in one molecule,

the generation of hydrogen radicals may be generated by the following reaction:



CONCLUSIONS

We studied TGA, IR, GPC, and GC/MS analysis of two types of perfluoropolyethers from the point of view of thermal stability. The results of this study are summarized as follows:

1. Perfluoropropylene oxide-type PFPE with a carboxyl terminal group at one end tends to lose its weight more rapidly than does copolymer-type PFPE with dihydroxyl or dicarboxyl methyl ester terminal groups at both ends.
2. The gradual weight decrease of copolymer-type PFPE with temperature may be attributed to irregular bonds in the chemical structure of copolymer-type PFPE.
3. The temperatures at which the weight decrease begins depend on the average molecular weight of PFPE for the same chemical structure, molecular weight, and molecular weight distribution.
4. We found that the number-average molecular weight of PFPE can be calculated from the peak intensity ratio of the polar end group and C—F stretching by the measurement of the IR spectrum of PFPE.
5. GC/MS analysis revealed that the main gaseous product of the pyrolysis of PFPE was hexafluoropropylene.
6. It is believed that the chemical structure of the most heat-stable PFPE combines the following three conditions in one molecule: first, PFPE with a trifluoromethyl group at both chain ends; second, PFPE with a sequence of copolymer type units; and third, PFPE with a high number-average molecular weight.
7. The degradation mechanism of the PFPE chain may be initiated at the end groups of the PFPE molecular chains and cause some radical reactions leading to some gaseous compounds. This degradation caused the change in average molecular weight and in molecular weight distribution.

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