

A Study on the Effect of Reaction Parameters on Viscosity and Molecular Weight of Hexafluoropropylene (HFP) based Perfluoropolyethers (PFPEs)

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ABSTRACT

Medium molecular weight liquid perfluoropolyethers (840 u to 1372 u) were synthesized by photopolymerization of hexafluoropropylene (HFP) in the presence of oxygen. Effects of various reaction parameters such as temperature, pressure, UV wattage and reaction time on yield, viscosity and molecular weight of PFPEs were studied. Out of all the parameters, the effect of reaction temperature was found the most significant on molecular weight of PFPEs. By increasing reaction temperature, viscosity and molecular weight of PFPEs were decreased. By increasing the wattage of the lamp, viscosity and molecular weight of PFPEs were also decreased. PFPEs obtained from reactions were subjected to FTIR and ¹⁹F-NMR analysis for structural confirmation.

KEYWORDS: Hexafluoropropylene, Bulk polymerization, Photopolymerization, Perfluoro polyethers, Acyl fluorides

1. INTRODUCTION

Medium molecular weight perfluoro polyethers** [PFPEs] are colorless liquid

polymers which find high-end application as a lubricant in various fields where conventional lubricants cannot be used.^[1-4]

**IUPAC Name of perfluoropolyethers [PFPEs]:

Trifluoromethylether-poly[oxy-1-trifluoromethyl-1,2,2-trifluoroethylene]-poly[oxydifluoromethylene]-acylfluoride

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PFPEs unique properties such as high oxidative resistance, thermal resistance, chemical resistance, good lubricity without additives, low volatility, low pour point, radiation resistance, high specific gravity, low surface tension, high viscosity index, non-flammability and compatibility with most elastomers and metals make them suitable for the use of lubrication.^[5-8]

HFP based PFPEs were first synthesized by the photopolymerization of HFP in presence of oxygen in 1965.^[9] Since then a lot of work has been reported related to the synthesis of PFPEs.^[10-13] The detailed mechanism of photopolymerization of HFP in gas and liquid phase has been established.^[11, 14] Different molecular weight PFPEs can be obtained by distillation due to the wide distribution of molecular weight obtained from photo polymerization of HFP.^[15] The Molecular structural studies such as geometries, net charge, bond stretching force constants, vibrational frequencies and infrared intensities are also reported.^[16] The Effect of the polymer composition and molecular weight on physical properties of PFPEs such as glass transition temperature and density has also been studied^[7].

PFPEs obtained by photo-oxidation of HFP possess highly reactive acyl fluoride end groups. Various methods have been reported to neutralize PFPEs such as fluorine end capping, UV end-capping or end group conversion in other groups such as amide, ester, and hydroxyl group according to their requirements in different fields.^[10]

The objective of the present paper is to study the effect of various process parameters such

as temperature, pressure, time and lamp wattage on molecular weight and viscosity of PFPEs.

EXPERIMENTAL

Materials

High-pressure mercury vapor [HPMV] lamps of 125W were purchased from Philips, India. Hexafluoropropylene [HFP] [Purity 99 %] was purchased from M/s Gujarat Fluorochemicals Limited, Gujarat [India]. Oxygen [Purity: 99.9 %] was purchased from M/s Air products, Delhi [India]. The quartz tube was fabricated by M/s Gaurav Enterprises, Delhi [India]. Low-temperature bath [room temperature to -80°C] was fabricated by M/s Southern scientific, Chennai [India].

Reactor Design

Reactor [MOC: SS 316] containing coaxial quartz tube was fabricated by a local manufacturer to carry out photopolymerization reactions. Internal diameter, outer diameter, and length of the reactor were 55.0 mm, 58.0 mm and 230 mm respectively. The reactor had one inlet port at the bottom of the reactor, one outlet port at the top of the reactor and one thermo well to measure the reactor temperature. Double walled quartz tube with the vacuum was used in the reactor to decrease the heat transfer between the inner wall and outer wall of the quartz tube. The outer diameter of the quartz tube was 45 mm and internal diameter was 35 mm and length was 280 mm. The distance between the quartz tube and the bottom of the reactor was 30 mm [Figure. 1].

Bulk Polymerization Method

A reactor of 250 ml capacity [Figure 1] was placed in a low-temperature bath to bring the reaction temperature to -60°C. Propan-2-ol [IPA] was used as a cooling media in low-temperature bath. Pressurizing and depressurizing of the reactor was performed by oxygen and the vacuum pump. The vacuum was created upto 100 mmHg in the reactor to remove the other gases from the reactor. 200 g of HFP was charged into the reactor at -60 °C. UV lamp [125 W] was placed in the quartz tube, switched on and oxygen was introduced into the reactor up to 1

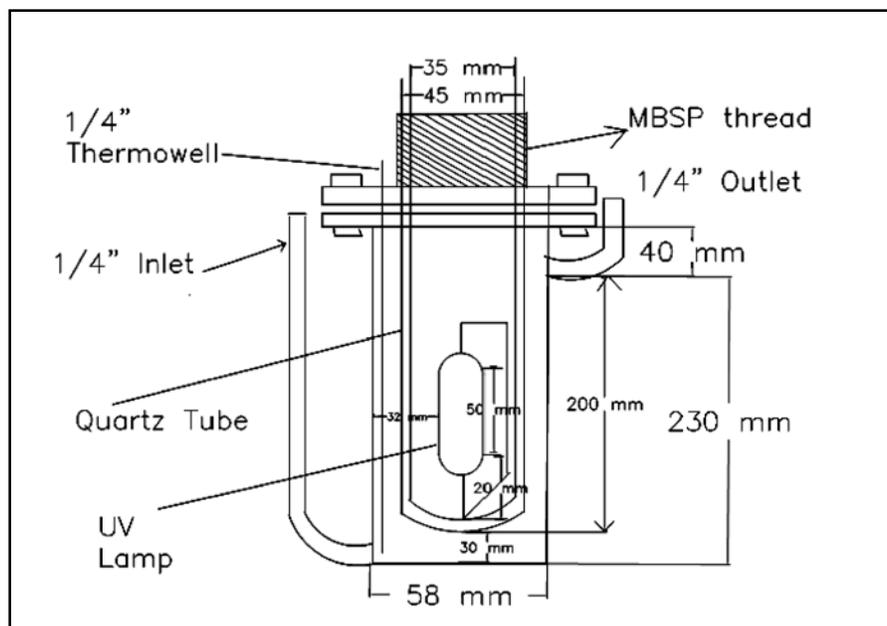


Fig. 1. Design of Photo-reactor [250 ml]

bar [gauge pressure] simultaneously and circulated by diaphragm pump at a flow rate of 5 l/min throughout the reaction. Gases from the outlet were continuously scrubbed by passing them through KOH bubbler to remove the acidic byproducts such as CF_2O and CF_3CFO . After completion of the reaction, perfluoropolyethers with acyl fluoride end groups were obtained.

Characterization

Fluorine-19 nuclear magnetic resonance [^{19}F -NMR]

For determining the structure, PFPEs were subjected to ^{19}F -NMR analysis. ^{19}F -NMR spectra were recorded on Bruker NMR spectrometer at a frequency of 376 MHz in the CDCl_3 solvent. CFCl_3 was used as an internal reference. 30 mg of PFPEs were dissolved in 1 ml of CDCl_3 .

Fourier-transform infrared spectroscopy [FTIR]

The Structural analysis of PFPEs was performed by using

the FTIR technique. FTIR spectra for the polymer samples were recorded using IR Affinity-1 S Shimadzu in the scanning range of $4000\text{--}400\text{ cm}^{-1}$ with 4 cm^{-1} spectral resolution.

Thermogravimetric Analysis [TGA]

The Thermal stability of the PFPEs was determined by the TGA. Thermogravimetric analyzer [NETZSCH STA model 449F3 Jupiter] was used to determine the amount of weight change as a function of temperature over time in an inert atmosphere. Analysis was performed from room Temperature to $500\text{ }^\circ\text{C}$ at the rate of $10\text{ }^\circ\text{C}/\text{min}$. in inert conditions.

Differential Scanning Calorimetry [DSC]

The Glass transition temperature of PFPEs was determined by using a TA Instrument Q 200 differential scanning calorimeter [DSC]. Experiments were performed at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ over temperatures ranging from $-70\text{ }^\circ\text{C}$ to $0\text{ }^\circ\text{C}$ under N_2 atmosphere with a gas flow rate of $50\text{ mL}/\text{min}$.

Kinematic Viscosity

Kinematic viscosity of PFPEs was determined by using Cannon-Fenske viscometer at 20°C.

Average Molecular weight

The average molecular weight of PFPEs was determined from the kinematic viscosity at 20°C by applying the empirical equation:

$$\eta_{kin}^{20} = 5.3 \times 10^{-7} M_n^{2.47} \quad [4]$$

Where η_{kin} is kinematic viscosity at 20°C and M_n is number average molecular weight.

Peroxide value

PFPEs [1 g] were dissolved in 30 ml of Galden SV 55 and acetic acid solvent [1:1 by weight] and then 0.5 ml of saturated potassium iodide solution was added. Peroxide value was determined by titrating PFPEs solution with 0.1 N sodium thiosulfate solution in presence of starch indicator.

Acid Value

The Acid value was determined by titrating PFPEs with KOH solution. 1 gm of PFPEs were dissolved in 10 ml of Galden HT 55 solvent and then titrated with 0.1 N alcoholic KOH.

$$\text{Acid Value} = [56.1 \cdot N \cdot V] / [\text{weight of Oil [gms]]}$$

Where N is normality of KOH solution, V is volume [ml] of KOH solution employed for titration

Density

The Density of PFPEs was determined by using 10 ml of pycnometer.

RESULTS AND DISCUSSION

Perfluoropolyethers were synthesized by photo-oxidation of hexafluoropropylene [HFP] and effects of various reactions parameters such as reaction time, reaction temperature, reaction pressure, and lamp wattage on yield and viscosity were studied.

The Effect of reaction time on yield, molecular weight and viscosity of PFPEs was studied by varying the reaction time from 1 h to 12 h. As reported in the literature^[14], short induction period was required to initiate the reaction and during initiation period [~30 min] consumption rate of oxygen was high. The viscosity of PFPEs was high initially due to the higher amount of peroxide

TABLE 1. Effect of Reaction Time

S. No.	Reaction Time (h)	HFP (g)	Oxygen (g)	Viscosity @ 20°C (cSt) (Mean)	SD (Viscosity)	Number average Molecular weight (M_n) (Mean)	SD (M_n)	Specific Gravity	Peroxide value (meq/Kg)
1	1	200	8-9	22.00	1.2	1213.85	26.83	~1.81	165.8
2	2	200	12-14	13.87	0.85	1006.90	25.05	~1.78	98.5
3	5	200	22-25	8.87	0.55	840.14	21.18	~1.76	81.3
4	9	200	35-38	9.90	1.08	877.93	38.46	~1.77	74.3
5	12	200	38-43	15.33	1.33	1048.42	36.60	~1.78	72.4

Reaction Temperature : -30 °C, Lamp wattage: 125 W and Pressure: 1 Kg/cm² were the same for all reactions

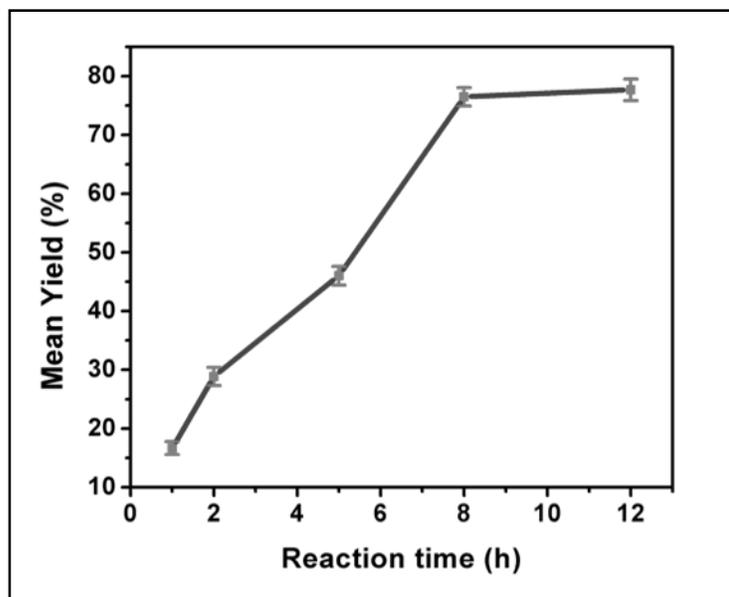


Fig. 2. Effect of reaction time on yield of PFPEs

present in the polymer chain [Table 1] while yield was very low due to incomplete propagation or less conversion of HFP. By increasing the reaction time from 1 hr to 12 h, yield increased from 16.6 % to 77.7 % [by weight of HFP] [Figure 2]. During propagation, viscosity and

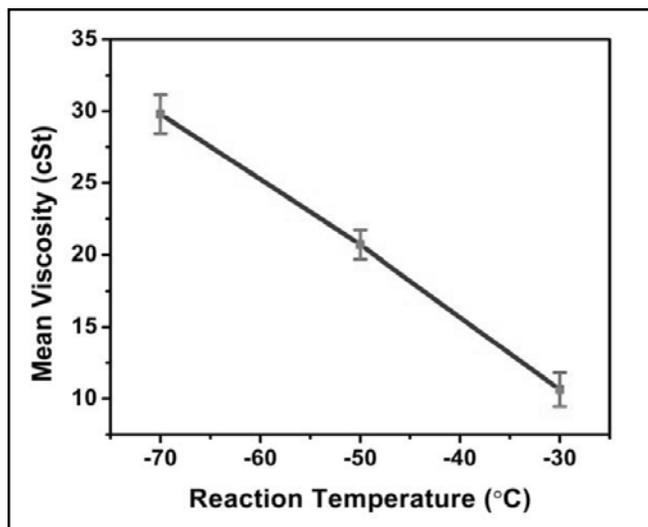


Fig. 3: Effect of reaction temperature on viscosity of PFPEs

molecular weight of PFPEs increased gradually with time and yield was also increased till 9 h [Table 1]. By increasing the reaction time beyond 9 h, yield of PFPEs did not change which indicates complete conversion of HFP into byproducts and PFPEs [Table 1]. The Number average molecular weight was found between 877 u to 1213 u. The Specific gravity was found between 1.76- 1.81 at 20°C [table 1]. 9 h of reaction time was found optimum to carry out photopolymerization of HFP and oxygen.

The Effects of reaction temperature on molecular weight and viscosity of PFPEs were

also studied. By increasing the reaction temperature from -70 °C to -30 °C, viscosity of the product decreased drastically from 29.9 cSt to 10.6 cSt [Figure 3]. Yield of PFPEs was slightly lower at -70 °C in comparison to other reaction temperatures [-30°C & -50 °C] possibly due to slightly lower reaction rate. The Number average molecular weight [M_n] decreased from 1372 u to 877 u by increasing the reaction temperature from -70°C to -30°C [Table 2]. As reported in literatures, at higher reaction temperature [> -50 °C] β -scissioning reaction become dominant to propagation reaction and

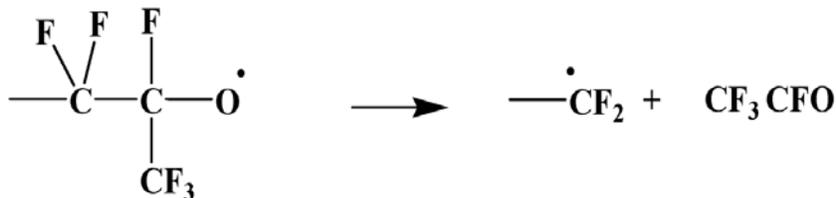
TABLE 2. Effect of Reaction Temperature

S. No.	Reaction Temperature (°C)	HFP (g)	Oxygen (g)	Yield (%) (Mean)	SD (Yield)	Number average Molecular weight (M_n) (Mean)	SD (M_n)	Specific Gravity
1	-70	200	26-28	71.73	1.53	1372.63	25.27	~1.81
2	-50	200	30-33	74.37	1.78	1184.34	23.42	~1.79
3	-30	200	35-37	76.5	1.57	877	38.46	~1.76

three carbon units break down into single carbon unit which caused decrease in molecular weight of PFPEs. Structural changes due to β -scissioning reaction will be discussed later in this paper under ^{19}F -NMR analysis section.

β -Scissioning reaction

Effect of oxygen pressure on yield, viscosity and molecular was studied by varying the pressure from 0.2 kg/cm² to 1 kg/cm². The reaction rate was found to be unaffected by oxygen pressure in the whole range of 0.2



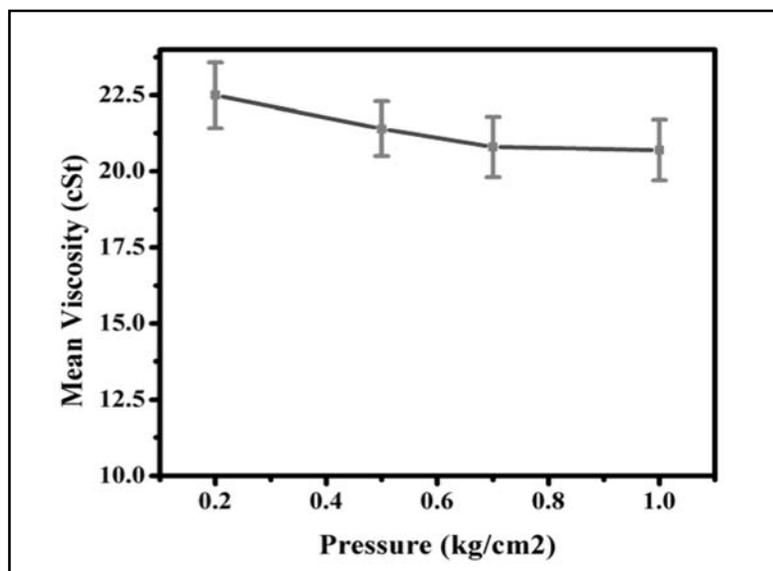


Fig. 4. Effect of reaction pressure on viscosity of PFPEs

kg/cm² to 1 kg/cm². By increasing pressure, yield increased slightly while no significant effect observed on molecular weight and viscosity of PFPEs. Viscosity was changed marginally from 22.5 cSt to 20.7 cSt [Figure 4] by increasing pressure from 0.2 kg/cm² to 1 kg/cm², while molecular weight remains in the range of 1184 u -1225 u. The Specific gravity was around 1.8 at 20 °C [Table 3].

The Effect of UV lamp wattage on viscosity and molecular weight of PFPEs was also studied. Two types of UV lamps, high-pressure mercury vapor lamp [HPMV] and low-pressure mercury vapor lamp [LPMV] were used to provide sufficient energy to initiate the reaction. It is reported that low-temperature mercury vapor lamp contributes to higher number of peroxide groups^[9]. Three HPMV lamps of 80W, 125W,

TABLE 3. Effect of Reaction Pressure

S. No.	Pressure (kg/cm ²)	HFP (gms)	Oxygen (gms) (Mean)	Yield (%)	SD (Yield) Molecular weight (M _n) (Mean)	Number average	SD (M _n)	Specific Gravity
1	0.2	200	27-29	67	2.7	1225.01	23.99	~1.8
2	0.5	200	28-30	69	1.25	1200.46	20.45	~1.8
3	0.7	200	30-32	76	1.76	1188.20	23.07	~1.8
4	1	200	30-33	78	1.57	1184.34	23.43	~1.8

Reaction time: 9 h, reaction temperature: -50°C and lamp wattage: 125 W were same for all the reactions.

and 250W were used to observe the effect of intensity of UV radiation on molecular weight and viscosity of PFPEs. As expected higher viscosity product was obtained when 80W of HPMV UV lamp was used in comparison to the 125W of HPMV lamp [Table 4]. By increasing wattage from 80W to 125W, yield increased

from 66 % to 74 % which indicated the increase in reaction rate due to the increase in wattage. The Increasing in wattage from 80 W to 125 W resulted in the decreased in viscosity from 26 cSt to 22 cSt [table 4] and the molecular weight [Table 4].

TABLE 4. Effect of Lamp Wattage

S. No.	Lamp wattage (W)	Lamp Intensity (W/m ²) r (mm):.02	Reaction Time (h)	Oxygen (g)	Mean Yield (%)	SD (Yield)	Viscosity @ 20°C (cSt)	SD (Viscosity)	Number average Molecular weight (M _n)	SD (M _n)	Specific Gravity
1	80	15923.57	9	28-30	66.40	1.25	26.36	1.20	1306.26	24.43	~1.82
2	125	24880.57	9	30-33	74.37	1.78	21.9	2.00	1211.08	45.22	~1.82
3	250	49761.15	9*	12-14	4.6	0.53	Insufficient quantity				

**Reaction could not be completed because of uncontrollable UV lamp temperature. Reaction was stopped after 3 h. Reaction time: 9 h, reaction temperature: -50 °C, lamp wattage: 125 W, Pressure: 1 kg/cm² were same for all the reactions.

Characterization

¹⁹F-NMR Analysis

Effect of reaction temperature on the structure of PFPEs was studied by using ¹⁹F-NMR technique. In the case of PFPEs, the fluorine-fluorine coupling can occur for fluorine nuclei up to 6 bonds so broad and unresolved spectra result. Due to the broad and unresolved peaks, chemical shift gives more reliable information rather than coupling constant.^[17] Second order ¹⁹F-NMR spectra were analyzed with the help of data reported in the literature.^[18-19]

¹⁹F-NMR spectra of PFPEs [Figure 5 & Figure 6] obtained from photo-oxidation of HFP at reaction temperature -50°C and -30°C

showed similar peaks but the area under the peaks were different in both the spectrum.

The Signal attributed to tertiary fluorine of propylene oxide repeating unit showed the highest chemical shift and appeared at -146 ppm due to shielding effect [Internal Reference: CFCI₃]. The Chemical shifts of -CF₃ and -CF₂O groups of perfluoropropylene oxide coincided and appeared downfield at -82 ppm, which confirmed the presence of three carbon repeating unit in the polymer chain. Chemical shifts of -OCF₂O- and -CF₃O decreased further due to the presence of the higher number of electronegative atoms and peaks appeared at -54 ppm and -57.8 ppm respectively. The Acyl fluoride end group showed the lowest chemical shift due to an isotropic effect and peak appeared at -13 ppm.

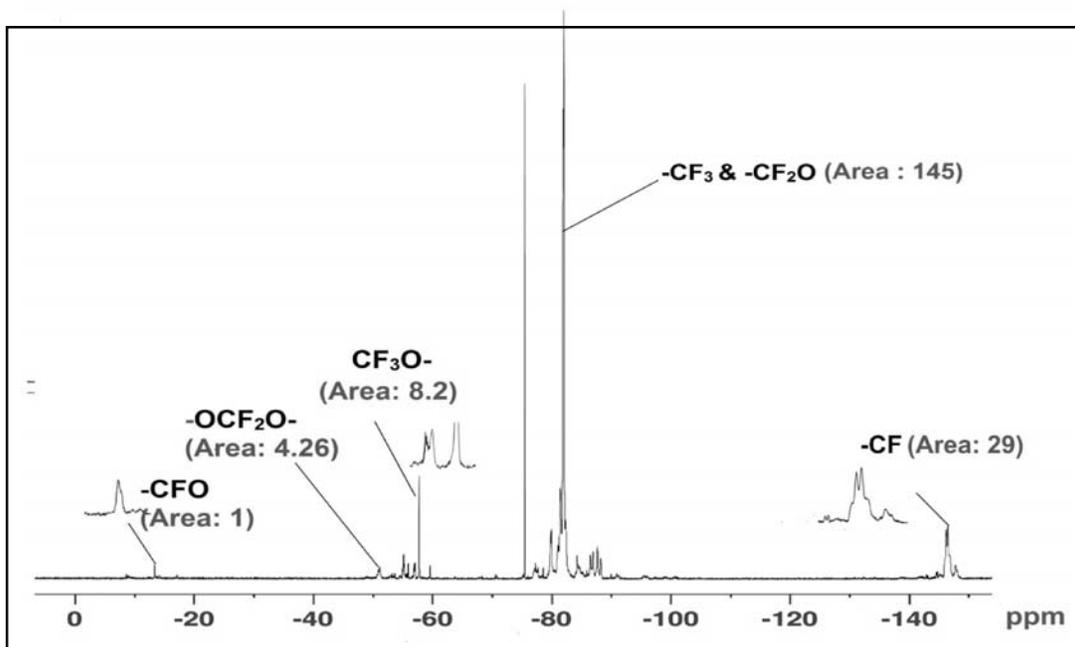


Fig. 5. ¹⁹F-NMR spectrum of perfluoropolyethers [PFPEs] obtained at -50 °C reaction temperature

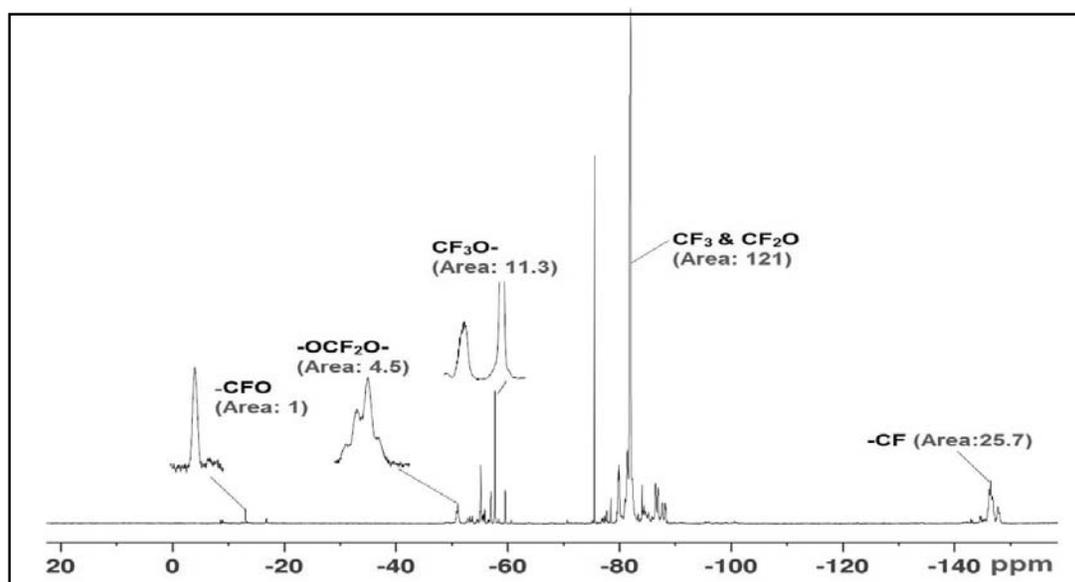


Fig. 6. ¹⁹F-NMR spectrum of perfluoropolyethers [PFPEs] obtained at -30 °C reaction temperature

Similar peaks appeared in both the graphs indicated the similarity in structure of PFPEs obtained at $-50\text{ }^{\circ}\text{C}$ and $-30\text{ }^{\circ}\text{C}$ and the difference in the areas under the peaks of both the spectrum indicated the change in the number of repeating units due to the polymerization temperature. By comparing the areas of both the ^{19}F -NMR spectrum it can be concluded that at the higher polymerization

temperature, number of $-\text{OCF}_2\text{O}-$ repeating unit increased and repeating unit of propylene oxide decreased possibly due to β -scissioning reaction. ^{19}F -NMR analysis explained the reason behind the decrease in molecular weight and viscosity of PFPEs due to the increase in polymerization temperature. Figure 7 shows the structure of PFPEs interpreted from NMR analysis.

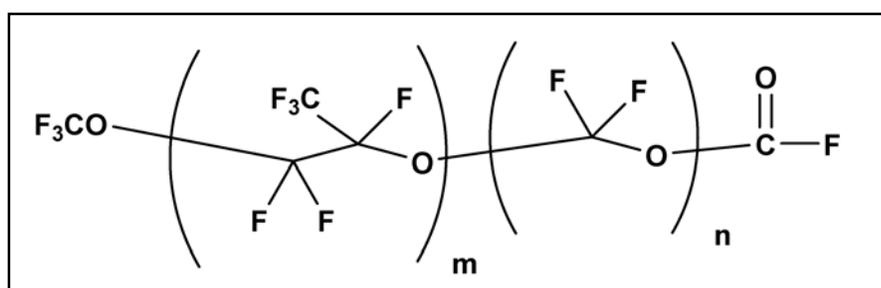


Fig. 7. Structure of PFPEs interpreted from ^{19}F -NMR

FTIR Analysis

Figure 8 shows the FTIR spectrum of PFPEs. A sharp band appeared at 1894 cm^{-1} was

assigned to the vibrations of the carbonyl group of acyl fluoride end group. A sharp band related to the carbonyl group of carboxylic acid end

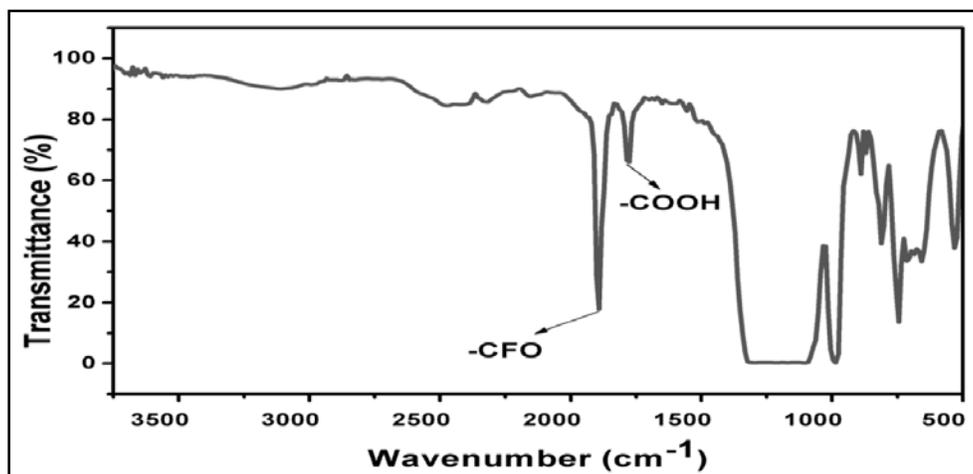


Fig. 8. FTIR spectra of Perfluoropolyethers with acyl fluoride end groups

group also appeared at 1780 cm^{-1} which confirmed the hydrolysis of acyl fluoride end group in presence of atmospheric moisture.^[20] Presence of carboxylic acid and acyl fluoride bands confirmed the acidic behaviour of PFPEs. The broad band from $1310\text{--}1080\text{ cm}^{-1}$ was assigned to the ether bond and CF stretching of perfluoromethylene oxide and perfluoropropylene oxide group. A sharp band around 1000 cm^{-1} was appeared due to the coupled stretching motion of C-O, C-F and C-C bonds.^[20-21] Bands between 700 cm^{-1} to 800 cm^{-1} were assigned to the valence angle bending of CF₃, CF₂ and C-O-C bond^[21].

Thermal Analysis

First low volatiles were removed by heating PFPEs at 100°C for 30 min. avoid the oxidation reactions, TGA analysis was performed under nitrogen environment. 25% weight loss was observed at 228°C while 50 % weight loss of PFPEs observed at 284°C .

The Glass transition temperature of PFPEs was also determined by DSC analysis. Glass transition temperature of PFPEs depends on molecular weight and ranges from -130°C to -60°C ^[23]. DSC analysis of PFPEs obtained from photo-oxidation of HFP at -50°C showed a sharp Tg at -26.23°C [Figure 10]. Presence of carboxylic acid and acyl fluoride end-groups

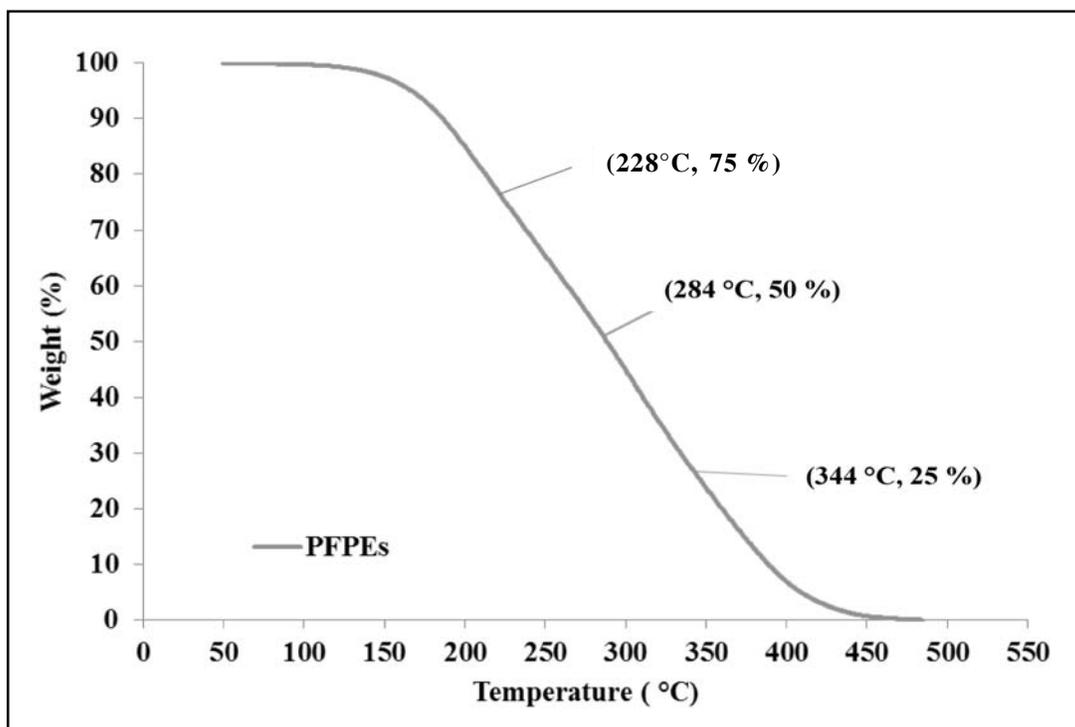


Fig.9. Thermal stability analysis of PFPEs by TGA

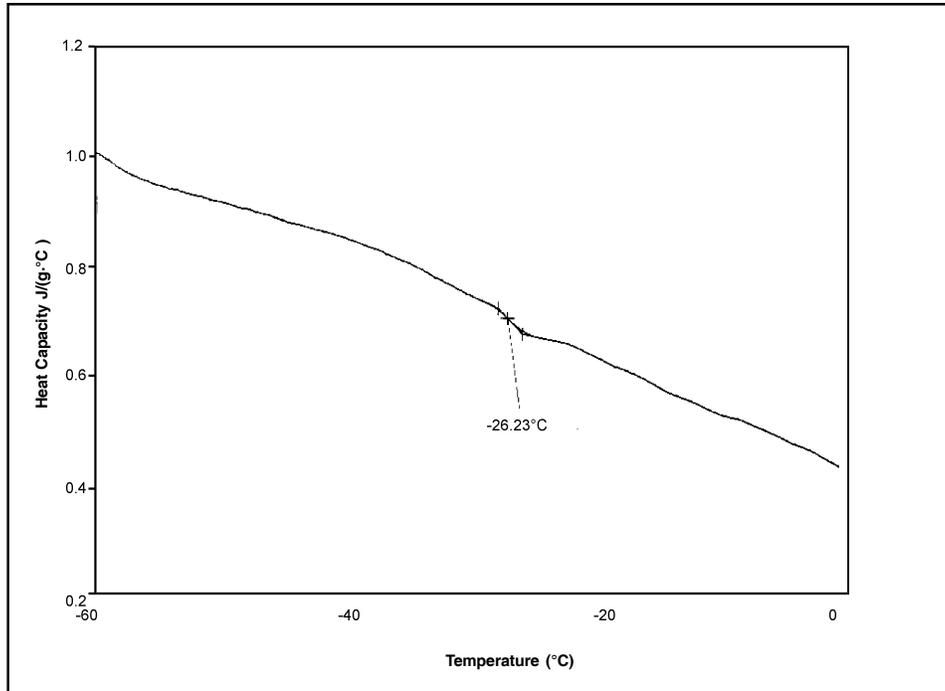


Fig. 10. DSC curve of PFPEs

would have caused the stiffening of chain segments which resulted in high glass transition temperature. It is expected that after stabilization of perfluoropolyethers by fluorination, glass transition temperature will decrease further due to removal of polar groups from polymer chain.

CONCLUSIONS

The following conclusions can be drawn from the results presented above:

- Effect of reaction parameters such as reaction time, reaction temperature and lamp wattage on yield, viscosity and molecular weight of PFPEs was found significant.

- By varying the polymerization temperature, PFPEs of different viscosities and molecular weight can be obtained
- By using UV lamps of different wattage, PFPEs of different viscosities and molecular weight can be prepared.
- Effect of oxygen pressure was found insignificant on polymerization rate.

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