

Method development to synthesize Low molecular weight Perfluoropolyethers (PFPEs)

Saurabh Saxena^a, Prateek Malik^a, Geetha Seshadri^a, Ajay K. Tyagi^a, Uttam Kumar Mandal^{b,*}

a: Shriram Institute for Industrial Research, New Delhi 110007, INDIA.

b: University School of Chemical Technology, Guru Gobind Singh Indraprastha University, Sector-16C, Dwarka, New Delhi 110078, India.

Abstract

Low molecular weight perfluoropolyethers (PFPEs) based on hexfluoropropylene (HFP) were synthesized by avoiding the direct exposure of UV to liquid HFP. Product of 1.5 cSt viscosity with 45 % yield was obtained after 9 hrs of reaction. Effect of temperature variation on yield and viscosity was also studied. Acidic characteristic of perfluoropolyethers was determined by titrating it with KOH. Acid values were found very high which confirmed the higher no of chains in product. Perfluoropolyethers were subjected for thermal analysis and were analysed by TGA which revealed the higher proportion of low molecular weight perfluoropolyethers in the product. Structural analysis of Perfluoropolyethers was also performed by FT-IR. FT-IR analysis confirmed the presence of COOH and COF group at the end of the polymer chain.

Keywords

Low molecular weight perfluoropolyethers (PFPE's), Photooxidation, Hexafluoropropylene

Introduction

Hexafluoropropylene (HFP) based perfluoropolyethers are liquid polymers with unique properties such as highly oxidative and thermal resistance, chemically inert, radiation resistance, low surface tension, no flash and fire point and also possess good dielectric properties. Because of these unique properties they find wide application in different industrial sectors such as Aerospace, Electronic, chemical, pharmaceutical, nuclear etc, as a lubricant, solvent, dielectric fluid and heat transfer fluid [1-8].

Mainly four types of perfluoropolyethers are commercially available and being synthesized from Tetrafluoropropylene (PFPE-Z), Hexafluoropropylene (Fomblin and Galden), Hexafluoropropylene oxide (Krytox) and tetrafluoroxyetane (Demnum) [9-22]. HFP based perfluoropolyethers have advantage over other perfluoropolyethers due to wide range of molecular weight distribution and can be used as a solvent, heat transfer fluid and lubricant.

HFP based Perfluoropolyethers were synthesized by photo-oxidation of HFP in the presence of oxygen by many researchers. Perfluoropolyethers with wide distribution of molecular weight were obtained. After distillation, low molecular weight perfluoropolyethers find application as a solvent, heat transfer fluid whereas medium molecular weight PFPE's can be used as a lubricant [10-11].

Generally perfluoropolyethers obtained by photooxidation of HFP contains low proportion of low molecular weight PFPE's (10- 15 % by wt) while low molecular weight PFPE's finds various applications in different industries as a heat transfer fluids, solvents and etchers because of its properties like dielectric, nonflammability, low thermal expansion, inertness and low surface tension [23].

Various methods are reported to synthesise HFP based low molecular weight perfluoropolyethers. Richard J lagow et al 1991 [24] obtained low molecular weight perfluoropolyethers by cracking of high molecular weight perfluoropolyether above 350 °C.

A lot of studies have been reported on the decomposition of High molecular weight perfluoropolyethers in presence of catalysts to decrease the cracking temperature. Catalysts used for cracking composed of fluorides, oxyfluorides or oxides of transition metals or lewis acids such as Al_2O_3 , $AlCl_3$, AlF_3 , TiO_2 etc at temperature between 230 to 280 °C. High molecular weight perfluoropolyethers were cracked and simultaneously distilled to get desired fraction of low molecular weight. An improved method of catalytic cracking for preparing low molecular weight perfluoropolyethers by using combination of silicon dioxide with oxide, fluoride and oxyfluoride of metal selected from Al, Ti, Cr, Co, Zn, Cu, Cd, Mn etc was also reported by Marchionni et al., 1991. Mechanism of catalytic thermal degradation of perfluoropolyethers was studied by many researchers by using TGA and NMR. [25-34].

Catalytic cracking methods to synthesis of low molecular weight PFPE's involves two steps, first step is the synthesis of high molecular weight perfluoropolyethers and the second step is cracking and distillation of synthesized high molecular weight PFPE's, which doesn't possess economic viability.

Therefore, the objective of the present paper is to develop a method to increase the proportion of low molecular weight perfluoropolyethers in order to avoid cracking or pyrolysis process hence making it more an economical viable for the industries.

Materials

Hexafluoropropylene (HFP) (Purity 99 %) was purchased from M/s Gujarat fluorochemicals limited, Gujarat. Oxygen was obtained from M/s Air products, Delhi. HPMV lamps of 125 W for UV source was purchased from Phillips, India. Quartz tube was fabricated by local manufacturer. Low temperature bath (room temperature to -80 °C) was purchased from M/s Southern scientific, Chennai.

Experimental Method:

Reactor of 1200 ml capacity was placed in to the low temperature bath to bring the reaction temperature at -30 °C. Isopropanol-2 was used as a cooling media in low temperature bath. Pressurizing and depressurizing of reactor was performed by oxygen and vacuum pump. 200 g of HFP was charged in to reactor and at the bottom of quartz tube, aluminum foil was placed. UV lamp was placed into the quartz tube. UV lamp was switched on and oxygen was introduced in to the reactor up to 1 bar (gauge pressure) simultaneously and circulated by diaphragm pump at the flow rate of 5 ltr/min throughout the reaction. Gases from outlet were continuously scrubbed by passing them through KOH bubbler to remove the acidic byproduct such as CF₂O. After completion of reaction intermediate acyl fluorides were obtained.

Result and Discussion

Photo-polymerization of hexafluoropropylene was performed by above mentioned method. In the second method level of liquid HFP was maintained just below the quartz tube and direct radiation to liquid HFP was avoided by placing aluminum foil at lower inner surface of quartz tube. UV radiation was only provided to oxygen and gaseous products throughout the reaction. Purpose of doing so was to create higher no of peroxides during the reaction so that chain transfer reaction can play a significance role to decrease the molecular weight of perfluoropolyethers. Higher the concentration of peroxides will be in reaction media, higher will be the chances of chain transfer reaction to occur. After 9 hrs of reaction, perfluoropolyethers with acyl fluoride end group were obtained. Yield was between 38-42 % (by weight of HFP) and viscosity was between 3-4 cSt which is very low. Acid value of product obtained was 350 mg/gm, resulted due to chain transfer reaction. Effect of reaction time on yield and viscosity was also studied. By increasing the time from 3 hrs to 12 hrs, yield increased from 15 to 42 % and viscosity increased from 0.8 cSt to 4 cSt (Figure. 2&3)

Effect of temperature variation was also studied on molecular weight of perfluoropolyethers, Reaction temperature was varied throughout the reaction. After 9 hrs of reaction product of 1.5 cSt viscosity was obtained which was lower than the product obtained, when the reaction temperature was kept constant at -60 °C. β-scissioning or the breakage of more peroxidic bonds can be reason behind the reduction of molecular weight of perfluoropolyether. Yield was around 44 % and acid value was around 600 mg/g which is higher than product obtained at constant temperature (Table.1). Peroxide value was similar to earlier method. By increasing the time from 3 hrs to 12 hrs yield increased from 12 to 44 % and viscosity increased from 0.8 cSt to 1.6 cSt (Figure. 1&2)

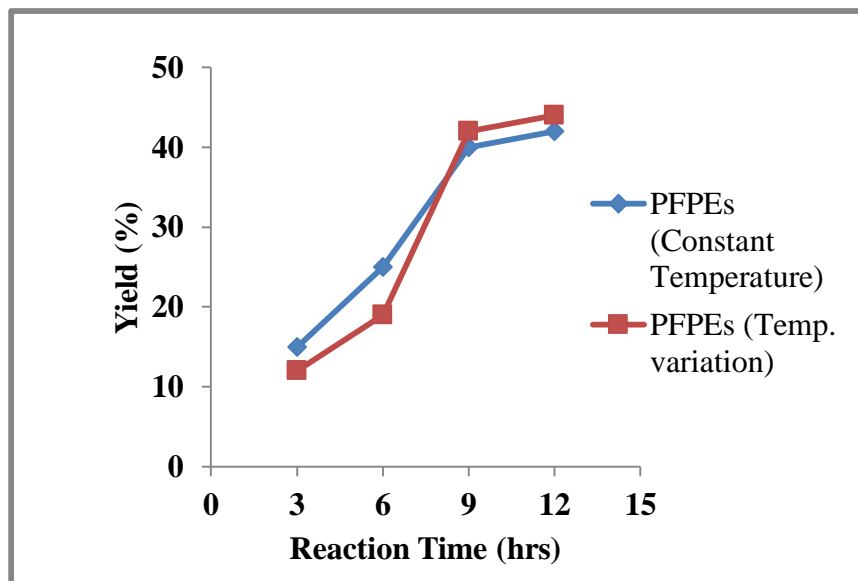


Figure.1 Effect of reaction time on Viscosity

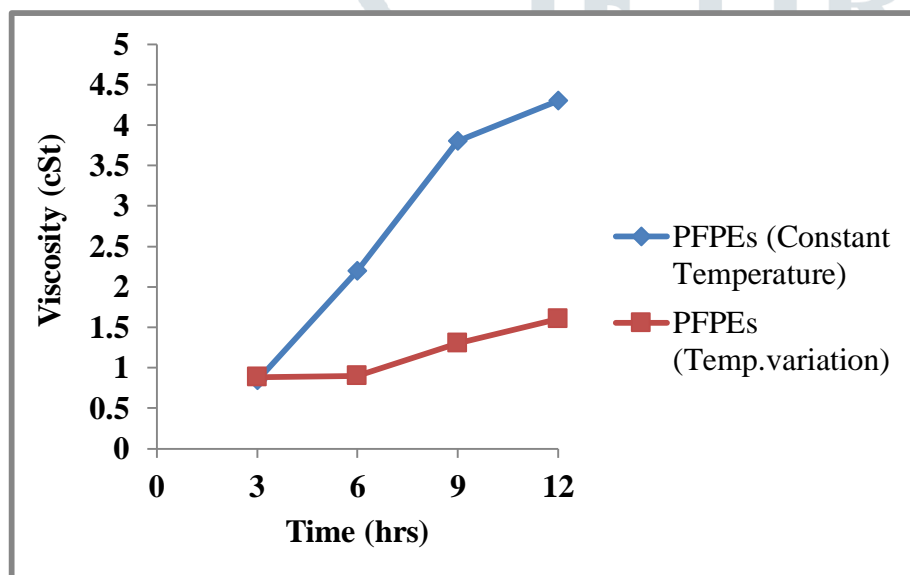


Figure.2 Effect of Reaction time on Yield

Table 1: Photooxidation of Liquid Hexafluoropropylene

Experiment	Method	
	Constant Temperature	Temperature variation
UV Source	125 W (HPMV)	125 W (HPMV)
Temperature (°C)	-50	-50 to -30
Reaction Time (hrs)	9	9
Pressure (bar)	1	1
Yield (%)	37-44	42-45
Viscosity (cSt) @ 20 °C	3.5-4.5	1.5-2
Density (g/ml)	1.78-1.8	1.74-1.76
Acid Value (mg/gm)	335-345	570-600
Peroxide Value (meq/kg)	90.5-95.3	90-98

Characterization

PFPEs obtained by photopolymerization of hexafluoropropylene were characterized by FT-IR for structural analysis and by TGA for thermal analysis.

TGA Analysis

Perfluoropolyethers with acyl fluoride end group were characterized by using thermogravimetric analyzer (NETZSCH STA model 449F3 Jupiter) to determine the amount or rate of weight change as a function of temperature over the time in an inert atmosphere. Heating rate was set at 10 °C/min and thermal loss was studied from room temperature to 600 °C. Figure 3 indicates that PFPEs obtained by temperature gradient method have higher proportion of low boiling products in compare to product obtained at constant temperature. PFPEs obtained at constant temperature showed the 50 % weight loss at 191 °C while PFPEs obtained by varying temperature showed 50 % weight loss at 100 °C which is much lower than product obtained at constant temperature. 75 % proportion of product obtained by temperature variation was below 130 °C which shows the higher proportion of low molecular weight of acyl fluorides in the product .

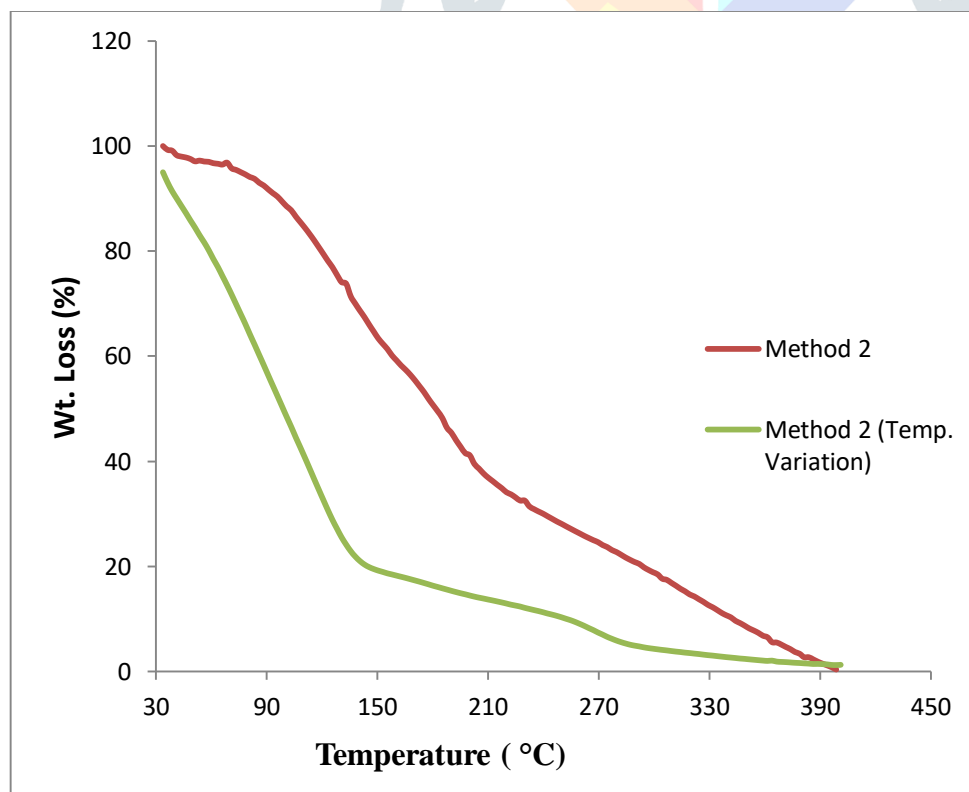


Figure 3: TGA analysis of Perfluoropolyethers

FT-IR Analysis

FT-IR spectra were recorded using IR Affinity-1S Shimadzu with scanning range of 4000-400 cm^{-1} and resolution of 4 cm^{-1} . Similar peaks observed in all the graphs of products obtained by above mentioned methods (Figure 4). Peak at 1894 cm^{-1} confirms the presence acyl fluorides at the end of chain and peak at 1780 cm^{-1} was observed due to presence of COOH group. Carboxylic groups formation can be due to the hydrolysis of COF group in presence of moisture. Broad spectrum from 1310-1080 cm^{-1} observed related to ether bond and CF stretching. Broad hump from 3500 to 2500 cm^{-1} in perfluoropolyethers obtained by method indicates the high reactivity towards moisture. (Figure 4)

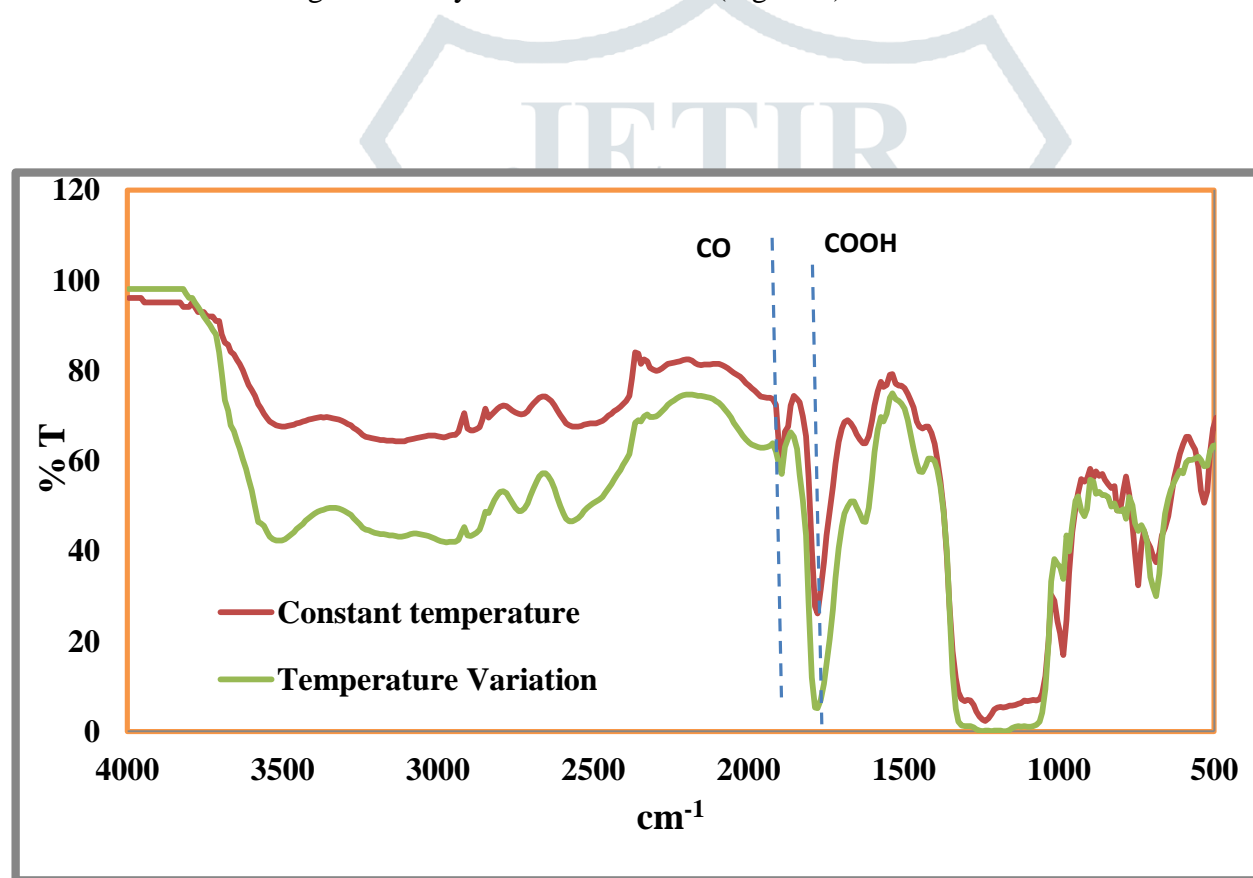


Figure.4 FT-IR analysis of perfluoropolyethers

Conclusion

Perfluoropolyethers with acyl fluoride end groups were synthesized by two methods. Low molecular weight perfluoropolyethers were obtained when direct UV radiation to HFP was avoided. Temperature variation caused further reduction in molecular weight and lower viscosity product was obtained. By generating more no of peroxy bonds in method 2, chain transfer and β scissioning reaction were promoted which resulted in higher no of CF_2O units in polymer chain and caused decrease in molecular weight of Perfluoropolyethers.

Acid value determination confirmed the higher no of chains in product obtained at temperature variation method in comparison to constant temperature method. Thermal analysis of PFPEs obtained by both the methods showed that weight loss was higher in product obtained by temperature variation method.

It can be concluded from present study that very low molecular weight Perfluoropolyethers with acyl fluoride end groups can be synthesized by avoiding direct UV exposure to liquid hexafluoropropylene and by varying temperature throughout the reaction.

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