제 1회
HOMRC 산학 클로퀴엄

2001. 6. 22

HOMRC

서울대학교
고차구조형 유기신연재료 연구센터

Preparation of Hexafluoropropylene Epoxide Using Phase Transfer Catalysis

이태환*, 김흥곤, 김훈식, 이희우*

한국과학기술연구원 환경공정연구부
*서강대학교 화학공학과

Hexafluoropropylene Oxide (HFPO)

- Raw material of fluorinated ion-exchange membrane such as Nafion®.
- Preparation of HFPO

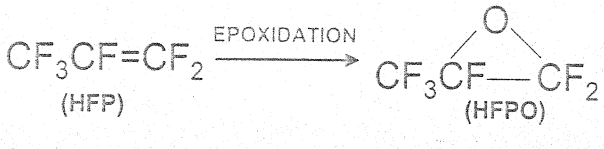
$HFP + O_2$

$HFP + NaOX$

$HFP + H_2O_2$

Electrochemical Oxidation

Objective

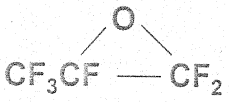


- Use of Hexafluoropropylene oxide(HFPO) as a comonomer appreciably enhances physical and chemical properties of fluoropolymers.
- HFPO is essential to the preparation of fluoritnated polyether which are the key material for manufacturing fluorinated ion-exchange membrane such as Nafion® and Flemion®.

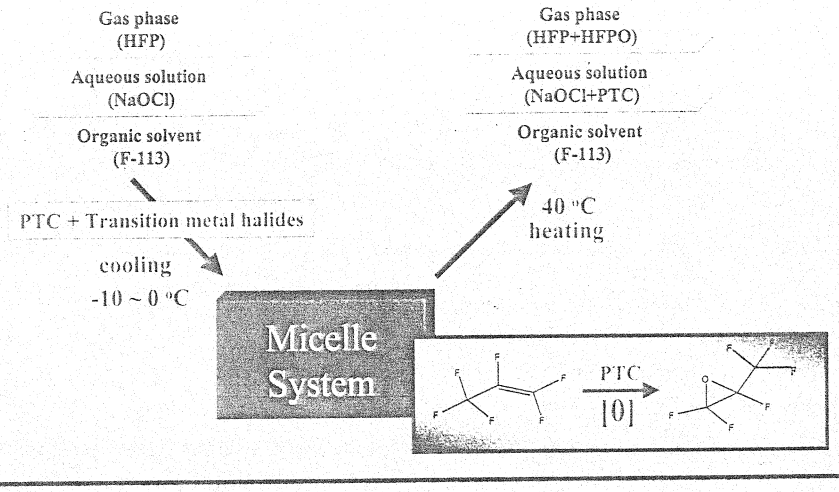
HFPO via Hypochlorite

- Hypochlorite regents
- Hexafluoropropylene
- Organic solvents
- Phase transfer catalyst
- Transition metal halides

Hexafluoropropylene oxide



Liquid-liquid phase



Mechanism of phase transfer catalysis

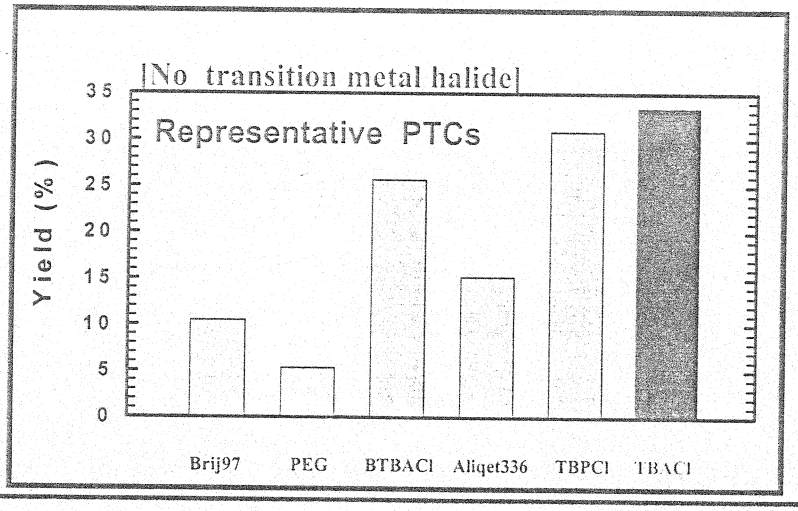
$$Q^+Y^- + R\text{-}X \quad \text{—} \quad Q^+X^- + R\text{-}Y \qquad \text{Organic phase}$$

Interface

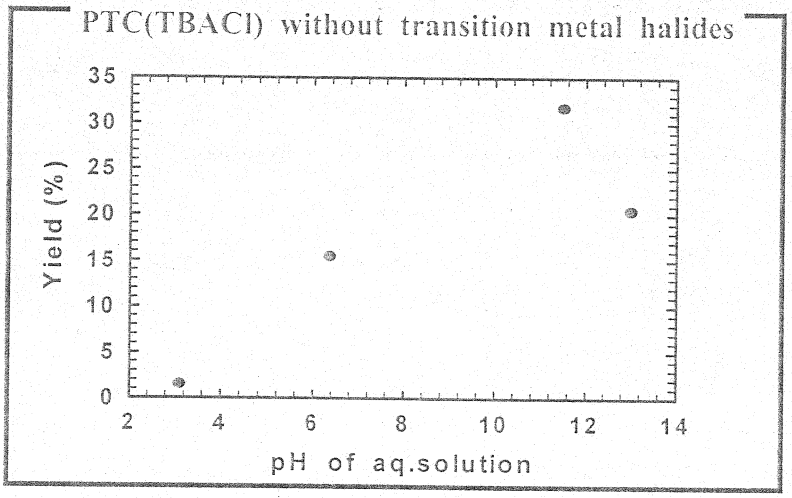
$$Q^+X^- + M^+Y^- \qquad Q^+Y^- + M^+X^- \qquad \text{Aqueous phase}$$

Q^+ : quaternary ammonium, phosphonium cation or crown ether- alkali metal cation
X^- : halide
M^+ : alkali metal Y^- : hypochlorite

Effect of PTC



Effect of pH



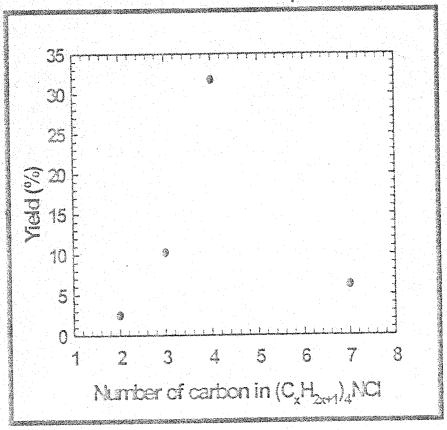
Effect of organic solvents

Organic solvents	Yield(%)
1,1,2-trichloro-1,2,2-trifluoroethane	31.77
1,1,1-trichloroethane	27.45
1,1,2-tetrachloroethylene	24.27
CCl_4	25.67
$CHCl_3$	20.24
CH_2Cl_2	14.25
methanol	10.25
toluene	5.86

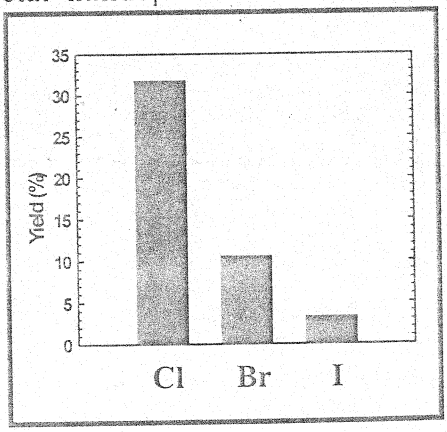
Only PTC(TBACl)

Effect of $(n\text{-}R)_4NX$

|No transition metal halide|



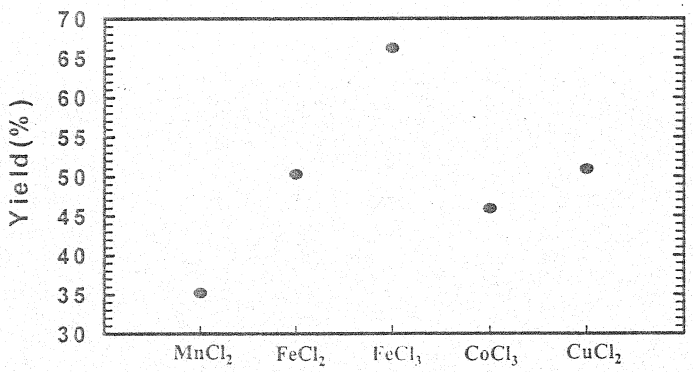
Effect of alkyl length $(n\text{-}R)_4NCl$



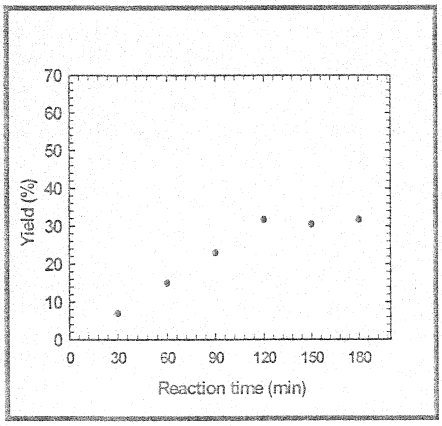
Effect of halides (X= Cl,Br,I)

Effect of transition metal halides

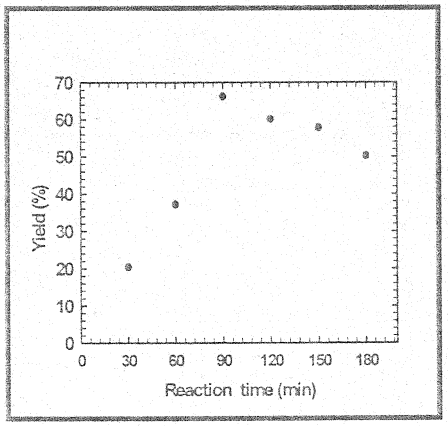
PTC(TBACl) + Transition metal halide



Effect of reaction time

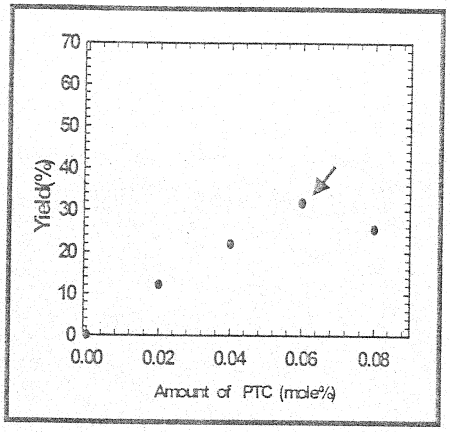


PTC Only

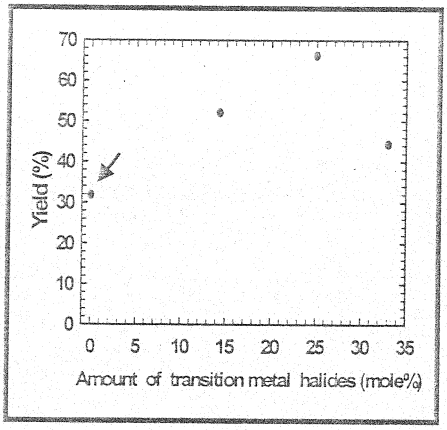


PTC + Transition metal halide($FeCl_3$)

Effect of PTC and transition metal halides



TBACl molar ratio to NaOCl



$FeCl_3$ molar ratio to TBACl

Conclusions

- HFPO was prepared by hypochlorite method.
- HFPO was sucessfully synthesized by liquid-phase epoxidation of hexafluoropropylene(HFP), which occurred at the interface between an aqueous hypochlorite and organic solvents.
- Addition of transition metal halides($FeCl_3$, $FeCl_2$, $CuCl_2$) increased yield and reaction rate of HFPO.
- Yield of HFPO changed with types and amounts of trransition metal halides as well as phase transfer catalysts.