CHAPTER 8

CATIONIC POLYMERIZATION

#### 8.1 INTRODUCTION

Cationic polymerizations are those in which the growing chain bears a positive charge. The active sites are either carbenium ions or oxonium ions. The monomers fitted for cationic polymerization include all those with electron donating substituents, in which the polarization of the double bond makes them sensitive to electrophilic attack by a carbenium site. Solvents used in cationic polymerizations should be stable towards acids and unable to react with electrophiles. Preferred are halogenated solvents (methylene chloride, methyl chloride, ethylene chloride, carbon tetrachloride), nitro compounds such as nitromethane or nitrobenzene, and also dioxane.

PST

#### 8.1.1 CATIONIC POLYMERIZATION OF VINYLIC MONOMERS

Cationic polymerizations are initiated by electrophilic agents such as the protonic acids (HCl,  $H_2SO_4$ , HClO<sub>4</sub>, etc.), lewis acids, which are electron acceptors by definition, and compounds capable of generating carbonium ions can also initiate polymerization. Examples of Lewis acids are AlCl<sub>3</sub>, SnCl<sub>4</sub>, BF<sub>3</sub>, TiCl<sub>4</sub>, AgClO<sub>4</sub>, and I<sub>2</sub>. Lewis acid initiators required a co-initiator such as  $H_2O$  or an organic halogen compound. Initiation by Lewis acids either requires or proceeds faster in the presence of either a proton donor (protogen) such as water, alcohol, and organic acids or a cation donor (cationogen) such as t-butyl chloride or triphenylmethyl fluoride. Actually, the protogen or cationogen is referred to as the initiator while the Lewis acid is the co-initiator, since the protogen or cationogen ultimately supplies the proton or cation that adds to monomer that initiates polymerization.

 $BF_3 + H_2O \leftrightarrow BF_3 \bullet OH_2$ 

$$BF_3 \bullet OH_2 + (C_6H_6) - CH = CH_2 \rightarrow (C_6H_6) - CH_2 - C^+ (BF_3OH)^-$$

The propagation reaction in the styrene/ $BF_3/H_2O$  system is through repeated addition of monomer.



Termination processes in these systems occur by transfer. For example, transfer of a proton to counterion, monomer, polymer, solvent, or some other added reagent can terminate the reaction. Transfer to counterion in the styrene/  $BF_3/H_2O$  system is illustrated by

Cationic Polymerisation of Heterocyclic Monomers



The initiators are the same as in cationic polymerization of vinylic monomers. The ring opening polymerization of several heterocyclic monomers proceeds by cationic initiation via oxonium sites that are formed upon alkylation (or protonation) of the monomer.

Protonation

$$BF_3 + H_2O + \bigcirc H^{\oplus}O$$
,  $BF_3^{\Theta}OH$ 

Acylation

$$R-CO^{\oplus}$$
,  $SbF_6^{\Theta}$  +  $\bigcirc O$   $\longrightarrow$   $R-CO-\Theta$ ,  $SbF_6^{\Theta}$ 

Alkylation

$$Et_3O^{\oplus}, BF_4^{\Theta} + \bigcirc^{O} \longrightarrow C_2H_5 - O^{\oplus} O$$
,  $BF_4^{\Theta} + Et_2O$ 

Hydrogen transfer



In general initiation step can be shown as,



The mechanism of chain growth involves nucleophilic attack of the oxygen of an incoming monomer onto a carbon atom in  $\alpha$  -position with respect to the oxonium site whereby the cycle opens and the site is reformed on the attacking unit,



Growing chain terminates with nucleophilic species as shown below.

$$\operatorname{matrix}_{\operatorname{H}} O_{-}(CH_2)_{4} \xrightarrow{+}_{1} O_{-}(CH_2)_{4} \xrightarrow{+}_{1} O_{+}(CH_2)_{4} \xrightarrow{+}_{1} O_$$

Triflic initiators like trifluoromethane sulfonic acid derivatives can also be employed as an initiator in the cationic polymerization of heterocyclics, in this case initiation step follows alkylation mechanism

$$CF_3 = SO_3CH_3 + \bigcirc O \longrightarrow CH_3 = O O, CF_3SO_3^{\Theta}$$

 $CH_3 \xrightarrow{\Theta} O$  + O  $\longrightarrow$   $CH_3 O(CH_2)_4 \xrightarrow{\Theta} O$ ,  $CF_3 SO_3^{\Theta}$  $CF_3 SO_3^{\Theta}$ 

lon pairs are in equilibrium with the ester form,

If instead of ester, triflic anhydride is used as initiator, the same reaction can occur at both chain ends and anhydride behaves as a bifunctional initiator.

In the case of living cationic polymerization, the growing sites are long living, provided the reaction medium does not contain any transfer agents such as alcohols, ethers, amines or acids. The reaction mechanism then involves only initiation and propagation steps and the polymers formed are living. The active sites are deactivated by addition of an adequate nucleophile, such as excess water, tertiary amines, alcoxides, phenolates or lithium bromide.

$$(CH_{2})_{4}^{-}O(CH_{2})_{4}^{-}OH + H^{\textcircled{0}}SbF_{6}^{\textcircled{0}}$$

$$+H_{2}O$$

$$+H_{2}O$$

$$+(CH_{2})_{4}^{-}O(CH_{2})_{4}^{-}O(CH_{2})_{4}^{-}NR_{3}SbF_{6}^{\textcircled{0}}$$

$$+(D-ONa)$$

$$SbF_{6}^{\textcircled{0}}$$

$$+LiBr$$

$$(CH_{2})_{4}^{-}O(CH_{2})_{4}^{-}O(CH_{2})_{4}^{-}O + NaSbF_{6}$$

## 8.2 **EXPERIMENTS**

### 8.2.1 LIVING CATIONIC POLYMERIZATION OF TETRAHYDROFURANE

Methyl trifluoromethane sulfonate (methyl triflate) or trifluoromethane sulfonic anhydride (triflic anhydride) has been described as initiators that lead, respectively, to monofunctional and bifunctional living PTHF with low polydispersity.



Living polymerization of THF is then terminated with a selected nucleophile to obtain functional polymers.

## 8.2.1.1 Materials Required

100-250 ml two-necked flask equipped with nitrogen inlet,

Syringe

Magnetic stirrer

Tetrahydrofurane (10 ml, purified and freshly distilled over sodium/benzophenone) Dichloromethane (purified)

Triflic anhydride (0.024 mol/l, 0.039 ml) or methyl triflate (0.024 mol/l, 0.026 ml) Methanol (100 ml)

Terminating agent like water, alcoxides, tertiary amines etc. (excess)

# 8.2.1.2 Experimental Procedure

Polymerization flask equipped with nitrogen inlet and a magnetic stirrer is flushed with dry nitrogen. Then 10 ml of freshly distilled THF is introduced with a syringe. The polymerization is started at room temperature by injecting 0.039 ml triflic anhydride (or 0.026 ml methyl triflate). After 30 minutes living polymerization of THF was terminated by adding an excess of a selected nucleophile (10x0.024 mol/l) and stirred additional 1 hr. Polymerization mixture was condensed in a rotary evaporated to remove unreacted THF and poured into a methanol and cooled down. Precipitated polymer was filtered off and dried in vacuum. % Conversion and the molecular weight of the polymer are determined.

# 8.2.2 LIVING CATIONIC POLYMERIZATION OF ISOBUTYLVINYL ETHER

Living polymerization of isobutylvinyl ether (IBVE) is initiated by the trifluoromethane sulfonic acid (triflic acid)/tetrahydrothiophene system.

# 8.2.2.1 Materials Required

100 ml two-necked flask equipped with nitrogen inlet Low temperature bath, Syringe Isobutylvinyl ether (1.3 ml, purified and distilled) Dichloromethane (4.4 ml, purified) Tetrahydrothiophene (0.22 ml, distilled) Triflic acid (0.25 mmol, 0.022 ml) Terminating agent like water, alcohol, alcoxides etc (2.5 mmol)

#### 8.2.2.2 Experimental Procedure

Polymerization flask equipped with nitrogen inlet and a magnetic stirrer is flushed with dry nitrogen. To this system 4.4 ml of freshly distilled  $CH_2Cl_2$ , 1.3 ml of IBVE and 0.22 ml of tetrahydrothiophene were injected under a nitrogen atmosphere. The solution was cooled down to  $-30^{\circ}C$  in a low temperature bath and 0.022 ml triflic acid was syringed into the system with stirring. The reaction was allowed to continue for 30 minutes. Then excess amount of a selected terminating agent is added, the cooling bath is removed and the system was allowed to warm up to room temperature. Stirring was continued for 1 hour then reaction mixture was evaporated in vacuo to give poly (IBVE). % Conversion and molecular weight of polymer is determined.

