

Polymerization of Tetrahydrofuran with New Transition Metal Catalyst and Its Mechanism: (*p*-Methylbenzyl)-*o*-cyanopyridinium Hexafluoroantimonate

Jun Won Kang and Yang-Kyoo Han*

Department of Chemistry, Hanyang University, Seoul 133-791, Korea

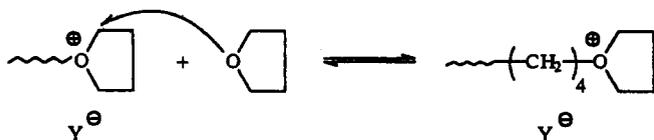
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(*p*-Methylbenzyl)-*o*-cyanopyridinium hexafluoroantimonate, a new catalyst, was synthesized by the reaction of *o*-cyanopyridine with α -bromo-*p*-xylene followed by exchange of counteranion with SbF_6^- . We examined the effect of the catalyst on the bulk polymerization of tetrahydrofuran under various conditions. The catalytic activity was best in the presence of 1 : 1 of epichlorohydrin used as cocatalyst versus catalyst concentration. The resulting polymers had relatively low conversions in 1.0-40%. Their number average molecular weights were in the range of 800 to 5300. Propagation rate increased with increase in temperature according to an Arrhenius expression giving an activation energy of 62 KJ/mol. We also found that the polymerization of THF with new catalyst proceeds *via* a cationic mechanism.

Introduction

Polytetrahydrofuran (polyTHF), well known as polytetramethylene glycol, is a very important soft segment for producing thermoplastic elastomers such as polyester (Hytrel[®]) and polyurethane (Spandex[®]).¹ THF reacts with cationic initiators to give polyTHF. Such reactions has been the subject of a number of papers²⁻⁴ since Meerwein reported trialkyloxonium salt as initiator.⁵

Polymerization of THF proceeds *via* a cationic mechanism, in which the propagating species is an oxonium ion that is ring-opened by nucleophilic attack of the additional THF monomer.



In the above scheme Y^- denotes the counter anions derived from the polymerization initiators. A counter anion of relatively low nucleophilicity, however, is required to achieve a controlled polymerization. Examples of anions are BF_4^- , PF_6^- , CF_3SO_3^- , FSO_3^- and so on.

On the other hand, only some limited catalyst systems such as FSO_3H , $\text{H}_2\text{SO}_4/\text{SO}_3$, $\text{HClO}_4/\text{acid anhydride}$, and ClSO_3H are used for industrial production of polyTHF of medium molecular weights (M_n : 600-3000) suitable for thermoplastic elastomers. The molecular weights depend on the concentration and the nature of catalyst and chain transfer agents like acid anhydride and SO_3 . But these catalyst systems also have several serious problems: One is higher concentration of catalyst is necessary for desired molecular weight polymers. The other is they require either alkaline or acid hydrolysis after polymerization to yield hydroxyl groups at both ends of the polymer and to produce relatively narrow molecular weight distribution (M_w/M_n) of below 2.0. Another is the hydrolysis reaction results in the production of large amounts of strong acids such as HF and sulfuric acid.^{6,7}

In order to overcome these disadvantages, we need to at-

tempt the study on new catalyst systems. Recently Pappas and Endo have reported latent thermal catalysts effective for the polymerization of epoxy resins, styrene, bicyclic ortho esters, and spiro ortho carbonates.⁸⁻¹⁰ They used various onium salts such as sulfonium, iodonium, phosphonium, or quaternary ammonium salt.¹¹

This paper describes the synthesis of new transition metal catalyst, a quaternary ammonium salt, and the catalytic activity for the bulk polymerization of THF under various conditions. We will also discuss its polymerization mechanism.

Experimental

Materials. Potassium hexafluoroantimonate, α -bromo-*p*-xylene (98%), and *o*-cyanopyridine (99%, OCP) were purchased from Aldrich Chemical Co. and used without purification for the synthesis of new initiator. Commercially available polymerization grade tetrahydrofuran (Shinwha Petrochemical Co. Ltd., Korea) was used as a monomer without purification. Epichlorohydrin was distilled after removal of water by usual methods and stocked over molecular sieves (4 Å). Pyridine was dried over CaH_2 for 24 h and distilled.

Synthesis of (*p*-methylbenzyl)-*o*-cyanopyridinium bromate salt. Into a 2-neck round bottom flask, α -bromo-*p*-xylene (14.95 g, 70.2 mmol) and OCP (8.53 g, 81.15 mmol) and acetonitrile (45 mL) were charged and stirred for 8 days at room temperature. After the reaction were completed, acetonitrile was evaporated and the residual solid was stirred for 12 h in diethyl ether (150 mL) to remove unreacted reactants. A greenish precipitate was filtered and dried under reduced pressure at 30 °C for 24 h: yield 18 g (78%); mp 168 ± 1 °C; $^1\text{H NMR}$ (D_2O) δ 9.21 (d, 1H, pyridine), 8.83 (t, 1H, pyridine), 8.73 (d, 1H, pyridine), 8.42 (t, 1H, pyridine), 7.43-7.39 (dd, 4H, phenyl), 6.12 (s, 2H, $-\text{CH}_2-$), 2.41 (s, 3H, $\text{ph}-\text{CH}_3$); IR (KBr) 3120, 3029, 2250 ($-\text{CN}$), 1614, 1489, 1434 cm^{-1} .

Synthesis of (*p*-methylbenzyl)-*o*-cyanopyridinium hexafluoroantimonate, new catalyst. The prepared pyridiniumbromate salt (1.0 g, 3.35 mmol) was dissolved in a distilled water (20 mL) and stirred for 2 h under nitrogen

atmosphere. Into the mixture, a solution of potassium hexafluoroantimonate (0.95 g, 3.45 mmol) in distilled water (20 mL) was added and stirred for 10 min. A white precipitate was collected and then dried *in vacuo* at 50 °C for 24 h: yield 40%; mp 136 ± 1 °C.

Polymerization of THF. A homogeneous mixture of THF (10 mL), initiator and/or cocatalyst in an one-neck round bottom flask equipped with a condenser was polymerized in a silicone oil bath. Polymerization was terminated with the addition of 1 N-HCl (1 mL) and then stirred for 10 min. The reaction mixture was extracted with benzene/distilled water (40 mL/120 mL). Anhydrous MgSO₄ (2 g) was added to the organic layer and stirred for 3 h to remove remaining water. The filtrate benzene solution was distilled off by using a rotary evaporator. The residual viscous polymer was dried under vacuum for 24 h at 30 °C. We carried out the polymerization varying concentration of catalyst, reaction time, temperature, and concentration of cocatalyst.

Measurement of viscosity. Inherent viscosity of polyTHF obtained was measured in benzene solution at 30 °C by using a Ubbelohde type viscometer. The number average molecular weight (M_n) was calculated by the following equation¹²:

$$[\eta] = 2.9 \times 10^{-4} M_n^{0.74}$$

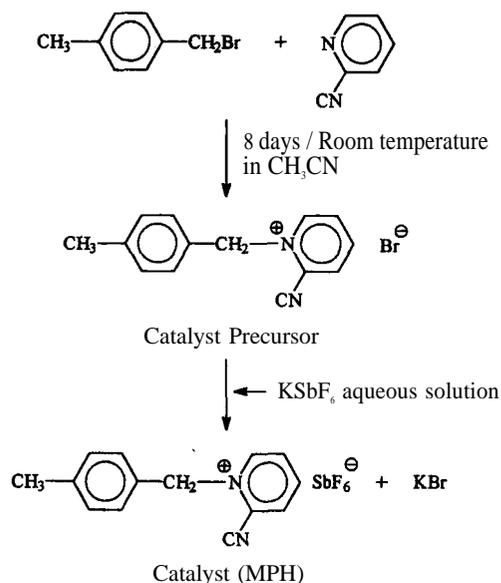
Hydrolysis of polyTHF. A mixture of the prepared polyTHF (0.61 g) and 1 N-HCl (60 mL) was refluxed for 12 h and cooled to room temperature. The solution was extracted with methylene chloride/distilled water (50 mL/50 mL) three times until pH was naturalized. The organic layer was dried over anhydrous MgSO₄ and then filtered. The filtrate solution was evaporated to remove methylene chloride solvent. The resulting viscous polymer was dried for 24 h under reduced pressure to give a waxy type poly(THF) having hydroxyl groups at both ends in 80% yield.

Characterizations. H-NMR spectra were recorded on a Varian Gemini-300 spectrometer. FT-IR spectra were obtained on a Bruker IFS 48 spectrometer. Thermal transition temperatures (T_g and T_m) were measured on a Perkin-Elmer 7 series DSC at a heating rate of 10 °C/min under nitrogen atmosphere. Molecular weight distributions were performed with a Shimadzu LC-4A GPC using Styragel columns with THF as solvent and polystyrene for calibration.

Results and Discussion

Synthesis of catalyst. (*p*-Methylbenzyl)-*o*-cyano-pyridinium hexafluoroantimonate (MPH), a new catalyst, was prepared by the reaction of *o*-cyano-pyridine with an equimolar amount of α -bromo-*p*-xylene followed by exchange of counteranion with SbF₆⁻ in water (Scheme 1).¹¹

We confirmed the structure of the catalyst by H-NMR and FT-IR spectra. In Figure 1-(a) characteristic peaks assignable to methyl, methylene in benzyl group, and phenyl group appeared at 2.4, 6.1, and 7.4 ppm, respectively. Four kinds of protons in pyridinium group were also observed at 9.2, 8.8, 8.7, and 8.4 ppm, respectively. Their integration ratio matched well as we expected. The IR spectrum of the catalyst showed weak bands around 3000 cm⁻¹ and several medium absorption in the 1614-1434 cm⁻¹ region, which are due to the aromatic and aliphatic C-H groups and to the



Scheme 1.

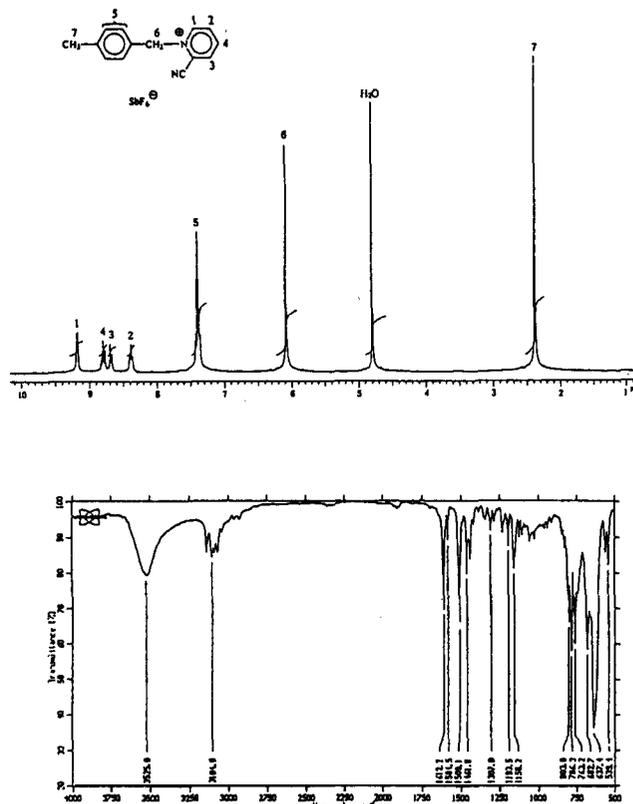


Figure 1. H-NMR (in D₂O) and FT-IR (KBr) spectra of catalyst.

pyridinium group. We also observed the strong peak due to the hexafluoroantimonate (SbF₆⁻) at 637 cm⁻¹. Especially, the catalyst was very hygroscopic, so that water absorbed from air appeared at 3525 cm⁻¹.

It, therefore, is essential to remove water (below 20 ppm) from the catalyst for polymerization.

Polymerization. In order to investigate the activity of the catalyst system, we carried out the bulk polymerization of THF changing concentration of catalyst, polymerization

time and temperature, and concentration of epichlorohydrin (EPH), cocatalyst. Their results are listed in Table 1.

The prepared polyTHF had relatively low conversion to polymer in the range of 1.0-40%. Its number average molecular weight ranged from 800 to 5300 and increased with increase in conversion. The resulting polymers had fairly narrow molecular weight distribution (M_w/M_n) ranging from 1.4 to 1.6. It has a great advantage in industrial point of view, since commercial polyTHF being used as a soft segment for thermoplastic elastomer requires another fractionation process after polymerization in order to prepare the polymer with narrow molecular weight distribution of below 2.0. The melting range of the synthesized polyTHF was 17 °C ($M_n=830$) to 42 °C ($M_n=5210$). These results are consistent well with those of commercial products (Dupont Terathane[®]).¹

Hydrolysis of polyTHF with 1 N-HCl solution readily provides hydroxyl groups at both ends of the polymer chain. Hydroxyl number was determined by end group analysis, by reaction with acetic anhydride and by back-titration with 1 N-NaOH (ASTM D-1638). The measured hydroxyl values are comparable to those of commercial product.¹ In case of $M_n=1980$, the value was about 50.

Effect of polymerization temperature. Figure 2 showed a trend that molecular weight and conversion increased with increase in polymerization temperature from 30 to 55 °C, but drastically decreased above 55 °C. This is due to the equilibrium polymerization of THF and also to the low ceiling temperature ($T_c=83 \pm 2$ °C) in bulk polymerization: At T_c or above no polymer is formed. Below T_c , there is an equilibrium monomer concentration below which no further polymerization occurs.³

Thus to obtain significant conversions to polymer and desirable molecular weight, we carried out the polymerization at either 45 °C or 55 °C under various conditions. We figured out the activation energy (E_a) for the bulk po-

lymerization of THF with our catalyst system (MPH-EPH) using an Arrhenius expression and a least square method. E_a from a slope in Figure 3 was 62 kJ/mol.

Effect of polymerization time. The effect of polymerization time on the molecular weight and the conversion of polyTHF is shown in Table 1 (Exp. # 2 and 3). We obtained higher molecular weights and conversions at 55 °C than at 45 °C. They, however, decreased rapidly after two days at all the both temperatures. It is probably due to the reason why depolymerization of polyTHF predominates over propagation reaction in the following equilibrium polymerization of THF. Thus we tried the polymerization

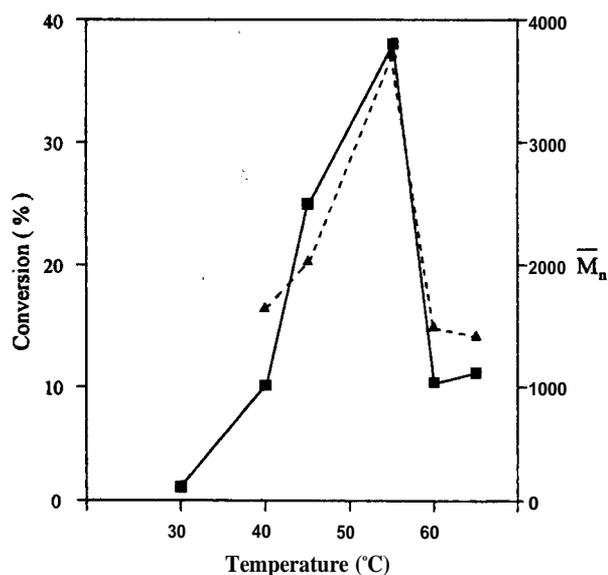


Figure 2. Effect of polymerization temperature on conversion (■) and M_n (▲): [Catalyst]=1.0 mol%; [EPH]=1.0 mol%; time, 2 days.

Table 1. Polymerization of THF with new catalyst system

| EXP. # | Catalyst (mol %) | EPH ^a (mol) | Temp. (°C) | Time (day) | Conv. (%) | M_n | T_m^b (°C) |
|--------|------------------|------------------------|------------|------------|-----------|-------|--------------|
| 1 | 1.0 | 1.0 | 30 | 2 | 0.5 | - | |
| | 1.0 | 1.0 | 40 | 2 | 2.6 | 1650 | |
| | 1.0 | 1.0 | 45 | 2 | 25.0 | 1980 | 26 |
| | 1.0 | 1.0 | 55 | 2 | 37.9 | 3890 | 32 |
| | 1.0 | 1.0 | 60 | 2 | 10.4 | 1590 | |
| | 1.0 | 1.0 | 65 | 2 | 10.7 | 1380 | |
| 2 | 1.0 | 1.0 | 45 | 1 | 0.8 | - | |
| | 1.0 | 1.0 | 45 | 2 | 25.0 | 1980 | |
| | 1.0 | 1.0 | 45 | 3 | 2.3 | 1500 | 25 |
| 3 | 1.0 | 1.0 | 55 | 1 | 12.1 | 1150 | |
| | 1.0 | 1.0 | 55 | 2 | 37.9 | 3890 | |
| | 1.0 | 1.0 | 55 | 3 | 10.4 | 1290 | |
| 4 | 1.0 | 0 | 55 | 2 | 0.9 | - | |
| | 1.0 | 0.5 | 55 | 2 | 4.7 | 830 | 17 |
| | 1.0 | 1.0 | 55 | 2 | 37.9 | 3890 | |
| 5 | 1.0 | 2.0 | 55 | 2 | 8.2 | 1520 | |
| | 0.25 | 0.25 | 45 | 2 | 11.6 | 5210 | 42 |
| | 1.0 | 1.0 | 45 | 2 | 25.0 | 1980 | |
| | 2.0 | 2.0 | 45 | 2 | 35.1 | 1050 | 21 |

^aEPH; epichlorohydrin. ^bMeasured after hydrolysis.

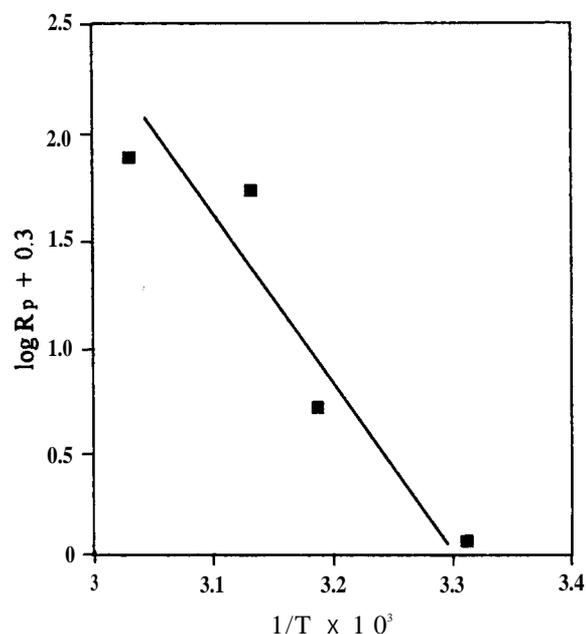
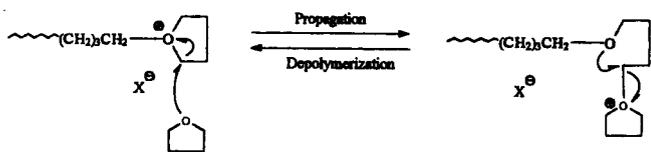


Figure 3. Logarithmic plot of rate of polymerization versus temperature.

time for 2 days in further experiments.

Effect of concentration of cocatalyst. In case we



proceeded the polymerization only with 1.0 mol% of the catalyst without cocatalyst (EPH), little polymerization occurred. Effect of concentration of cocatalyst on molecular weight and conversion was best, when the mole ratio of cocatalyst to catalyst was 1.0 (Figure 4). On the contrary, the activity of the cocatalyst drastically decreased in the presence of over 1.0. This will be described in more detail in polymerization mechanism later.

Effect of concentration of catalyst system. In polymerization with 1 : 1 of the ratio of catalyst to EPH, the conversion of polymer increased with increase in the concentration of catalyst system, whereas the molecular weight decreased gradually (Exp. # 5 in Table 1).

Polymerization Mechanism. Based on the results discussed so far, we propose a possible mechanism of the cationic polymerization with new catalyst (MPH), as shown in Scheme 2 and 3.

In Scheme 2 MPH salt dissociates by heating and reaches an equilibrium between *p*-xylene cation and OCP. The cation (II) stabilized by a resonance effect of benzyl group and the pyridinium cation (I) destabilized on pyridine shift the equilibrium to the forward reaction (k_1). Moreover, the cyano group in OCP causes a steric hindrance of MPH salt (I) and enhances the cleavage of the C-N bond. The resulting *p*-xylene cation (II) acts as an initiating species in the polymerization of THF. In other words, the cation (II) reacts with THF to produce the THF oxonium ion salt (IV), which propagates additional THF monomer to give a poly-THF. However, the propagation with the oxonium ion (IV) gives rise to very low conversion and molecular weight *via* a path 1 in Scheme 3. This is the reason why the cation salt

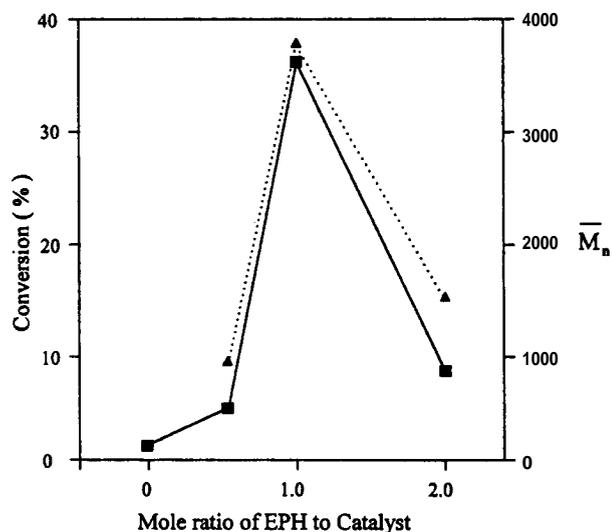
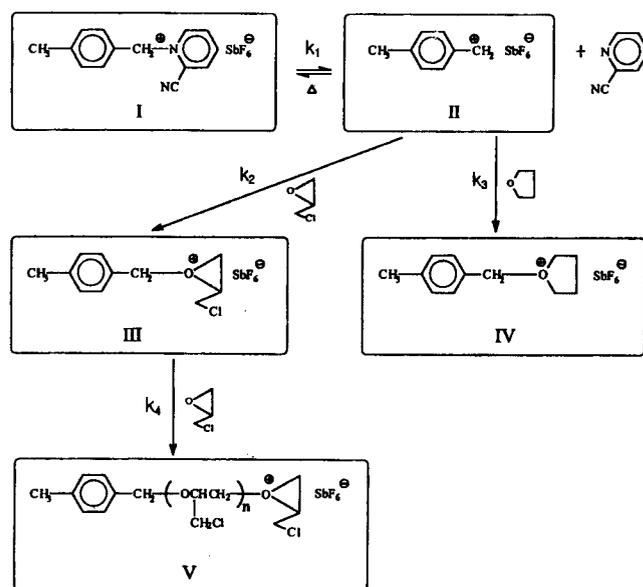


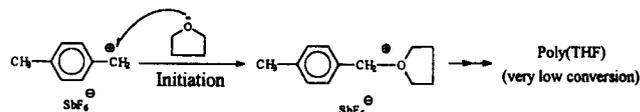
Figure 4. Effect of concentration of EPH on conversion (■) and \bar{M}_n (▲): [Catalyst]=1.0 mol%; time, 2 days; temperature, 55 °C.

(II) is much more stable than the THF oxonium ion salt (IV) and little polymerization occurs. On the other hand, when EPH is present as a cocatalyst, the reaction of the cation (II)

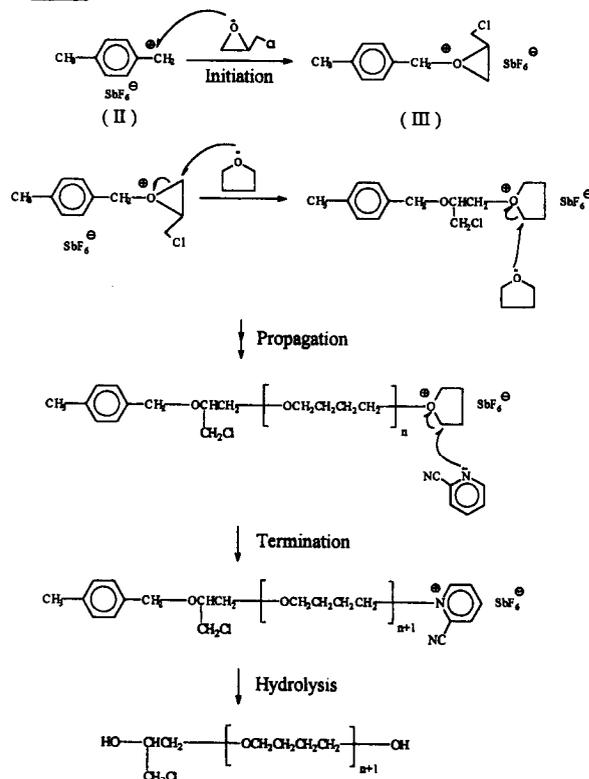


Scheme 2.

Path 1



Path 2



Scheme 3.

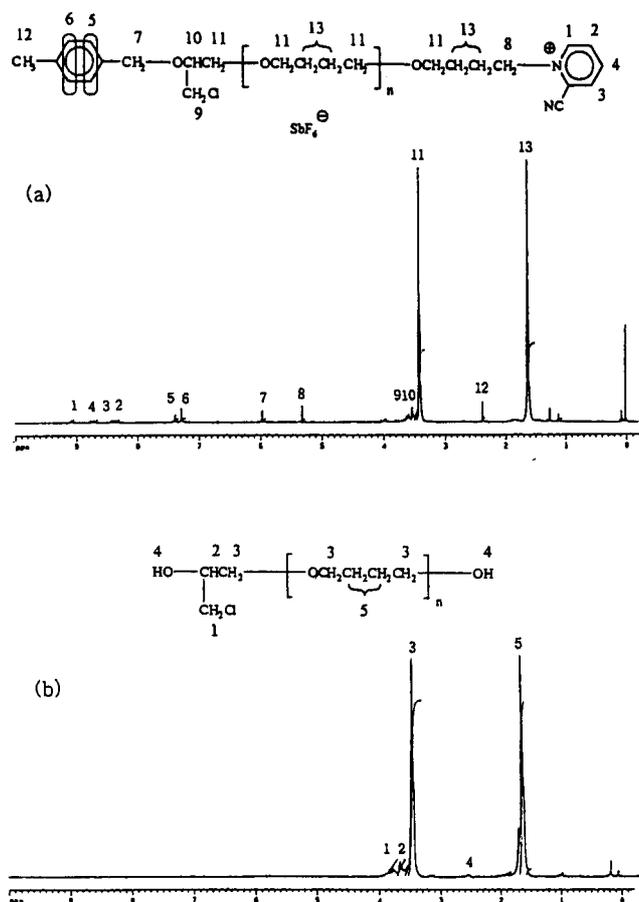


Figure 5. NMR spectra of Poly(THF) (M_n : 3890) in $CDCl_3$: (a) before hydrolysis; (b) after hydrolysis.

with oxirane ring of EPH produces new oxonium ion salt (III) shown in Scheme 2. It initiates THF monomer and then propagates to yield medium molecular weight polymers ($M_n=800-5300$) we expected *via* a path 2 in Scheme 3. Effect of concentration of cocatalyst discussed earlier supports these results. In addition, when the concentration of cocatalyst (EPH) is more excess than that of catalyst, the cation (III) propagates remaining EPH to produce oligomers (V), as shown in Scheme 2. Such a side reaction results in the decrease of molecular weight and conversion in the polymerization of THF (Exp. # 4 in Table 1).

In the termination step, the liberated pyridine from the catalyst attacks the THF oxonium ion in the growing chain end to terminate the polymerization of THF (Scheme 3). The chain end groups terminated with pyridinium salt readily converts into hydroxyl groups by the addition of 1N-HCl solution. Spectroscopic data from H-NMR and FT-IR strongly supports the proposed termination mechanism: H-NMR spectrum of polyTHF before hydrolysis showed weak *o*-cyano-pyridine and *p*-xylene groups, resulting from the termination step (Figure 5-a). They, however, disappeared after hydrolysis (Figure 5-b). In Figure 6-a, aromatic C-H in *p*-xylene, *o*-cyano-pyridine, and hexafluoroantimonate (SbF_6^-) absorption bands appeared around 3100, 1614, and 635 cm^{-1} , respectively. They also disappeared after hydrolysis (Figure 6-b). The IR spectrum of polyTHF after hydrolysis was consistent with that of commercially available product from

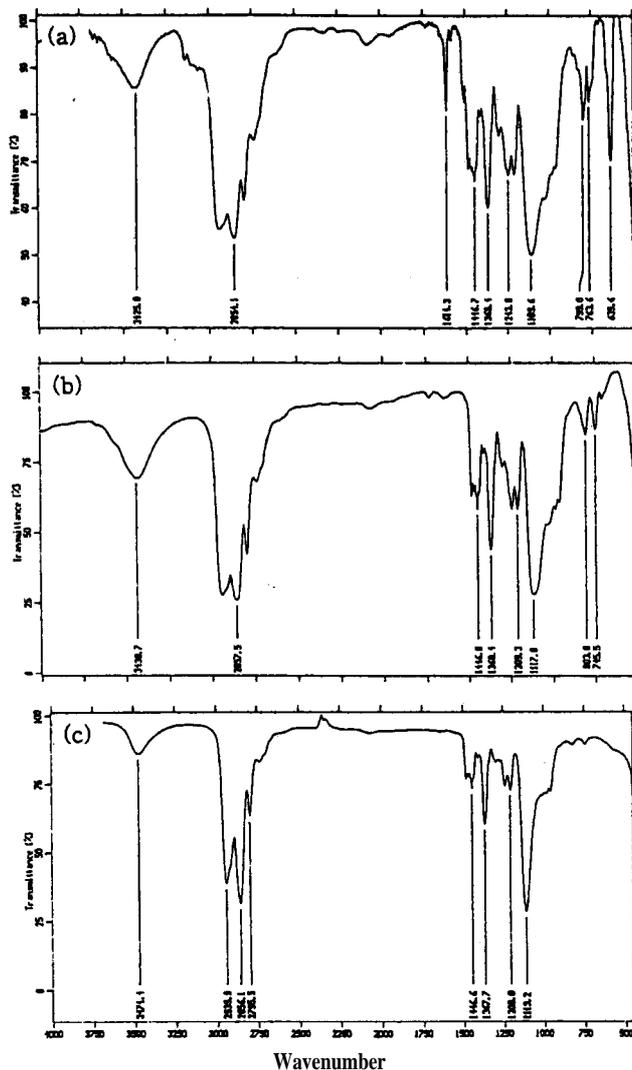


Figure 6. IR spectra of Poly(THF): (a) before hydrolysis; (b) after hydrolysis; (c) BASF product.

BASF Chemical company.

Conclusion. Synthesis of new catalyst was achieved by a nucleophilic substitution between *o*-cyano-pyridine and α -bromo-*p*-xylene followed by exchange of counteranion with SbF_6^- in water. The catalyst was very effective for the polymerization of THF in the presence of EPH as cocatalyst. The number average molecular weight of the obtained polymers was in the range of 800 to 5300 and they had relatively narrow molecular weight distribution ranging from 1.4 to 1.6. We also found that the polymerization of THF with new catalyst proceeds *via* a cationic mechanism. On the basis of above results, the catalyst system shows a strong potential as new initiator for preparing polyTHF suitable as a soft segment for thermoplastic elastomers.

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