COORDINATION POLYMERIZATION OF CYCLIC ETHERS BY METAL XANTHATES AND CARBAMATES

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ABSTRACT

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Zinc xanthates are active catalysts in stereoregular polymerization of propylene oxide. They are markedly more stable than that of known classical stereoregular catalysts in this field. But the steric control of zinc xanthates is weaker. With the purpose of finding more effective catalyst systems the xanthates of Cu, Pb, Ni, Fe, Al and Sn are investigated. Among these only copper isopropyl xanthate (Cu(isoPr)Xt) and tin isopropyl xanthate (Sn(isoPr)Xt) were appeared to be active, but Cu(isoPr)Xt yielded only low molecular weight product. Therefore Sn(isoPr)Xt system was investigated in detail in polymerization of propylene oxide (PO). Polymerization of PO with this catalyst produced two contrasting polymers, through out the process. High molar mass, crystalline (K-polymer) and low molar mass (D-polymer**).** D-polymers had both hydroxyl and double bond terminals. Formation of double bonds was thought to be due to as an anionic process. Polymerization reactions were studied keeping composition of polymerization mixture constant, but varying the polymerization time, keeping polymerization time but changing catalyst concentration, changing reaction temperature and reacting catalyst with predetermined amount of water. It's found that Sn(isoPr)Xt have considerably low efficiency than that of Zn(isoPr)Xt catalyst (about 6000 times smaller). The yield linearly increases by increasing catalyst concentration. The propagation is competed by a termination or transfer process hence overall activation energy is negative. On the bases of these experimental data some mechanistic features of this system was discussed.

The catalytical activity of carbamates in this field has also been reported, without any information about catalytical efficiency and stereoregularity of the process. For this reason zinc diethyl dithiocarbamate was also studied and found as an active catalyst in stereoregular polymerization but it showed weaker efficiency in the PO polymerization than that of Zn(isoPr)Xt catalyst (about 12 times weaker).

Keywords: Copper isopropyl xanthate, tin isopropyl xanthate, zinc diethyl dithiocarbamate, crystalline-polymer, amorphous-polymer, propylene oxide.

ÖZ

HALKASAL ETERLERİN METAL KSENTATLAR VE KARBAMATLARLA KOORDİNASYON POLİMERLEŞMESİ

Taş, Hüseyin

Yüksek Lisans, Polimer Bilimi ve Teknolojisi Bölümü
Tez Yöneticisi: Prof. Dr. Kemal Alyürük

Eylül 2003, 64 sayfa

Çinko ksentatlar propilen oksitin stereoregüler polimerizasyonunda aktif katalizörlerdir. Bu alanda bilinen klasik stereospesifik katalizörlerden daha kararlıdırlar. Ancak çinko ksentatların polimerleşmelerdeki sterik kontrolleri düşüktür. Bu araştırmada daha etkin katalizör sistemleri bulmak amacı ile Cu, Pb, Ni, Al ve Sn ksentatlar incelendi. Bunların arasında sadece bakır izopropil ksentat ve kalay izopropil ksentatın aktif olduğu gözlendi, ancak bakır izopropil ksentat düşük moleküler ağırlıklı ürün verdi. Bu nedenle propilen oksitin polimerizasyonunda kalay izopropil ksentat sistemi detaylı olarak incelendi. Bu katalizör kullanılarak polimerleştirilen propilen oksit, yüksek molar kütleli, kristallenebilen K-polimer ve düşük molar kütleli D-polimer ürünlerini birarada verdi. D-polimerin hem hidroksil hem de çifte bağ uç grupları içerdiği gözlendi. Çift bağ oluşumu anyonik mekanizma varlığı şeklinde yorumlandı. Polimerizasyon tepkimeleri; polimerleşme karışımının bileşimi sabit tutulup polimerleşme zamanı değiştirilerek, polimerizasyon zamanı sabit tutulup katalizör derişimi ve tepkime sıcaklığı değiştirilerek ve daha önceden belirlenen miktarda su ile tepkimeye girmiş katalizör kullanılarak incelendi. Kalay izopropil ksentatın çinko izopropil ksentata göre çok düşük etkinliğe sahip olduğu saptandı (yaklaşık 6000 kez düşük). Katalizör derişimi arttıkça yüzde verimin de doğrusal olarak arttığı gözlendi. Toplam aktivasyon enerjisinin negatif olması büyümenin sonlanma ya da transfer reaksiyonu ile yarıştığı şeklinde yorumlandı. Yapılan bu deneylerin sonuçlarına bağlı olarak bu sistemin mekanizması tartışıldı.

Karbamatların da bu alanda katalitik etkinlikleri rapor edildiği halde stereospesifik özellikleri ile ilgili bir kayıt yoktur. Bu nedenle bu çalışmada çinko dietil ditiokarbamat da kullanıldı ve propilen oksitin stereoregüler polimerizasyonunda aktif olduğu gözlendi. Ancak çinko izopropil ksentat katalizöründen daha zayıf (12 kez) etkinliği olduğu saptandı.

Anahtar Sözcükler: Bakır izopropil ksentat, kalay izopropil ksentat, çinko dietil ditiokarbamat, kristal-polimer, amorf-polimer, propilen oksit.

To my FATHER and ELDER BROTHER,

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CHAPTER I

INTRODUCTION

The earliest report on epoxides polymerization was the work of Wurtz in 1859 where ethylene oxide was polymerized through a Lewis base [1]. The fundamental studies on epoxides polymerization began in 1930's with the work of Staudinger [2]. However, only low molecular weight polymers of epoxides were known to any great extent before 1950. Pruitt and Baggett first disclosed the preparation of high molecular weight polypropylene oxide with a stereospecific catalyst in a patent in 1955 [3]. Their catalyst was the reaction product of ferric chloride and propylene oxide. The initial studies on this system were subsequently published by Price and his co-workers [4,5]. A few years later, various types of catalysts for stereospecific polymerization of epoxides were found and developed by a number of researchers. These catalysts included: aluminum isopropoxide-zinc chloride by Price et al. [6], zinc alkyl-water and zinc-alcohol by Furukawa [7] and aluminum alkyl-water-acetylacetone by Vandenberg [8].

1.1. Stereoregular Polymers

Stereoregular polymers constitute a large class of macromolecular compound that are endowed with many interesting and valuable properties. A large part of the properties that possess by these polymers are determined by their steric regularity. Wislicenus recognized the essential role of stereochemistry in determining the physical and chemical properties of a chemical compound more than one hundred years ago [9]. However, the fundamental studies on the influence of stereoregularity on the physical and chemical properties of polymers started only in the 1940s. A great impute to the development in this field was given by the first synthesis of a highly stereoregular polypropylene by Natta and his group in 1955 [10]. From this development it clearly emerged that stereochemistry has a strong influence on the reactivity, the conformational equilibria and many other properties of polymers in dilute solution and in the melt. The stereochemistry of a regular polymer determines the type of crystal structure and the degree of crystallinity, and thus determines the properties of this polymer in the solid state. Therefore, it is not surprising that in some cases even the success of the industrial application of a polymeric product may be determined by the stereochemistry of this polymer.

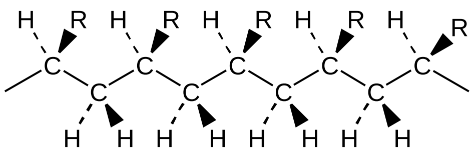
The definition of a stereoregular polymer was given by the IUPAC commission on macromolecular nomenclature [11] as “a regular polymer whose molecules can be described by only one species of stereo-repeating unit in a sequential arrangement”. A stereo-repeating unit is further defined as “a configurational repeating unit having defined configuration that all sites of stereoisomerism in the main chain of a polymer molecule”.

The concept of stereoregularity is most important in polymers with mono or asymmetrically disubstituted carbon atoms on the polymer backbone. These substituents create sites of asymmetry in the polymer chains. The regularity with which successive asymmetric centers show the same configurations determines the overall stereoregularity of the polymer chain.

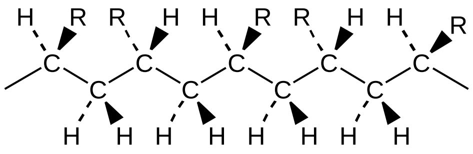
There are three possible stereochemical arrangements for a substituted polymer chain.

(i) If each asymmetric carbon has the same configuration, it is called isotactic chain.
(ii) If successive asymmetric centers have the opposite configuration the chain is in syndiotactic structure.

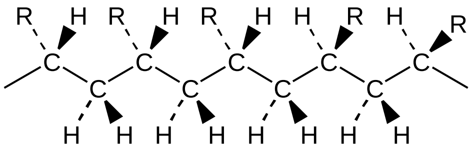
(iii) If the configuration of carbons is completely random the polymer is called as atactic chain polymer.



i) isotactic polymers



ii) syndiotactic polymers



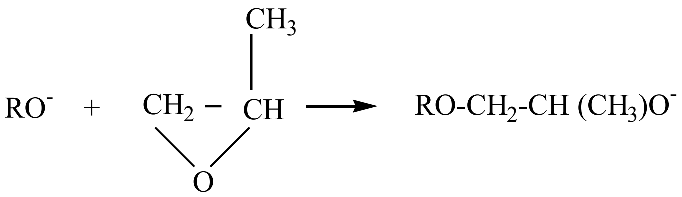
iii) atactic polymer

The definition of stereoregularity given by the IUPAC commission refers to ideal structure but may be applied to practical cases when deviation from ideality is not too large. A polymer, which contains a significant amount of steric irregularity, is usually considered as " partially stereoregular ".

1.2. Polymerization of Epoxides

1.2.1. Simple Anionic Polymerization

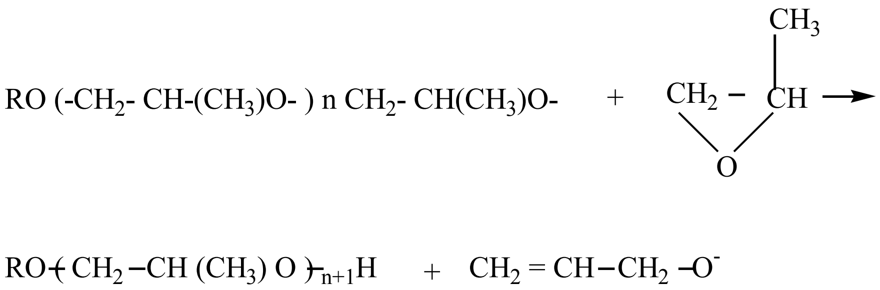
The anionic polymerization of epoxides can be initiated by nucleophiles such as alkali metal hydroxides and alkoxides [12-14]:



For most epoxides containing one substituent (as propylene oxide), the attack of the nucleophile on the primary carbon is favored. Ring opening at the primary carbon-oxygen, almost exclusively, in an anionic polymerization was indicated by the formation of a crystalline, optically active polymer in the polymerization of l-propylene oxide with potassium hydroxide [15].

The use of nucleophilic initiators for propylene oxide polymerization yields a relatively low molecular weight (5.000-10.000 g/mol), viscous polymers containing unsaturated end groups.

There is no kinetic termination reaction in the anionic polymerization of PO, but the chain length is limited by a proton transfer reaction with solvent or monomer. In the case of transfer to monomer, the growing end abstracts a proton from the methyl group of the monomer by forming an allyl oxide ion [16,17], where the formed allyl oxide ion is also a strong nucleophile and can initiate a new chain.



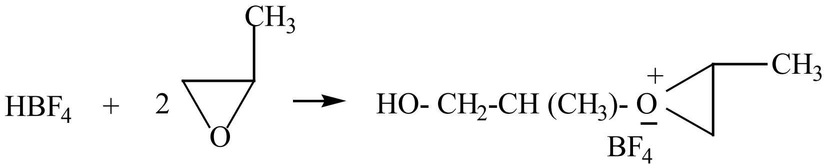
$$RO\,(-CH_2-CH-(CH_3)O-)\,n\,CH_2-CH(CH_3)O^- + \underset{\diagdown O \diagup}{CH_2-\overset{CH_3}{\overset{|}{C}H}} \longrightarrow$$

$$RO\!\left(CH_2-CH\,(CH_3)\,O\right)_{n+1}H + CH_2=CH-CH_2-O^-$$

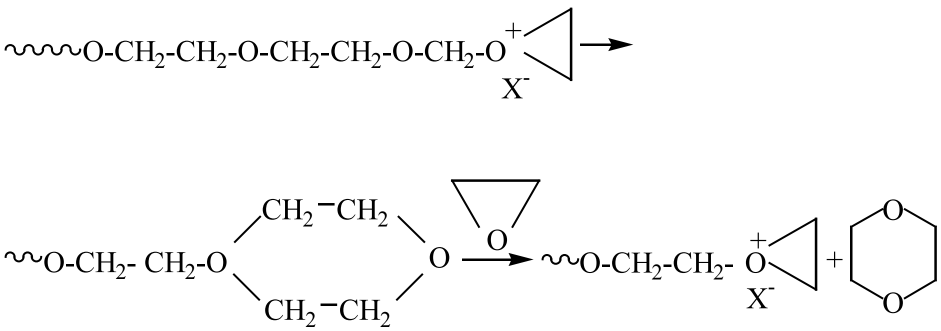
Transfer to solvent is especially important when the initiator is an alkoxide ion, since an alcohol is usually used as a solvent. In this case the growing end abstracts the hydroxylic proton of the alcohol.

1.2.2. Simple Cationic Polymerization

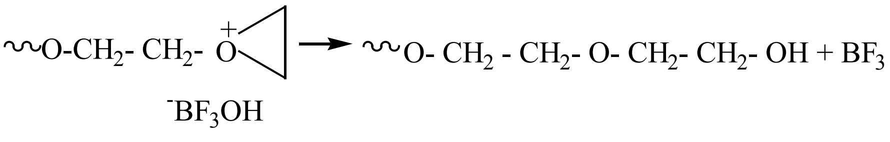
The cationic, ring-opening reactions of all cyclic ether monomers are believed to involve the formation and the reaction of oxonium compound [18], the oxonium ion is formed by the reaction of Friedel-Crafts type catalyst as HBF_4, HBF_3OH, HSbCl or $SnCl_4$ with the monomer [12-14]:



Since the polyether chains contain oxygen atoms in their backbone, these atoms have the capability of oxonium ion formation. The growing end of the polymer chain may “bite back” to form an oxonium ion with an oxygen in the polymer chain which is already formed. This process leads to the formation of cyclic products, which one of the characteristics of the cationic polymerizations of epoxides.



As a result of cyclization, the molecular weights of the polymers obtained by cationic polymerization cannot grow above a limiting value (4000-10000 g/mol). Termination occurs by combination of the propagating oxonium ion with either the gegen-ion or, more likely with an anionic fragment from the gegen-ion.



1.2.3. Stereospecific Polymerization of Epoxides

Pruitt and Baggett published the first report on the stereospecific polymerizations of epoxides in 1955 [3]. Few years later it was found that a number of organometallic compounds could also polymerize epoxides to stereoregular polymers [19-20]. It was also recognized that some modifiers are necessary to have an active catalyst. Some reagents were reported as effective modifiers as water, oxygen [21], hydrogen sulfide [22], alcohols [7,23], and amines [24]. The most studied stereospecific catalysts are iron-propylene oxide-water, alkyl zinc-water and alkyl aluminum-water systems.

The function of the modifiers is to react with the organometallic compound to form a new catalytic species, which are active in the stereospecific polymerization. The most widely used modifier is water. It reacts with the organometallic compounds to yield a metal-hydroxide as an intermediate product:

$$R_XM + H_2O \longrightarrow R_{X-1}MOH + RH$$

The intermediate is not stable and may undergo either a self-condensation reaction or reacts with another organometallic species to give a metal-oxygen-metal bond.

$$2R_{X-1}MOH \longrightarrow R_{X-1}M-O-R_{X-2}OH + RH$$

or

$$R_{X-1}MOH + R_XM \longrightarrow R_{X-1}M-O-MR_{X-1} + RH$$

The reaction of metal hydroxides with the organometallic compounds may continue to form a polymeric product with a metal-oxygen-metal linkage. The formation of the degree of the polymerization depends on the nature of the used organometallic compound and the reaction conditions.

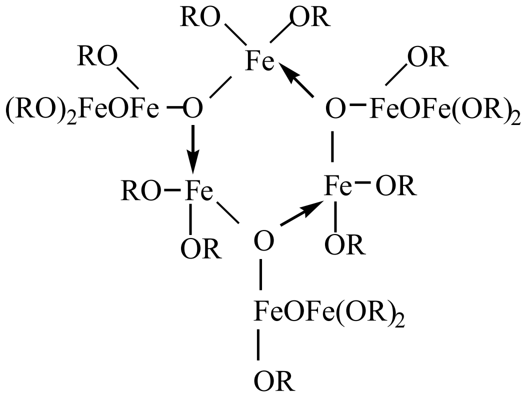
1.3. Stereospecific Catalyst Systems

1.3.1. The Pruitt-Baggett Catalyst System

In 1955, the first report of the stereospecific polymerization of propylene oxide, was published by Pruitt and Baggett [3]. In their work, the complex formed from the reaction of ferric chloride ($FeCl_3$) and propylene oxide was used for the polymerization of propylene oxide. The polymerization of propylene oxide with $FeCl_3$ was investigated in more detail by Price et al. [4,5]. They observed that the polymerization process falls into two defined stages. The first stage occurs at room temperature to give an adduct of $FeCl_3$ and propylene oxide while the second stage, in which a high molecular weight polymer is formed, occurs at elevated temperature.

The hydrolysis of Pruitt-Baggett adduct (PBA) at different mole ratios of water and the effect of this on the solubility and the catalytic activity of the formed Pruitt-Baggett catalyst (PBC) were studied in detail by Çolak et al. [25]. It was found that the formed PBC was soluble in the polymerization medium as the mole ratio of H_2O/Fe was kept in the range between 0 and 1. As the ratio was increased from 1 to 5, larger amounts of precipitation which did not dissolve in the polymerization medium was observed. The maximum conversion of propylene oxide to polymer was observed at a hydrolysis ratio of 0.5; however, the maximum yield of stereoregular polymer was obtained at a ratio of 0.67. Aksoy et al. [26] showed that PBC, as synthesised Çolak et al. would dissociate in dioxane into free ions showing a remarkable electrical conductivity, however with a time taking process conductivity fades away due to combination of anion and cation through a solvent molecule. It was possible to remove the solvent molecule that binds the opposite ions by evaporation and regenerate free ions by successive addition of solvent. Aksoy et al. showed that PO can also bind ions together to form “monomer bound ion-pairs” and argued that these ion-pairs are responsible of stereoregular polymerization.

The structure of Pruitt-Baggett and the polymerization mechanism of PO were studied in some detail by Takrouri et al. [27]. Study of the polymerization in the presence of anion and cation scavengers and in different dielectric media supported the conclusion that neither free anions nor cations were solely responsible for the stereoregular polymerization but together with a monomer molecule they combine to yield catalytically active monomer-bound ion pairs. PBC produces low molecular weight mainly cyclic by-product polyethers (D-polymers), together with high molecular weight stereoregular poly(propylene oxide)s (K-polymer). The study of the product showed that high molecular weight stereoregular polymers (K-polymers) were connected to each other with Fe atoms. The suggested structure of PBC is as follow:



1.3.2. Zinc Alkyl-Water Catalyst System

Diethyl zinc ($ZnEt_2$) was the first organozinc compound used for stereoregular polymerization of propylene oxide [19]. It was found that $ZnEt_2$ in the absence of water was catalytically inactive. However, the catalytic activity for the polymerization of propylene oxide is much enhanced when a controlled amount of water is added as a modifier [7]. The maximum polymer yield was obtained with a catalyst consisted of an equimolar mixture of $ZnEt_2$ and water.

The addition of water to $ZnEt_2$ in hexane leads to the ethane gas evolution and the formation of salt-like precipitation [28]. The reaction was formulated as follows:

$$(C_2H_5)_2Zn + H_2O \longrightarrow (C_2H_5)ZnOH + C_2H_6$$

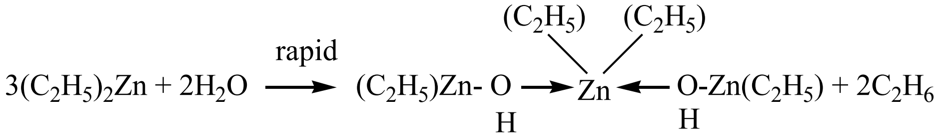
$$(C_2H_5)Zn + (C_2H_5)ZnOH \longrightarrow (C_2H_5)\ ZnOZn\ (C_2H_5) + C_2H_6$$

$$(C_2H_5)\ ZnOZn\ (C_2H_5) + H_2O \longrightarrow (C_2H_5)\ ZnOZnOH + C_2H_6$$

$$(C_2H_5)\ ZnOZnOH + (C_2H_5)_2Zn \longrightarrow (C_2H_5)\ ZnOZnOZn\ (C_2H_5) + C_2H_6$$

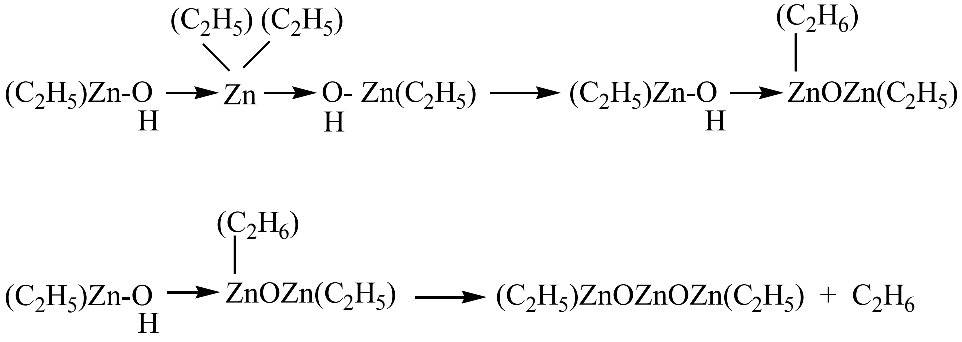
$$\longrightarrow \quad \longrightarrow \quad \longrightarrow \quad (C_2H_5)\ Zn\ (\text{-}OZn\text{-})_n\ OZn\ (C_2H_5)$$

Alyürük [29] found that the observed stoichiometry and the analysis formula of the resulting product of the reaction between $ZnEt_2$ and water did not depend on the initial $H_2O/ZnEt_2$ ratio, as this ratio was ≤ 0.66:



$$3(C_2H_5)_2Zn + 2H_2O \xrightarrow{\text{rapid}} (C_2H_5)Zn\text{-}\underset{H}{O} \longrightarrow \overset{(C_2H_5)\quad(C_2H_5)}{Zn} \longleftarrow \underset{H}{O}\text{-}Zn(C_2H_5) + 2C_2H_6$$

It was assumed that the protons of the product had a Bronsted acid character and catalyzes the decomposition in two stages:



$$(C_2H_5)Zn\text{-}\underset{H}{O} \longrightarrow \overset{(C_2H_5)\ (C_2H_5)}{Zn} \longrightarrow \underset{H}{O}\text{-}\ Zn(C_2H_5) \longrightarrow (C_2H_5)Zn\text{-}\underset{H}{O} \longrightarrow \overset{(C_2H_6)}{Zn}OZn(C_2H_5)$$

$$(C_2H_5)Zn\text{-}\underset{H}{O} \longrightarrow \overset{(C_2H_6)}{Zn}OZn(C_2H_5) \longrightarrow (C_2H_5)ZnOZnOZn(C_2H_5) + C_2H_6$$

1.3.3. Aluminum Alkyl-Water Catalyst System

The first aluminum alkyl used as a stereospecific catalyst was $AlEt_3$ [19]. Polymerization of epoxides with this catalyst gave only low molecular weight atactic polymers in the absence of a modifier [30]. Similar behavior was observed when $AlMe_3$ was used as a catalyst [31]. For aluminum alkyls, water was found to be the most effective modifier [31,32].

The kinetics of the hydrolysis of aluminum alkyls was studied first by Amdurski et al. [33] and from the result obtained the formation of Al-O-Al linkages was predicted. Ishida [34] and Saegusa et al. [35] suggested that the reaction product of $AlEt_3$ and water has the following formula:

$$(C_2H_5)\ [\ \text{-}Al(C_2H_5)O\text{-}\ ]_n\ Al(C_2H_5)_2 \qquad \text{where } n= 1,2,3,4.....$$

The value of n=1 predominates when the $H_2O/AlEt_3$ molar ratio was 0.5. However, when the ratio was between 0.5-1.0 the predominating products were those with n>1. As the ratio increased more than 2, some precipitation was observed.

The hydrolysis of $AlEt_3$ in etheric solution, was studied by Tani et al. [36] and the following reactions were suggested:

$$(C_2H_5)_3Al + H_2O \longrightarrow (C_2H_5)_2AlOH + C_2H_6$$

$$(C_2H_5)_2AlOH + H_2O \longrightarrow HO(C_2H_5)AlOH + C_2H_6$$

$$(C_2H_5)_2AlOH + (C_2H_5)_3Al \longrightarrow (C_2H_5)_2AlOAl(C_2H_5)_2 + C_2H_6$$

$$\longrightarrow \quad \longrightarrow \quad \longrightarrow \quad (C_2H_5)_2Al\ [\text{-}OAl(C_2H_5)\text{-}\ ]_n\ OAl(C_2H_5)_2$$

The product in the third reaction predominates, as the ratio of $H_2O/AlEt_3$ was less than 0.5 however, a polymeric product was obtained as the ratio was increased from 0.5 to 1.0. For higher ratios, the formation of insoluble products was observed.

The hydrolysis of $AlMe_3$ was the subject of a number of studies carried out in this department [37-41]. It was found that upon the addition of water to dilute dioxane solution of $AlMe_3$, one mole of methane gas evolved for each mole of H_2O used in 5 to 10 minutes, which indicated the complete consumption of H_2O at the beginning of the reaction. Then another mole of methane was formed slowly and the reactions were completed in about 8 hours. The proposed reactions were as follows:

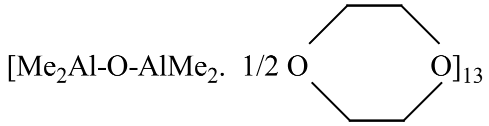
$$Al(CH_3)_3 + H_2O \xrightarrow{\text{very rapid}} (CH_3)_2AlOH + CH_4$$

$$(CH_3)_2AlOH + Al(CH_3)_3 \xrightarrow{k_1} (CH_3)_2AlOAl(CH_3)_2 + CH_4$$

$$2(CH_3)_2AlOH \xrightarrow{k_2} (CH_3)_2AlOAl(CH_3)OH + CH_4$$

$$(CH_3)AlOAl(CH_3)OH + Al(CH_3)_3 \xrightarrow{k_3} (CH_3)_2AlOAl(CH_3)OAl(CH_3)_2 + CH_4$$

In order to prepare $Me_2AlOAlMe_2$ as a major product, the molar ratio of $AlMe_3/H_2O$ was taken quite large. The analysis results of the hydrolysates were consistent with the calculated values for $Me_2AlOAlMe_2.1/2$ Dioxane structure. The obtained hydrolysis product was confirmed by analytical results to be a 13-mer form of bis dimethylaluminum oxide dioxane complex.



$$[Me_2Al\text{-}O\text{-}AlMe_2.\ 1/2\ O \qquad O]_{13}$$

However these analytical results do not necessarily prove that the proposed catalyst is catalytically pure. Detailed kinetic studies show that even at very low $H_2O/AlMe_3$ molar ratios, the specific rate constants of k_2 and k_3 are large enough to induce –O-Al-O- units in the hydrolysis products. But amount of such impurities was small enough not to be detected by analytical methods.

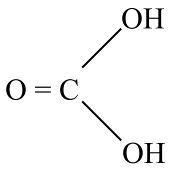
Öktem [42] reported that poly(methylaluminum oxide)s, $Me_2Al(OAlMe)_xMe_2$, PMAO, which are the products of partial hydrolysis of $Al(CH_3)_3$ formed aggregates containing 6 Al atoms per molecule in dioxane solution. It was found that PMAO partially dissociated into free ions in diethyl ether solution and such a solution was conductive. By using different ion scavengers and solvents with different dielectric constants, the ionic nature of the polymerization of propylene oxide with PMAO was studied. It was suggested that the ion-pairs of PMAO and not free ions are the responsible species for stereoregular polymerizations of propylene oxide. Öktem also argued that both the coordination of the incoming monomer and the growing of the polymer chains were taking place at the cationic fragment of the ion-pairs.

In summary, coordination catalysts produce high molecular weight isotactic poly(propylene oxide). However; they are very sensitive to moisture and air. It is difficult to prepare and store them. The catalytical efficiency of these catalysts is usually very low, such as; 400-4000 metal atom can only produce one stereoregular chain. The products obtained with these catalysts are high molecular weight tactic polymer together with rather large quantities of low molecular weight polymer.

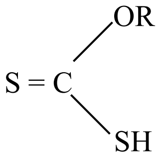
It appears that, this field of polymer chemistry requires a new coordination catalyst that is simpler in nature, more stable to atmospheric contaminations and produce higher molecular weight polymers with higher efficiency.

1.4. Polymerization of Propylene Oxide with Metal Xanthates

Xanthates are salts of xhantic acid, which is alkyl dithiocarbonic acid, which two oxgen atoms in carbonic acid replaced by sulfur and one hydrogen atom replaced by an alkyl group [43]:



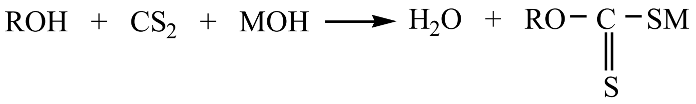
Carbonic acid



Xanthic acid, (where R donates an alkyl or aryl group)

The hydrogen atom of xhantic acid is replaceable by a metal atom. Xanthates of transition metals are sparingly soluble. Xanthates were discovered by Zeise [43] in 1822, but not much work was recorded on the study of their properties and reactions during the 19th century, although some of their general characteristics had been recognized.

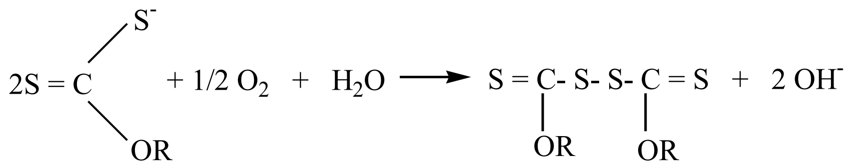
Xanthates are the reaction products of carbon disulfide with an alkoxide. They are formed by combination of the three reactants in the stoichiometric ratio 1:1:1, with the elimination of water. The general reaction is:



$$ROH + CS_2 + MOH \longrightarrow H_2O + RO-\underset{\underset{S}{\|}}{C}-SM$$

Where R stands for an alkyl radical and M denotes a monovalent metal such as sodium or potassium.

On standing in atmosphere, the aqueous solution of xanthate becomes turbid and gives out a disagreeable odor as a result of hydrolysis and oxidation of the xanthate. In the presence of oxygen, xanthate is oxidized to dixanthogen according to the following reaction:



The resulting dixanthogen causes turbidity in a xanthate solution kept standing in the atmosphere.

A variety of catalyst systems comprising metal-oxygen, metal-sulfur or metal-nitrogen bonds have been reported for the polymerization of olefin oxides and of olefin sulfides to high molecular weight polymers [44]. Many such catalysts are prepared by the reaction of alkyl metals (for instance dialkyl zinc, trialkyl aluminum) with active hydrogen compounds, oxygen or sulfur. Alkylmetals are partially hazardous and it is necessary to take extreme caution during handling. Xanthates, dithiocarbamates, and thiocarboxylates of metals are reported as new catalysts in this communication. Unlike alkyl metals, these new catalysts are relatively quite safe.

Polymerization of olefin oxides with xanthates was first studied by Lal [44]. Potassium alkyl xanthates were synthesized by reacting carbon disulfide with an excess amount of the corresponding alcohol in the presence of potassium hydroxide. The isolated materials were treated in aqueous solution with equivalent amounts of zinc sulfate, cadmium chloride and ferric sulfate to form the corresponding zinc, cadmium, and ferric alkyl xanthates. The precipitates where filtered, washed with water and dried. The catalyst was purified by recrystallization from suitable solvents. Polymerizations were carried out under nitrogen in 4-oz. bottles. The bottle was tumbled in a constant temperature bath for a specified interval. In the case of propylene oxide, the polymerization was stopped by chilling the bottle in cold water and adding methanol containing phenyl β-naphtylamine stabilizer. The swollen mass was isolated and dried under vacuum, then inherent viscosity of the polymer was determined. Lal showed that olefin oxides undergo polymerization in the presence of metal alkyl xanthates. Zinc isopropyl xanthate was outstanding among the three metal isopropyl xanthate in polymerizing propylene oxide in regard to both the yield and inherent viscosity of the polymer. However, Lal did not characterize polymers, on the basis of stereoregularity. Hence whether the polymers were crystalline or amorphous were not clear.

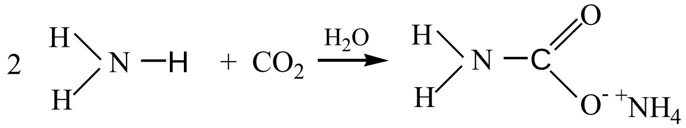
In 1999, Bolat [45] studied metal xanthates as potential catalysts for stereoregular polymerization of propylene oxide in order to define and improve these systems. Zinc isopropyl xanthate was used for polymerization of propylene oxide. Stability and catalytic activity of Zn(isoPr)Xt in different conditions were tested. For this purpose several catalyst solutions were prepared and kept under different conditions like open, semi-closed, closed to atmosphere. The polymerization experiments with these catalyst solutions showed that $ZnXt_2$ is stable and reproducible results can be obtained if prepared and stored in the absence of atmospheric agents (O_2, H_2O). It was also observed that $ZnXt_2$ polymerizes PO into high molecular weight polymer with high efficiency. Bolat [45] investigated the polymers in the view of stereoregularity using polarized microscope, DSC and ^{13}C-NMR. No spherulites were detected with polarized microscope. No endothermic peak corresponding to solid-liquid phase transition was observed in DSC examinations. The results of DSC, which denote that only atactic product is produced by using $ZnXt_2$, was also confirmed by ^{13}C-NMR spectroscopy. According to these results it was proposed that $ZnXt_2$ is a unique catalyst in the polymerization of propyleneoxide since there was no other reported catalyst that produce high molecular weight atactic polypropyleneoxide. But recently Tarkın [46] has shown that carefully fractionated poly(propyleneoxide) samples were crystalline, hence Bolats conclusion was not correct. Bolat also studied the nature of the polymer growth by changing the allowed polymerization time and suggested that polymerization shows chain-growth features, a chain transfer to monomer competes with propagation and finally polymerization is a typical coordination process.

In 2001, catalytical activity of several transition metal xanthates as potential coordination catalysts in the polymerization of propylene oxide, was studied by Soysal [47]. Tin, copper and iron isopropyl xanthates were found to be catalytically active. In order to complete the work initiated by Bolat [45], zinc xanthate catalysts were examined in detail. Soysal showed that polymerization results obtained with zinc isopropylxanthate by Bolat was also reproducible. The effect of alkyl group on the catalytical activity studied, by synthesizing isopropyl, ethyl, 2-octyl catalysts. It was observed that as the alkyl groups become larger, stability of zinc xanthate catalysts against atmospheric impurities increase. It was also observed that ZnEtXt catalyst seemed to yield polymers with considerably lower rates than that of isopropyl and 2-octyl catalysts. The lower yields of polymerization with ZnEtXt was not directly attributed to alkyl group effect and explained with the presence of a high-activation energy termination process. For ZnOcXt catalyst, like Zn(isoPr)Xt, such effective termination reactions can be ignored considering much higher activation energy and percent yields which are close to %100. The possibility of stereoelective polymerization, which might be an effect of alkyl group, was also studied by Soysal. For this purpose zinc 2-(+)-octyl xanthate catalyst was used. It was observed that $Zn^{*}OcXt$ produced less low molecular weight oily polymer than that of the ZnOcXt which might indicated a chiral control of process. However, since no optical activity in the unreacted monomer or in the polymer could be detected it is concluded that the control is not strong enough to perform a stereoelective polymerization. The polymer samples obtained with all these catalysts were practically uncrystallizable. However, ^{13}C NMR studies showed the presence of some partial stereoregularity on the polymer chains, which indicates a steric control that is not strong enough to form isotactic and structurally regular chains that can crystallize.

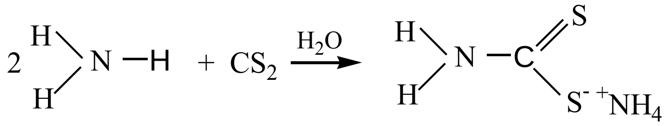
The research on metal xanthates up to now show that metal xanthate catalysts produce high molecular weight, atactic poly(propyleneoxide) with high percent conversion. Because of their stability, they can be used without high vacuum conditions that simplify the polymerization conditions. They have high catalytical efficiency than organometallic catalysts. The polymerization time can also be reduced by metal xanthate catalyst.

1.5. Polymerization of Propylene Oxide by Dithiocarbamates

Carbamates are the half-amides of carbonic acid. Their sulfur analogs, the dithiocarbamates, are the half-amides of dithiocarbonic acid. The synthesis of these two types of compounds in their simplest form are given by the following equations:



The ammonium salt of carbamic acid



The ammonium salt of dithiocarbamic acid

The dithiocarbamates were discovered as a class of chemical compounds early in history of organo-sulfur chemistry. Debus [48], for example, wrote in ‘Liebig’s Annalen der Chemie’ on the synthesis of dithiocarbamic acids in 1850. The strong metal-binding properties of the dithiocarbamates were recognized early. Delépine was one of the pioneer workers in the field. It is now known that this characteristic is due to the insolubility of the metal salts, with the exception of those of sodium and other alkali and the alkaline earth metals, and to the capacity of the molecules to form chelate complexes. Various dithiocarbamates, notably sodium diethyldithiocarbamate, have found practical outlet in the field of inorganic analysis because of these characteristics.

N- Substituted dithiocarbamic acid, RNHCSSH or R_2NCSSH, are formed as their substituted ammonium salts by reaction of CS_2 with a primary or secondary amine, usually in alcoholic, or aqueous solution. In order to conserve the more valuable amine, it is common practice to use an alkali metal hydroxide to form the salt:

$$RNH_2 + CS_2 + NaOH \rightarrow RNHCSSNa + H_2O$$

Many of the heavy metal salts of the dithiocarbamates are colored. They are prepared simply by the addition of a solution of the heavy metal as its chloride, sulfate, etc., to a solution of an ammonium or alkali metal salt of the dithiocarbamic acid, preferably with exclusion of oxygen. The heavy metal salts are more soluble in organic solvents such as chloroform, carbon tetrachloride and diethyl ether. They can be crystallized from such solvents as benzene and ligroin.

Other applications for the dithiocarbamates have been found in the field of rubber chemistry as vulcanization accelerators, in biology as inhibitors in research on enzymes due both to their metal-combining capacity and to their ability to interact with sulfhydryl-containing compounds. Due to their biological activity they have been also used in the fields of medicine and agriculture.

Polymerization of propylene oxide by dithiocarbamates, was studied by Lal [44]. Polymerizations were carried out with the same procedure followed for polymerization of olefin oxides with metal alkyl xanthates as described in section 1.4. Lal showed that dithiocarbamates of zinc and cadmium are effective in polymerizing propylene oxide. It is observed that zinc dimethyldithiocarbamate was outstanding among the other metal alkyl dithiocarbamates in polymerizing propylene oxide in regard to both the yield and inherent viscosity of the polymer.

Lal [49] also studied the effect of alkyl group of dithiocarbamates on polymer yield. It was found that the effectiveness of the various catalysts studied is in the following order: zincdimethyldithiocarbamate > zincpentamethylene dithiocarbamate >> zincdiethyldithiocarbamate. The substitution of methyl groups in the dithiocarbamate by a pentamethylene group or ethyl group markedly decreases the catalytical activity. It was also found that zinc di-n-butyl dithiocarbamate was a significantly slower catalyst than zinc diethyl dithiocarbamate. The author stated that steric factors associated with ethyl and particularly with n-butyl groups are responsible for the decrease in the catalytic activity of zinc diethyl- and dibutyl-dithiocarbamates. Etyl groups may be able to block the entry of propylene oxide for attack on the –CS_2Zn- structure in the catalyst. The n-butyl groups can shield the –CS_2Zn- structure much more effectively than ethyl groups. In contrast, the six-membered ring present in the pentametylenedithiocarbamate has fewer conformations, which shield the –CS_2Zn- structure.

Lal didn't characterize the polymers obtained by dithiocarbamates on the basis of stereoregularity. Therefore, didn't conclude whether the polymers were crystalline or amorphous.

1.6. Aim of This Work

High molecular weight isotactic PPO can only be obtained by using organometallic catalyst as it is explained in the previous chapters. These catalysts are difficult to prepare and store, also they are complicated and have low catalytical efficiencies.

Bolat [45] and Soysal [47] showed that metal alkyl xanthate catalysts give high molecular weight atactic PPO. Present work aimed to a closer look to several transition metal xanthates as potential coordination catalysts in cyclic ether polymerizations. The catalytic activity of Sn(isoPr)Xt catalyst on polymerization of PO was planned to study in details.

Lal [44] proposed dithiocarbamates as potential catalysts besides xanthates. Although this was a remarkable contribution no other work about these systems appeared in literature. Even the tacticity of poly (propylene oxide) obtained with these systems was not studied. Thus characterization of PPO synthesized by dithiocarbamates was also aimed in this work.

CHAPTER II

EXPERIMENTAL

2.1. Purification of Materials

All solvents and reagents were purified by standard procedures prior to fractionation by distillation on a 1-meter column packed with Fenske helices, with an efficiency of approximately 20 theoretical plates.

2.1.1. Solvents

Benzene, was supplied by Merck. It was distilled over CaH_2 with high vacuum system and stored in dry N_2 box.

Isooctane, was supplied by Merck. It was distilled without any other purification.

Toluene, was supplied by Merck. It was used for viscosity measurements.

1,4 Dioxane was supplied by Merck, distilled by using sodium metal for several days and distilled over CaH_2 with high vacuum system and stored in vacuo.

2.1.2. Reagents

Diethyl ether, was supplied by Merck.

Acetone, was supplied by Merck.

Potassium hydroxide (Riedel-de.Haën), carbon disulfur (Merck), $SnCl_2.2H_2O$ (Merck), Sodium diethyldithiocarbamate (Aldrich) were used without purification.

Isopropyl alcohol, was supplied by Merck. It was distilled by fractionation column.

Propylene oxide, was supplied by Merck. It was distilled by fractionation column and stored over CaH_2 in vacuo.

2.2. Apparatus

2.2.1. The Vacuum-Line

An all-glass vacuum-line shown in Figure A.1. was used for polymerization experiments. The assembly allows;

i) Storage and transferring of reagents with measuring in vacuo.
ii) Mixing the reagents in vacuo.

The vacuum-line evacuated by;

i) Fore pump, a Sargent-Welch Scientific Co. rotary pump which can provide an evacuation below $1.0x10^{-4}$ torr.
ii) Liquid nitrogen traps, which are chilled with liquid nitrogen in order to evacuate the system. One of the traps is placed between the mercury

diffusion pump and the rotary pump; the other one is placed between the diffusion pump and the main body of the line.

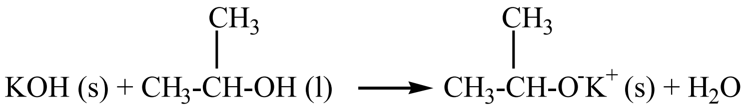
2.2.2. Dry N_2 Box

The dry N_2 box allows handling air sensitive reagents with gloves, under inert gas (N_2) atmosphere. Before using dry box, it was filled with N_2 gas. The interior moisture was dried by placing P_2O_5 in the box. Keeping the inside pressure of the box slightly higher than the atmospheric pressure prevented leakage of the air. As a precaution for the accidental drop in the interior pressure of the box, an oil trap was used at the outlet of N_2 stream.

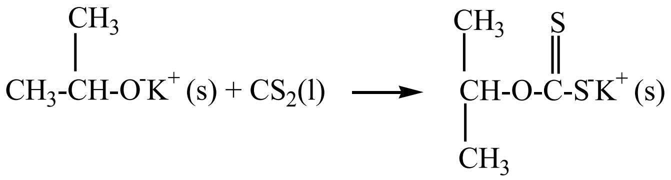
2.3. Procedure

2.3.1. Preparation of Potassium Isopropyl Xanthate

KOH and isopropyl alcohol were refluxed for one hour. At the end of reflux, the warm solution was decanted. CS_2 was added dropwisely to the solution, in an ice bath with continuous shaking. The addition of CS_2 is done in an ice bath because the reaction with CS_2 is highly exothermic and xanthates are susceptible to thermal decomposition. 20 ml of dry diethyl ether was added and the resulting potassium isopropyl xanthate was filtered on a funnel, and washed with few ml of dry ether. The product was purified by dissolving in the minimum volume of hot acetone, by filtering and cooling the filtrate in an ice bath. Precipitation was completed by addition of 20 ml of dry ether. The recrystallized solid was filtered off and washed with few ml of dry ether. This process was done twice. The reactions are as follows;



$$\mathrm{KOH\ (s) + CH_3\text{-}\overset{\overset{CH_3}{|}}{C}H\text{-}OH\ (l)} \longrightarrow \mathrm{CH_3\text{-}\overset{\overset{CH_3}{|}}{C}H\text{-}O^{-}K^{+}\ (s) + H_2O}$$



$$CH_3\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}O^-K^+ (s) + CS_2(l) \longrightarrow \underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{CH}}}}\text{-}O\text{-}\overset{S}{\overset{\|}{C}}\text{-}S^-K^+ (s)$$

potassium isopropyl xanthate

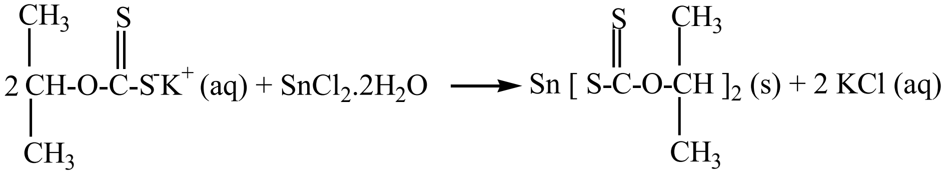
2.3.2. Preparation of Several Transition Metal Xanthates

Transition metal (Cu, Pb, Ni, Fe, Al) isopropyl xanthates were prepared with same procedure. The aqueous solution of recrystallized potassium isopropyl xanthate was mixed with stoichiometric amount of transition metal salt. In this process degassed-water was used, because of instability of metal xanthates in the presence of oxygen. Upon mixing, metal isopropyl xanthates precipitated. They were filtered, washed with water to remove the excess ions and dried in vacuo. Obtained metal isopropyl xanthates were not further purified with recrystallization.

2.3.3. Preparation of Tin Isopropyl Xanthate

1 Metal xanthates are quite stable, but they would decompose in prolonged exposure to moist air. In this synthesis maximum care was taken to protect the product from air; therefore, all process was carried out in dry N_2 box.

2 Potassium isopropyl xanthate was dissolved in degassed water and mixed with water solution of $SnCl_2.2H_2O$. The reaction is as follows;



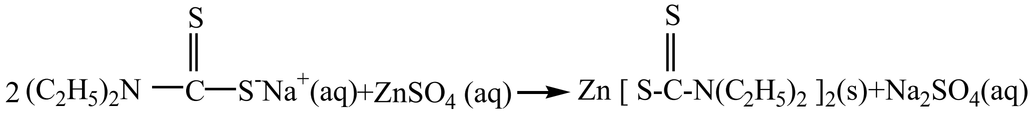
$$2\,\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{CH}}}}\text{-}O\text{-}\overset{S}{\overset{\|}{C}}\text{-}S^-K^+ (aq) + SnCl_2.2H_2O \longrightarrow Sn\,[\,S\text{-}\overset{S}{\overset{\|}{C}}\text{-}O\text{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{CH}}}}\,]_2 (s) + 2\,KCl (aq)$$

tin isopropyl xanthate

The formed precipitate was filtered and washed with cold water to remove water-soluble salts. Several attempts were done to recrystallize the formed product but due to decomposition of it at solving temperature in isooctane, further purification with recrystallization was failed. So, resulting tin isopropyl xanthate was dried in vacuo, then dissolved in benzene and filtered in order to remove insoluble particles. The catalyst solution was stored in vacuo (Figure A.2.). However initially clear solutions upon prolonged storage become turbid because of some decomposition. Such solutions were discarded and new ones were prepared instead.

2.3.4. Preparation of Zinc Diethyl Dithiocarbamate

Preparation of zinc diethyl dithiocarbamate was done in dry N_2 box. Sodium diethyl dithiocarbamate was dissolved in degassed-water and mixed with water solution of $ZnSO_4$. The reaction is as follows;



$$2\,(C_2H_5)_2N-\overset{\overset{S}{\|}}{C}-S^-Na^+(aq)+ZnSO_4\,(aq)\longrightarrow Zn\,[\,S-\overset{\overset{S}{\|}}{C}-N(C_2H_5)_2\,]_2(s)+Na_2SO_4(aq)$$

Sodium diethyldithiocarbamate zinc diethyldithiocarbamate

The formed precipitate was filtered, washed with water and dried in vacuo. Obtained zinc diethyl dithiocarbamate was dissolved in benzene and filtered to remove insoluble impurities. The catalyst solution was stored in dry N_2 box.

2.3.5. Concentration Determination of Catalyst Solutions

2.3.5.1. Determination by Gravimetrically

The molality of catalyst was determined by following procedure;

i. Measured volume of $SnXt_2$ in benzene was transferred into a specially designed ampoule.

ii. Benzene was evaporated by freeze-drying.

iii. The ampoule was sealed off by fire from the line A-B.

iv. The ampoule containing $SnXt_2$ was cracked open and weighed (w_1).

v. $SnXt_2$ in the ampoule was removed by washing and the empty ampoule was reweighed (w_2).

vi. The concentration of the catalyst was calculated as;

$$m = \frac{w_1 - w_2}{M_{SnXt2}\ V\ d} \times 1000$$

M : Molecular weight of $SnXt_2$
V : Volume of the solvent
d : Density of the solvent

2.3.5.2. Determination by Atomic Absorption Spectrometer (AAS)

For AAS measurements, a solution which has a Sn concentration higher than 120 ppm was prepared by decomposing $SnXt_2$ catalyst in 5M HCl.

2.3.6. Polymerization of Propylene Oxide

Polymerization experiments were carried out under high vacuum conditions. A defined amount of catalyst solution was taken into the polymerization tube. Catalyst was obtained in a tacky solid form by freeze drying the solution and pumping off the solvent to dryness. Measured amount of PO was distilled on to the catalyst under vacuum by chilling the polymerization tube with liquid N_2. The polymerization tube was sealed off by fire and placed in a constant temperature bath at definite temperature for a defined time. At the end of predetermined polymerization time, the polymerization tube was cracked open. Its content was dissolved in benzene, while heating and stirring, and transferred into a separatory funnel. Then, 50 ml. 5M HCl was added and shaked to decompose the catalyst and water was added and shaked in order to extract the water-soluble residues. Polymer solution and water phase were separated. The polymer solution was freeze-dried and weighed.

2.3.6.1. Polymerization with Transition Metal Xanthates

Polymerization experiments were carried out under high vacuum conditions. A defined amount of each transition metal xanthate catalyst solution was taken into the polymerization tube in dry N_2 box. The tube was closed with Rotaflo-greaseless tap to protect the catalyst from air and moisture. Freeze drying of the catalyst solution and pumping off the solvent to dryness was achieved. Measured amount of PO was distilled on to the catalyst under vacuum by chilling the polymerization tube with liquid N_2.

2.3.6.2. Polymerization with Tin Isopropyl Xanthate Catalyst

Since the catalyst stock solutions were kept in the vacuum system, its delivery from the storage flask to the polymerization tube was achieved by transferring a calculated volume of the catalyst solution by a vacuum burette equipped with Rotaflo-greaseless taps. The polymerization container was a tube specially designed for sealing off after the transfer of the catalyst and the monomer solutions were completed.

For polymerization experiments three stock solutions of Sn(isoPr)Xt were prepared and used by following same polymerization procedure as mentioned above. The effect of different catalyst/monomer ratio, polymerization time and polymerization temperature on catalyst efficiency was investigated.

The effect of water on catalyst and therefore polymerization was also investigated by changing H_2O/Sn (mol/mol) ratios between 0.0-2.0. For this purpose, 1,4-Dioxane was used to mix H_2O and catalyst solution. A definite amount of water vapour with known volume and temperature that was measured by using a mercury manometer was first transferred into polymerization tube by chilling to liquid nitrogen temperature. The number of moles of water was calculated from ideal gas equation. Then, definite amount of 1,4-Dioxane and catalyst solution were transferred into the tube respectively. Water, 1,4-Dioxane, and catalyst solution were mixed with a magnetic stirrer that was replaced into the tube previously. The final solution was allowed to stay overnight. The solution then freeze-dried and the polymerizations were carried out as described at section 2.3.6.

2.4. Fractionation of Polymer

The synthesized polymers were dissolved in isooctane at 70°C and chilled to 0^{o}C for 48 hours at which the supernatant solution was separated from the precipitated polymer rich phase by filtering with glass wool (Figure A.3.). Both polymers, which were insoluble (K-polymer having high molecular weight) and soluble (D-polymer having low molecular weight) in isoocatane at 0^{o}C, were isolated by freeze-drying in benzene.

2.5. Characterization of D-polymer

2.5.1. Determination of Number Average Molecular Weight

Number average molecular weight of the D-polymer was measured cryoscopically in recrytallized benzene. The empirical cryoscopic constant of benzene was determined by using azobenzene as a standard reagent. When the solution is dilute, the mole fraction is proportional to the molality of the solute, m, and its common to use this equation below;

$\Delta T = K_f\, m$

ΔT = freezing point depression (^{o}C)

K_f = cryoscopic constant of solvent (^{o}C/ mol kg^{-1})

m = molal concentration of the solute (mol/kg)

According to this equation the slope of ΔT vs. m graph gives the cryoscopic constant of benzene.

Molecular weight of the polymer was determined by using these equations:

$$\Delta T/c = K / M_n + A_2c + A_3c^2 + \ldots\ldots$$

$$\lim_{c\to 0} (\Delta T/c) = K / M_n$$

$$1/M_n = [\ \lim_{c\to 0} [\ (\ \Delta T/c)/c\ ]\ x\ \rho\ ] / 1000\ x\ K_f$$

ρ : solvent density (g/cm^3)

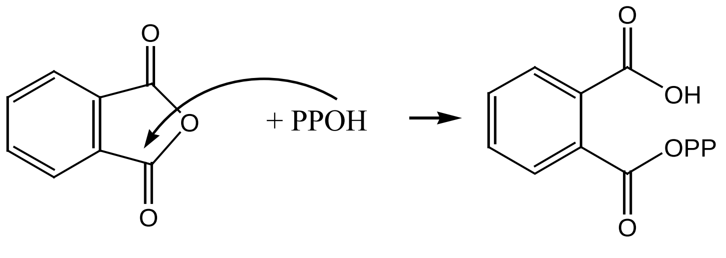
K_f : cryoscopic constant of solvent (^{o}C/ g cm^{-3})

c : solute concentration (g/cm^3)

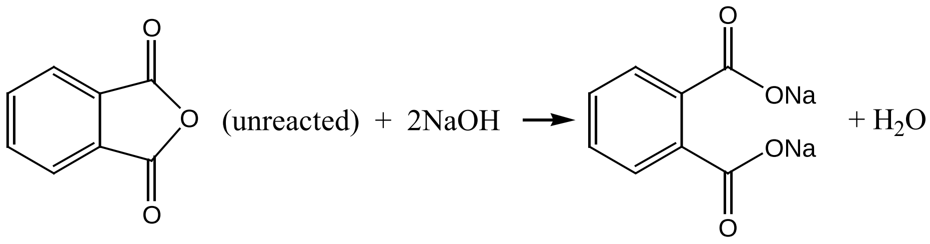
M_n : number average molecular weight

2.5.2. Determination of End Group Functionality

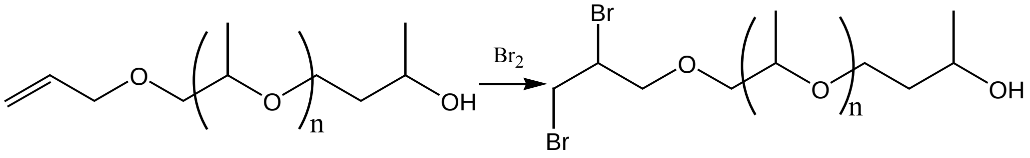
End group determination was performed in order to find out hydroxyl and double bond functionality of D-polymer. Hydroxyl group functionality was determined by phthalic anhydride esterification method. D-polymer was refluxed with phthalic anhydride in pyridine. After cooling the solution distilled water was added and titrated with NaOH by using phenolphthalein end point. The titration difference between the sample and blank gives the amount of hydroxyl terminals in the polymer. The mechanism is as follows:



Titration



Double bond content was determined on the basis of bromination of double bond. D-polymer was dissolved in a mixture of $CHCl_3$ + glacial acetic acid. The mixture was cooled in an ice bath and Br_2 in glacial acid was added slowly with a pipette. After standing exactly two minutes aqueous KI was added and the solution was titrated with $Na_2S_2O_3$ using starch indicator. The titration difference gave the amount of double bonds in polymer. The reactions are:



Titration

$$Br_2 \text{ (unreacted)} + 2I^- \longrightarrow 2Br^- + I_2$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2S_4O_6^{2-} + 2I^-$$

The amount of double bond and hydroxyl terminals in 1-gram polymer was calculated and number average molecular weight of the polymer was determined with the equation below;

$M_n =$ 1 g polymer / $(C_{OH} + C_{DB})/2$

C_{OH}: the amount of hydroxyl groups in 1-gram polymer

C_{DB} : the amount of double bonds in 1-gram polymer

2.6. Characterization of K-Polymers

2.6.1. Determination of Molecular Weight

Viscosity average molecular weights were calculated form intrinsic viscosities measured with Ubbelohde viscometer in toluene at 25^{o}C using Mark-Houwink Equation [50]:

$$[\eta] = K\ M^{a}$$

where $K = 1.29 \times 10^{-4}$ $a = 0.75$

2.6.2. Determination of Melting Point

Benzene solution of fractions (about 0.003g/ml) were put dropwisely on a glass plate. Benzene was evaporated under Infra-Radiator lamp. The deposited films of polymer on glass plates were melted in an oven by increasing temperature to 90^{o}C. The temperature of the oven was decreased gradually to room temperature in at least 12 hours. Such treated samples were crystallized in the form of spherulites. Melting point measurements were carried out on a hot stage polarizing microscope where the temperature was increased about 2^{o}C/min. The temperature at which spherulites were completely dissappeared was noted as the melting point.

2.6.3. Differential Scanning Calorimeter (DSC)

A Perkin-Elmer model 1-B differential scanning calorimeter was used to determine melting points and heat of fusion of some fractions. For DSC measurements, samples were heated from –60^{o}C to 100^{o}C at heating rate of 2^{o}C/min and then cooled to –60^{o}C at cooling rate 2^{o}C/min.

2.6.4. ^{1}H and ^{13}C NMR Measurements

Bruker-Spectroscopic Avance DPX 400 Ultra Shield instrument was performed. For ^{1}H and ^{13}C NMR measurements, 400 and 100 MHz frequencies were used respectively. Measurements were done in deuterio-chloroform.

2.6.5. IR Spectroscopy

A Nicholet 510 model FT-IR spectro-photometer was used to get IR spectra of the polymers. Polymers were dissolved in $CDCl_3$, then dropped on KBr pellets and dried in the vacuum desiccator.

2.6.6. Atomic Absorption Spectrometer (AAS)

A Philips PU 9200 model acetylene flame atomic absorption spectrometer was used. A 9 mA Philips lamp was used for Sn detection.

CHAPTER III

RESULTS AND DISCUSSION

3.1. Preparation of Metal Xanthates

Bolat [45] showed that Zn(isoPr)Xt was a suitable catalyst for polymerization of PO. Soysal [47] chose nine different metals (Mn, Co, Ni, Cu, Sn, Hg, Pb, Cr, Fe) and prepared their xanthate forms in order to observe their catalytical activities in the polymerization of PO. Soysal concluded that Fe, Cu and Sn isopropyl xanthates are active catalysts in the coordination polymerization of PO, but Cr, Mn, Co, Ni isopropyl xanthates are not. But Soysal didn’t define the preparation conditions of metal xanthates. In order to certify Soysal’s work, five different metals were chosen, their xanthate forms were prepared and polymerizations with these catalysts were attempted. Metal xanthates were used immediately after formation without further purification. The following table, Table 3.1, summarizes the observed formation of metal xanthates by precipitation upon mixing the reagent solutions (i.e. potassium isopropyl xanthate with transition metal salts).

Table 3.1. Description of Studied Metal Xanthates

Form of metal	ppt. Formation	Color of ppt.
$SnCl_2.2H_2O$	Instantaneous	Orange
$CuSO_4$	Instantaneous	Reddish brown
$Pb(NO_3)_2$	Instantaneous	White
$FeCl_2.4H_2O$	Instantaneous	Black
$NiSO_4$	Instantaneous	Dark green
$AlCl_3.6H_2O$	*	White

***:** Only a trace amount of ppt formed after 24 h cooling in refrigerator, hence catalytic activity of this system could not studied.

3.2. Catalytic Activity of Metal Xanthates

Polymerization experiments with all metal xanthate catalysts were carried out under the same conditions. Polymerizations are performed at 82°C for 17 hours and moles of metal atoms to monomer ratio were kept almost 1 to 1000 for all cases. Since only trace amount of precipitate (presumably aluminum xanthate) obtained; this system could not be used as catalyst. In the case of Cu, after 17 hours only a low viscosity was developed in polymerization mixture. Even after an additional 48 hours polymerization time viscosity of solution did not increase markedly. Although this experiment was repeated two more times no high polymers could be synthesized by Cu(isoPr)Xt. All of the precipitated potential catalysts immediately dissolved in monomer immediately after sealing off the polymerization tube. The color of solutions distinctly changed on placing at 82°C reaction bath. Table 3.2 summarizes the catalytical activity of used metals.

Table 3.2. Summary of Catalytical Activity of Metals.

Polymerization conditions: Temperature: 82 °C, polymerization time: 17h.

Metal	**Charge**	**Solubility**	**Color**		**Polym.**
			Initial	Final	
Sn	+2	+	yellow	colorless	+
Cu	+2	+	reddish brown	green	+
Pb	+2	+	champagne	black	-
Fe	+2	+	black	black	-
Ni	+2	+	Yellowish green	black	-

Solubility +: soluble. Polymerization +: polymerize PO, -: did not polymerize PO

3.3. Characterization of Sn(isoPr)Xt Catalyst by AAS.

The %Sn in Sn(isoPr)Xt catalyst was measured by AAS and compared with its theoretical value assuming the precipitate has the emprical formula of $SnC_8H_{14}O_2S_4$ with 30.5% Sn. Results are shown in Table 3.3.

Table 3.3. Characterization of Sn(isoPr)Xt by AAS

	Theoretical value (ppm)	**AAS measurement (ppm)**
% Sn	129	122

%Sn in Sn(isoPr)Xt measured with AAS was almost same as its theoretical value.

3.4. Polymerization of PO with Sn(isoPr)Xt Catalyst

It is observed that tin isopropyl xanthate catalyst polymerize propylene oxide. This result is consistent with Soysal’s [47] observations. Since Sn appeared the most active metal among the tested ones, catalytical activity of this metal was investigated in some detail.

During this research three stock solutions of Sn(isoPr)Xt were prepared, stored and used for polymerization purposes under same conditions. The color of initial precipitates changed from one batch to the other (Table 3.4).

Table 3.4. Color Change of Initial Precipitates from One Batch to The Other

	Batch I	**Batch II**	**Batch III**
Color of ppt.	Orange	Yellow	White
Color of benzene solution of Sn(isoPr)Xt	Orange	Yellow	Orange

This color change may be due to the dixanthogen formation (section 1.4) caused by oxygen and moisture in spite of maximum care taken to avoid air during preparation step. Apart from the color difference as expected some minor differences in catalytic activities of these were also observed (Table 3.5).

Table 3.5. Comparison of Catalytical Activities of Sn(isoPr)Xt from The First Batch (I) with That of Second Batch (II).

No	**Mole of Sn ($x10^4$)**	**Mole of monomer**	**Time (h)**	**Temp. (°C)**	**%K-polymer[(a)]**	**% conv.**	**$M_v x10^{-5}$ (b)**
I	7.2	0.143	17	82	39	9.1	8.05
II	7.2	0.143	17	82	28	6.1	7.92

(a) % high molecular weight fraction (b) Molecular weight of K-polymer

The catalyst stock solutions were clear and orange in color. Sn(isoPr)Xt residue after evaporation the solvent (benzene) readily dissolved in monomer to give clear polymerization mixture.

3.4.1. Effect of Catalyst Concentration on The Rate of Polymerization:

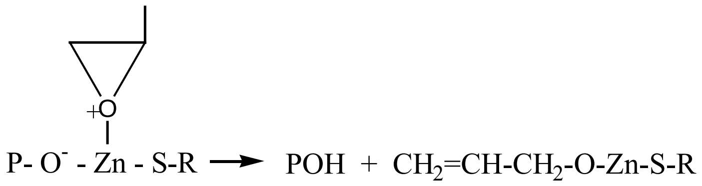
The relation between catalyst concentration and rate of the polymerization was studied by keeping all polymerization conditions except the catalyst concentration. The results are shown both in Table 3.3 and Figure B.1. In Figure B.1., it appears that % conversion increases at fixed reaction time, hence the rate of process linearly increases with the catalyst concentration. The relation between % conversion (P) and catalyst concentration ([C]) can be given as in Eq. I:

$P = 1.65 + 9513[C]$ (Equation I)

Table 3.6. Polymerization of PO with Different Moles of Sn(isoPr)Xt

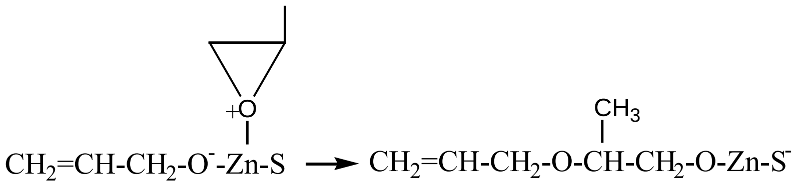
No	Mole of Sn ($x10^4$)	Mole of monomer	Time (h)	Temperature (°C)	Mass of polymer	% conversion	$M_v x10^{-5}$
1	1.8	0.143	17	82	0.264	3.2	2.36
2	3.6	0.143	17	82	0.403	4.8	2.31
3	7.2	0.143	17	82	0.760	9.1	1.98
4	18	0.143	17	82	1.544	18.6	1.4

On the other hand, viscosity average molecular weights (M_V) of polymers decrease with increasing concentration of catalyst. Bolat [45] observed the similar effects of Zn(isoPr)Xt catalyst concentration on the degree of polymerization: when concentration of catalyst was lowered by half, the yield almost decreased by two times. Bolat attributed this effect to the lessened interaction between active sites, which resulted the molecular weight of the product appreciably increased. However, a transfer to catalyst would be also a reason for this effect. Such transfer can be formulated as follows:



Where PO is the growing polymer, R is unknown group.

CH_2=CH-CH_2-O-Zn-S polymerizes propylene oxide as the original active sites:



According to this mechanism, double bonds are formed in the transfer reaction. In fact, analysis of end groups of D-polymers have revealed existence of such double bonds (see Section 3.5)

3.4.2. Growth of Polymer

Growth of polymer with reaction time was also studied. For this purpose identical polymerization mixtures were polymerized in identical conditions but for different reaction times. Results are shown in Table 3.7. Its apparent that molecular weights of polymer formed in different polymerization times were almost constant that is typical for a chain-wise process.

Table 3.7. Growth of Polymer with Time

Polymerization Conditions: mole of Sn: $7.2\mathrm{x}10^{-4}$, mole of monomer: 0.143, temperature: 82°C

No	Time (h)	Mass of polymer	% conversion	$M_v\mathrm{x}10^{-5(a)}$	%K-$^{(b)}$ polymer	%Conversion to K-polymer	$M_v\mathrm{x}10^{-5(c)}$
5	6	0.46	5.6	1.78	34.0	1.7	8.12
3	17	0.76	9.1	1.98	39.9	3.2	8.04
6	36	1.05	12.6	2.90	40.7	4.6	9.32
7	72	1.31	15.8	2.25	45.1	6.8	6.78
8	120	1.98	23.9	2.20	38.7	8.9	6.94
9	240	3.01	36.3	2.65	34.5	12.5	7.74

(a) Molecular weight of obtained polymer (b) % high molecular weight fraction (c) Molecular weight of K-polymer

In Figure B.2. increase of the % conversion of monomer, % conversion to K and D-polymers with different reaction times are shown in the same graph. It appears that the D-polymers are formed not only at the beginning of process but it is formed together through out the process. Further more the ratio of rate of formation of D-polymers to K-polymers is almost constant through out the process (1.8~ 2.0). This shows that D-polymers are formed from a transfer process.

Bolat [45] and Soysal [47] used Zn(isoPr)Xt catalyst in the polymerization of propylene oxide. They attained 24.2 and 25.5 % conversion respectively, by using $6.8\mathrm{x}10^{-6}$ mole catalyst and 0.074 mole monomer polymerized at 82°C for 5 hours. Thus, they obtained about 138 kg of K-polymer for each mole of zinc catalyst. However, the K-polymer yield of in experiment 5 in Table 3.7, which has been carried in comparable conditions, was only 0.2 kg /Sn catalyst. Thus the efficiency of tin catalyst appears to be much smaller than that of the zinc catalyst.

A termination reaction might be responsible for the low efficiency of tin catalyst. In fact initial rate of polymerization is about 3.5 times higher than that instantaneous rate at 120 h. (that is estimated by drawing tangents to the %conversion-time graph Figure B.2.). The decrease in the monomer concentration in this time interval is only ¼. Hence the decrease of the rate of the process can not be attributed to the monomer concentration but a process which deactivates the catalyst (see Eq. I)

3.4.3. Effect of Temperature on The Catalytic Activity of Sn(isoPr)Xt

The effect of temperature on Sn(isoPr)Xt catalyzed polymerizations was studied. Results are summarized in Table 3.8.

Table 3.8. Polymerization of PO with Sn(isoPr)Xt at Different Temperatures

No	Mole of Sn ($x10^4$)	Mole of monomer	Time (h)	T[(a)] (^oC)	% conv.	% K-Polymer[(b)]	%Conversion to K-polymer	$M_v x10^{-5}$ [(c)]
10	7.2	0.143	17	82	6.1	28.5	1.7	7.92
11	7.2	0.143	17	96	6.4	24.4	1.5	7.72
7	7.2	0.143	72	82	15.8	45.1	6.8	6.78
12	7.2	0.143	72	96	21.6	25.8	5.6	4.61

(a) Polymerization temperature. For b and c refer to Table 3.7

Increasing polymerization temperature about 14 °C at fixed polymerization time (No 10 and 11) slightly increased the percent conversion. However, percent conversion and molecular weight of high molecular weight fraction were decreased at elevated temperature. Polymerization No 12 that was done at increased temperature (96°C) and time (72h) could be compared with polymerization No 7 which was done at 82°C and for 72 hours. Increasing polymerization temperature increased the percent conversion. But, the conversion of monomer into K-polymer apparently decreased. Also, it can be seen from the Table 3.8 that there is a marked decrease in the molecular weight of high molecular weight fraction in 72 h polymerization. These results show that:

a) D-polymer formation has positive but K-polymer formation process has negative energy of activation.

b) In order to have negative activation energy rate law of K-polymer formation is expected to be in the following form (Eq.2)

$$R_K = A.k_K/k_D[C][M]^a \qquad \text{(Equation 2)}$$

Where A is a constant, k_K and k_D are specific rate constants of K and D polymer propagation's. The exponential 'a' is likely unity.

c) D- polymer formation can not be associated to a termination process, other wise amount of D-polymer would be limited by the moles of catalyst used (i.e. if each active center is deactivated by formation of a D-polymer in Ex.12 only $7.2x10^{-4}$ x500=0.36g. D-polymer would be formed where 500 is the cryoscopically measured molecular weight of D-polymers) but in this experiment 1.32 g D-polymer have formed and polymerization was still alive.

d) Hence D-polymer formation is likely due to a transfer reaction in the " back-biting" form.

3.4.4. Additive Effect of Water on The Catalytic Activity of Sn(isoPr)Xt

Since in this research semi-closed systems are used, water might be an important contaminant as a modifying, terminating or transfer agent. In order to study the effect of water on Sn(isoPr)Xt catalyst, various amount of water was added per mole of Sn, catalyst solution and water were allowed to stay over night (2.3.6.2). White precipitates were observed in the catalyst solution after this process for all polymerization experiments. Freeze-drying the solvent and polymerizations were carried out as usual. The white precipitates were dissolved in monomer and the polymerization mixtures were clear, homogeneous and yellow in color. The results are summarized in Table 3.9.

Table 3.9. Additive Effect of Water on The Catalytic Activity of Sn(isoPr)Xt in Polymerization of Propylene Oxide.

Polymerization conditions: Polymerization temperature: 82°C, Polymerization time: 17 hours

No	**H_2O/Sn (mol/ mol)**	**Mole of Sn ($x10^4$)**	**Mole of monomer**	**Mass of polymer**	**% conv.**	**% [(a)] K-polymer**	**%Conv. to K-polymer**	**M_v [(b)] ($x10^{-6}$)**
13	0	3.56	0.143	0.701	8.4	45.3	3.8	1.01
14	0.2	3.56	0.143	0.752	9.0	46.8	4.2	1.08
15	0.5	3.56	0.143	0.710	8.5	51.3	4.4	1.02
16	0.67	3.56	0.143	0.733	8.8	54.5	4.6	0.93
17	1.0	3.56	0.143	0.694	8.4	54.9	4.4	1.02
18	2.0	3.56	0.143	0.677	8.1	53.2	4.2	1.20

(For a and b refer to Table 3.7)

Treatment of catalyst with water, in the range of 0.0-2.0 H_2O/Sn (mol/mol), did not effect the percent conversion, however slightly increased the percent conversion of high molecular weight fraction. The added water also slightly increased the conversion of monomer into high molecular weight fraction up to a maximum at 0.67 H_2O/Sn (mol/mol) ratio. Therefore it appears that small quantities of water is not harmful as a terminating or transfer agent on the contrary it may have a slight activating effect which is maximized at 0.67 H_2O/Sn mol/mol ratio.

Bolat [45] studied the effect of water on Zn(isoPr)Xt catalyst by adding water in the range of 0.0-2.0 H_2O/Zn (mol/mol) and concluded that addition of water only increases the low molecular weight, oily polymer product. This conclusion is completely opposite to the results that obtained in this work.

3.5. Characterization of D-Polymer

D-polymer of polymer No 5 was characterized by determination of number average molecular weight, IR and double bond functionality. Number average molecular weight of the polymer was measured by cryoscopy. Emprical cryoscopic constant (K_f) of benzene was determined by using azobenzene as a standard reagent. It was found as 5.36 ^oC /mol kg^{-1} and used for determination of molecular weight of the polymers. Double bond terminals were measured by analytical methods. Although IR spectrum (Figure B.3.) showed the presence of hydroxyl groups, the hydroxyl functionality was not measured.

Table 3.10. Characterization of D-polymer

Sample	M_n [(a)]	C_{DB} [(b)] ($x10^{-4}$ mole)
D-polymer	500	5.7

(a) M_n: Number average molecular weight determined cryoscopically (b) C_{DB}: Double bond functionality in 1-gram polymer

3.6. Stereoregularity of PPO Polymerized by Sn(isoPr)Xt

Bolat [45] searched for any sign of steric control of Zn(isoPr)Xt catalyst by examination of the polymers with DSC, Polarized microscope and ^{13}C NMR. It's concluded that formed polymers were atactic; hence uncrystallizable. Soysal [47] also studied the polymers catalyzed by zinc xanthates in the view of stereoregularity. In polarized microscope measurements no spherulites were observed. It was observed from the DSC spectra that, the polymer has crystalline parts but both melting temperature and % crystallinity were very low. For ^{13}C NMR measurements the polymer was fractionated at 40°C, 25°C and 0°C respectively in dilute isooctane. ^{13}C NMR spectra of these fractions showed that degree of splitting both at methyl, methylene and methine peaks apparently increases from fraction precipitated at 40°C to others. Finally Soysal concluded that a steric control does exist in the addition of monomers into growing chain. However this control was not strong enough to form isotactic and structurally regular chains that can crystallize.

Polymers obtained by Sn(isoPr)Xt catalyst in this work were also examined for crystallinity. For this purpose, polymer No 9 (Table 3.7) was dissolved in isooctane at 70°C and allowed to stand at 40°C for 24 hours and polymer precipitated in the temperature range of 70°C - 40°C was collected. Same procedure was repeated by lowering the precipitation temperature to 25°C and 0°C respectively and three fractions were obtained.

Table 3.11. Fractionation of Polymer No 9

Fraction	**Mass of Fraction**	**Tp (a) (°C)**	**w_i (b)**	**$[\eta_I]$ (c)**	**$M_v x10^{-6}$**	**Tm (d) (°C)**
F_1	0.170	40	0.184	3.84	0.92	62
F_2	0.264	30	0.285	4.66	1.19	48
F_3	0.529	0	0.573	1.21	0.20	42

(a) precipitation temperature (b) weight fractions (c) intrinsic viscosity (d) melting point measured by hot-stage polarizing microscope

Polymeric films from F_1, F_2 and F_3 showed Maltese Cross-spherulitic structures under a plane-polarized microscope. The appearances of these spherulitic structures were in a definite order in F_1 but spherulites spread over a dark area in F_2 and F_3 under polarizing microscope. The photograph of spherulites observed at F_1 is shown in Figure3.1. DSC spectra of F_2 and F_3 are given in Figure B.4. and Figure B.5.

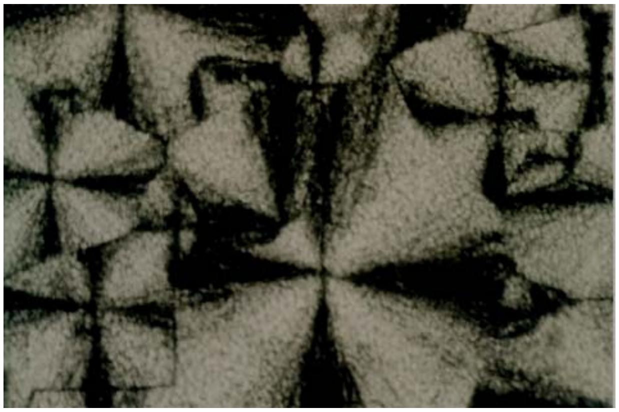


Figure 3.1. Photograph of Spherulites

Melting point of F_1, F_2 and F_3 decrease as precipitation temperature decreases. Because stereoregular polymers are usually crystalline materials; whereas stereoirregular polymers are amorphous and for this reason, stereoregularity and crystallinity are used synonymously in many cases. Therefore, results of T_m values shown in Table 3.11 show that stereoregularity and/or crystallinity of fractions decrease as the precipitation temperature decreases.

It's known that ^{13}C-NMR spectrum of isotactic poly(propyleneoxide) has three single peaks of almost equal intensity. The upfield peak at 17.33 ppm was assigned to methyl carbon, the center peak at 73.90 ppm to the methylene carbon and the peak at 75.90 ppm to the methine carbon. However, in fractions which suffers racemic additions on the growing chain and/or head to head and tail to tail additions: these peaks split into several additional minor peaks due to presence of stereo or regio-isomers. ^{13}C-NMR spectra of F_1, F_2 and F_3 are given in Figure B.6, B.7, and B.8. respectively. In spectrum of F_1, singlet methine peak at 75.9 ppm, singlet methylene peak at 73.8 ppm and singlet methyl peak at 17.8 ppm were observed with almost equal intensities. According to these observations it can be concluded that this fraction is highly isotactic. Degree of splitting both at methyl, methylene and methine peaks apparently increases from fraction F_1 to others which shows that steric irregularities increase with decreasing precipitation temperature.

Both ^{13}C-NMR studies and melting point measurements show that stereoregularity decreases with decreasing precipitation temperature of fractions.

3.7. Polymerization of PO with Zinc Diethyl Dithiocarbamate

In order to understand the catalytic activity of dithiocarbamates, zinc diethyl dithiocarbamate was prepared and two polymerization experiments were done with this catalyst at 82°C. The polymerization mixtures obtained by evaporating the solvent of the stock solution and distilling PO on the residue (which was white colored and non-sticky mass) were clear, homogeneous and champagne in color. Polymerization results are shown in Table 3.12.

Table 3.12. Polymerization of PO with Zinc Diethyl Dithiocarbamate

No	**Mole of catalyst ($x10^4$)**	**Mole of monomer**	**Time (h)**	**% conv.**	**%$^{(a)}$ K-polymer**	**%Conversion to K-polymer**	**$M_v^{(b)}$ ($x10^{-6}$)**
19	2.91	0.143	17	2.14	-	-	-
20	2.91	0.143	90	60.0	65.0	38.2	1.2

(For a and b refer to Table 3.7)

Although the efficiency of zinc diethyl dithiocarbamate catalyst is higher than that of Sn(isoPr)Xt catalyst (i.e. 1 mol metal yields 11kg K-polymer instead of 0.2 kg), it is less efficient than that of Zn(isoPr)Xt catalyst (138kg-pol/molZn) K-polymer of PPO synthesized by zinc diethyl dithiocarbamate catalyst, was crystalline and gave an endothermic peak at 57°C in DSC spectrum (Figure B.8).

3.8. Future Research

In order to enhance catalytical activity of Sn(isoPr)Xt following research might be caried out:

1. Due to negative activation energy of process system should be studied at lower temperatures.

2. Polymerization in different solvents (to change dielectric constant of medium) should be studied.

3. Effect of water and other possible additive might be studied.

4. The alkyl group effect on the xhantate group can be investigated.

5. Same points can also be considered for carbamates and several metal carbamates might be studied.

CHAPTER IV

CONCLUSIONS

1. Among Cu, Pb, Ni, Fe and Sn isopropyl xanthates only Cu(isoPr)Xt and Sn(isoPr)Xt was found to be active catalyst in polymerization of PO. Since Sn(isoPr)Xt appeared to be more active this system was investigated in some details.

2. Analysis (AAS) of stored catalyst has shown that the used catalyst had identical emprical composition to that of Sn(isoPr)Xt.

3. Polymerization of PO with this catalyst produced two contrasting polymers together, through out the process. High-molar mass, crystalline (K-polymer) and low molar mass (D-polymer).

4. D-polymers had both hydroxyl and double bond terminals.

5. The polymer yield increase with catalyst concentration but molar mass of product decreases. This effect is attributable to a transfer or termination process.

6. Molar masses of product almost stay constant through out polymerization process as expected from a chain-wise growth.

7. Overall activation energy of K-polymer formation is negative, as a result of a termination or more likely a transfer reaction.Water as a adduct have a weak activating effect on the catalytical activity. This effect is maximum if H_2O/Sn molar ratio is 0.67.

8. Sn(isoPr)Xt have very poor efficiency with respect to Zn(isoPr)Xt catalayst.

9. Zinc diethyl dithiocarbamate is also active catalyst in stereoregular polymerization but it is not as efficient as Zn(isoPr)Xt catalyst.

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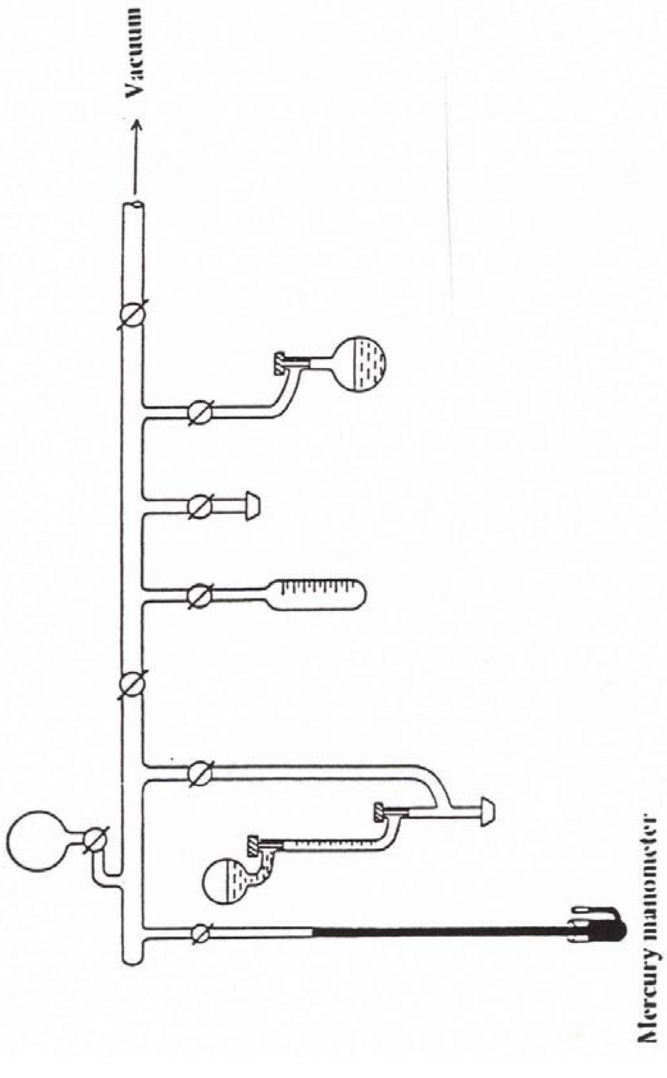
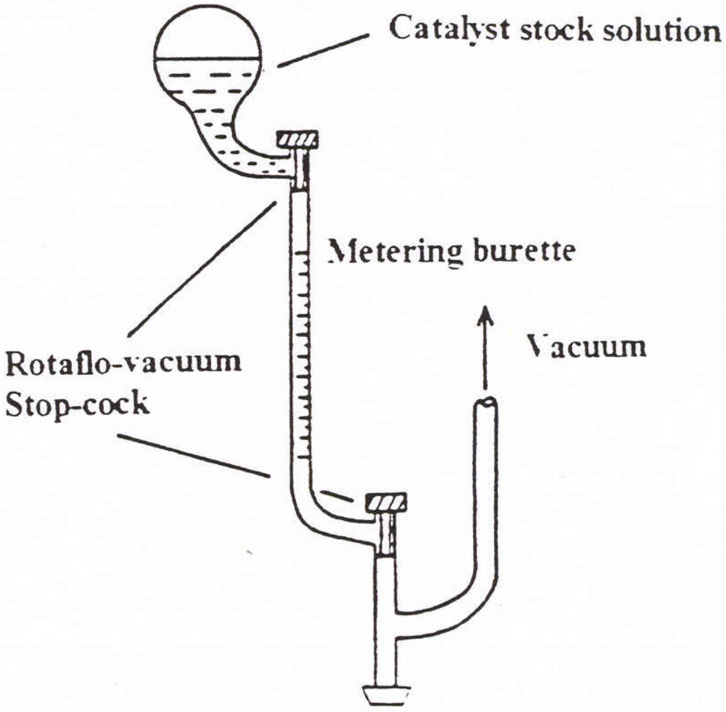
APPENDIX

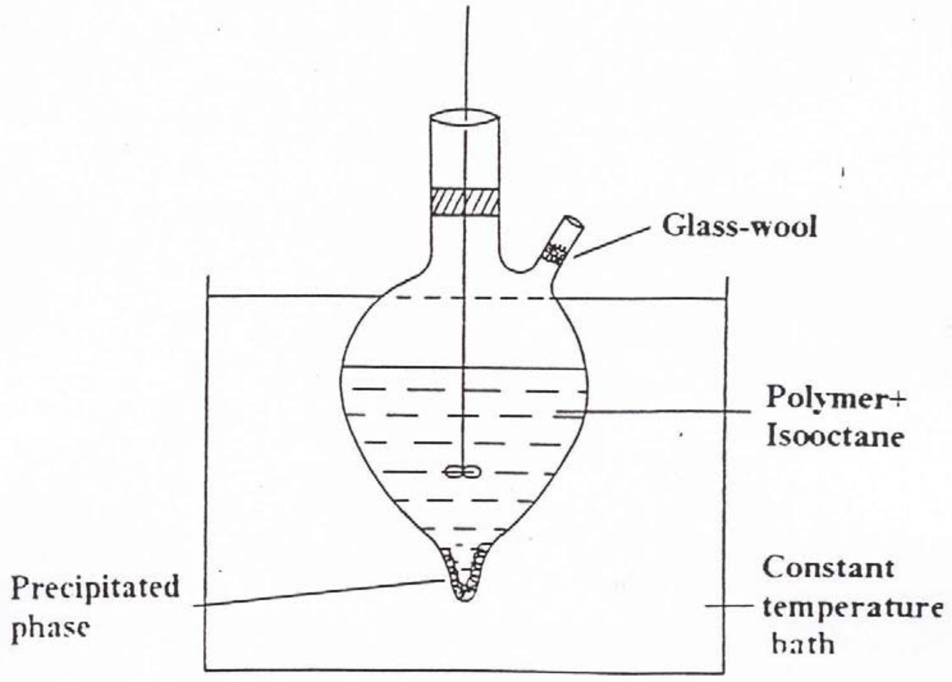
A. APPARATUS



FigureA.1. Vacuum-Line



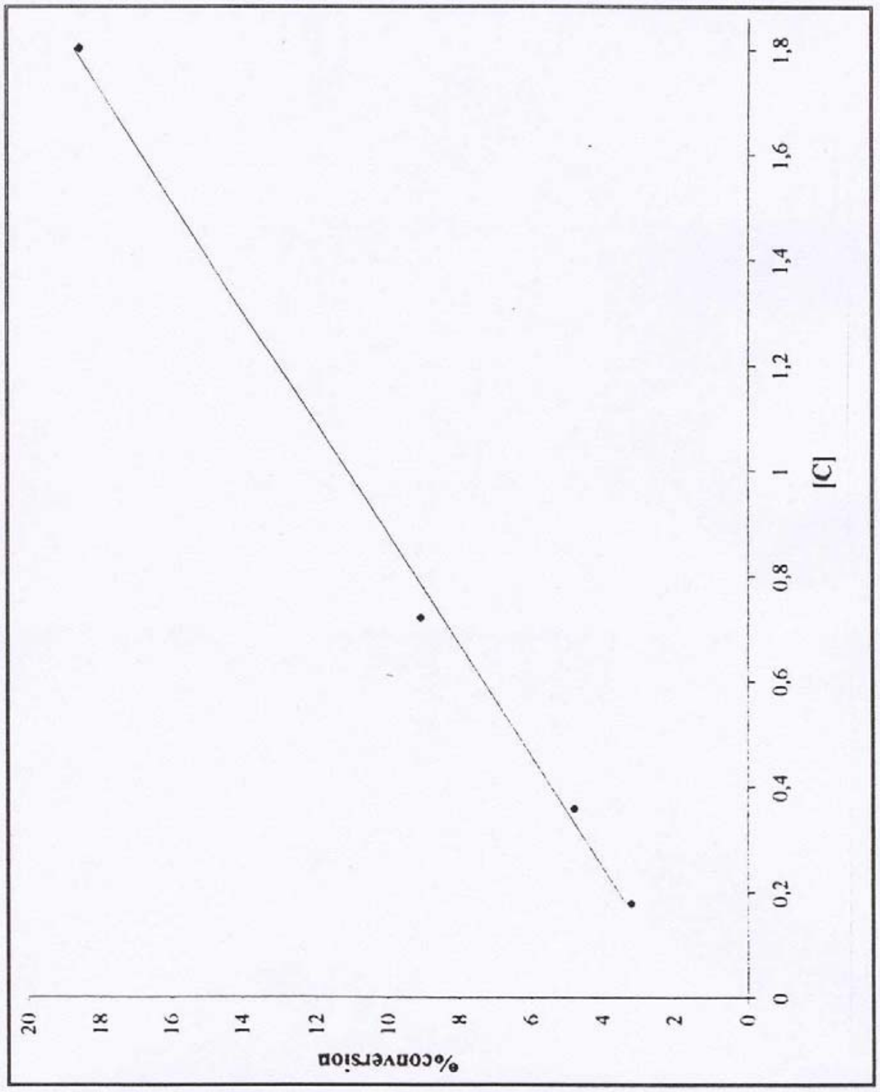
FigureA.2. Catalyst Storage System



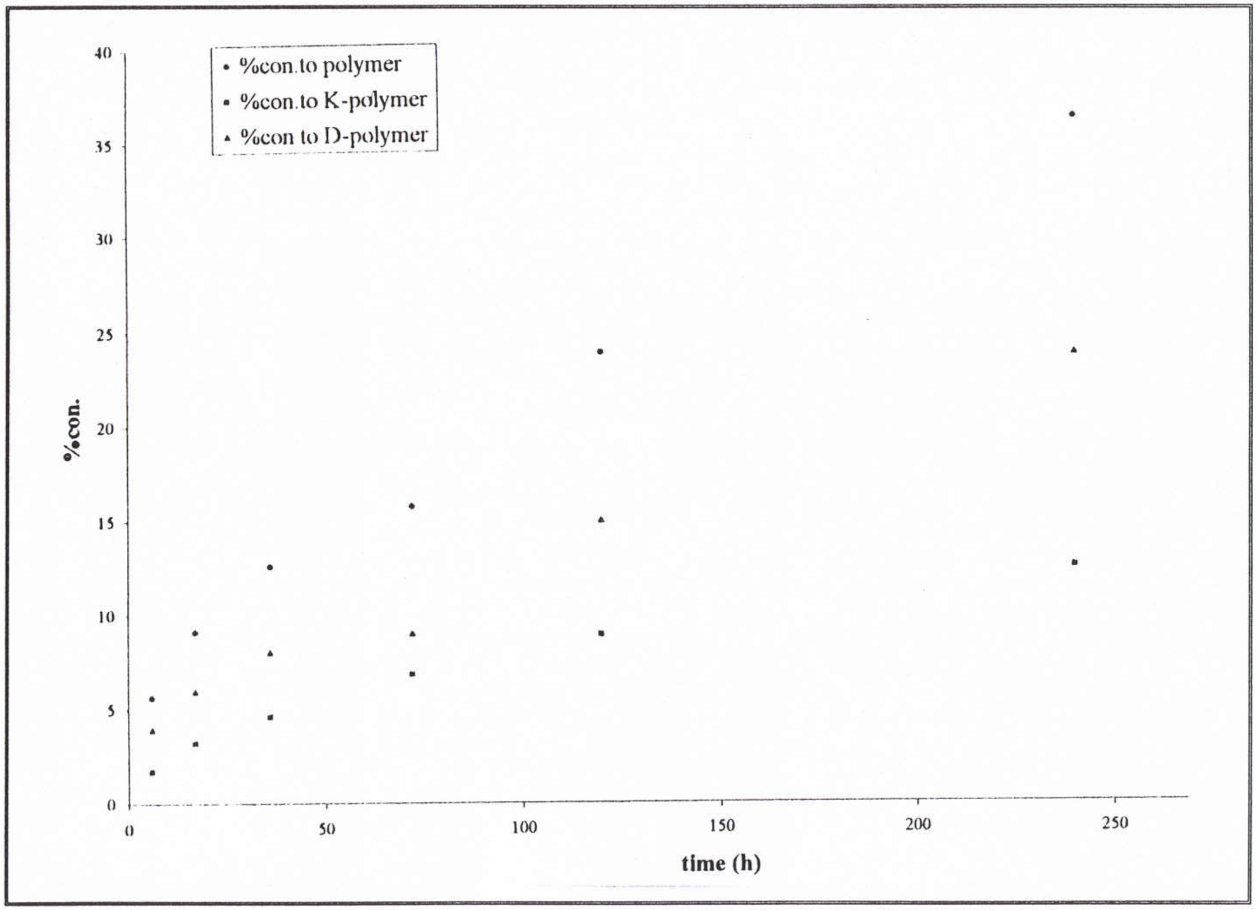
FigureA.3. Fractionation System

APPENDIX

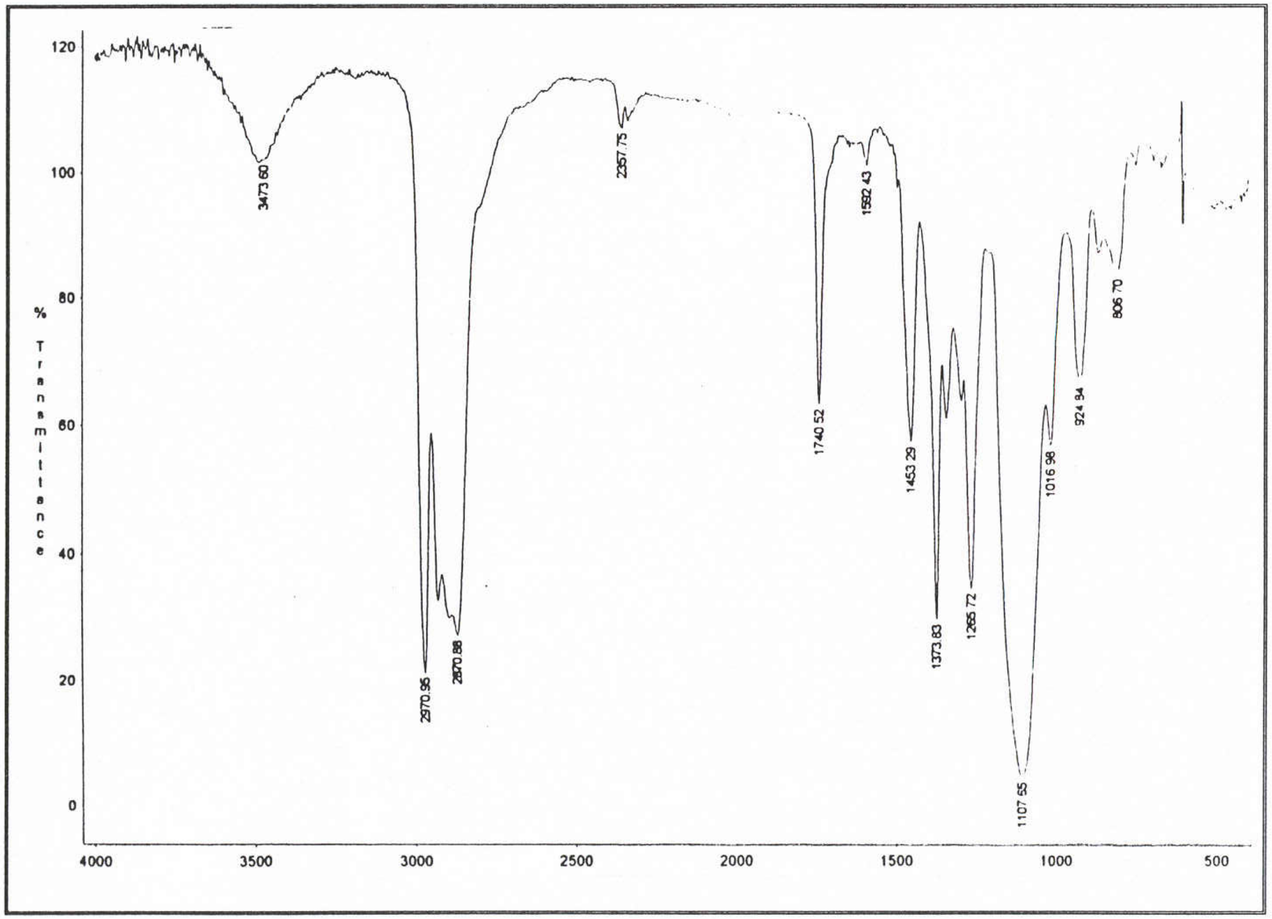
B. SPECTRA AND GRAPHICS



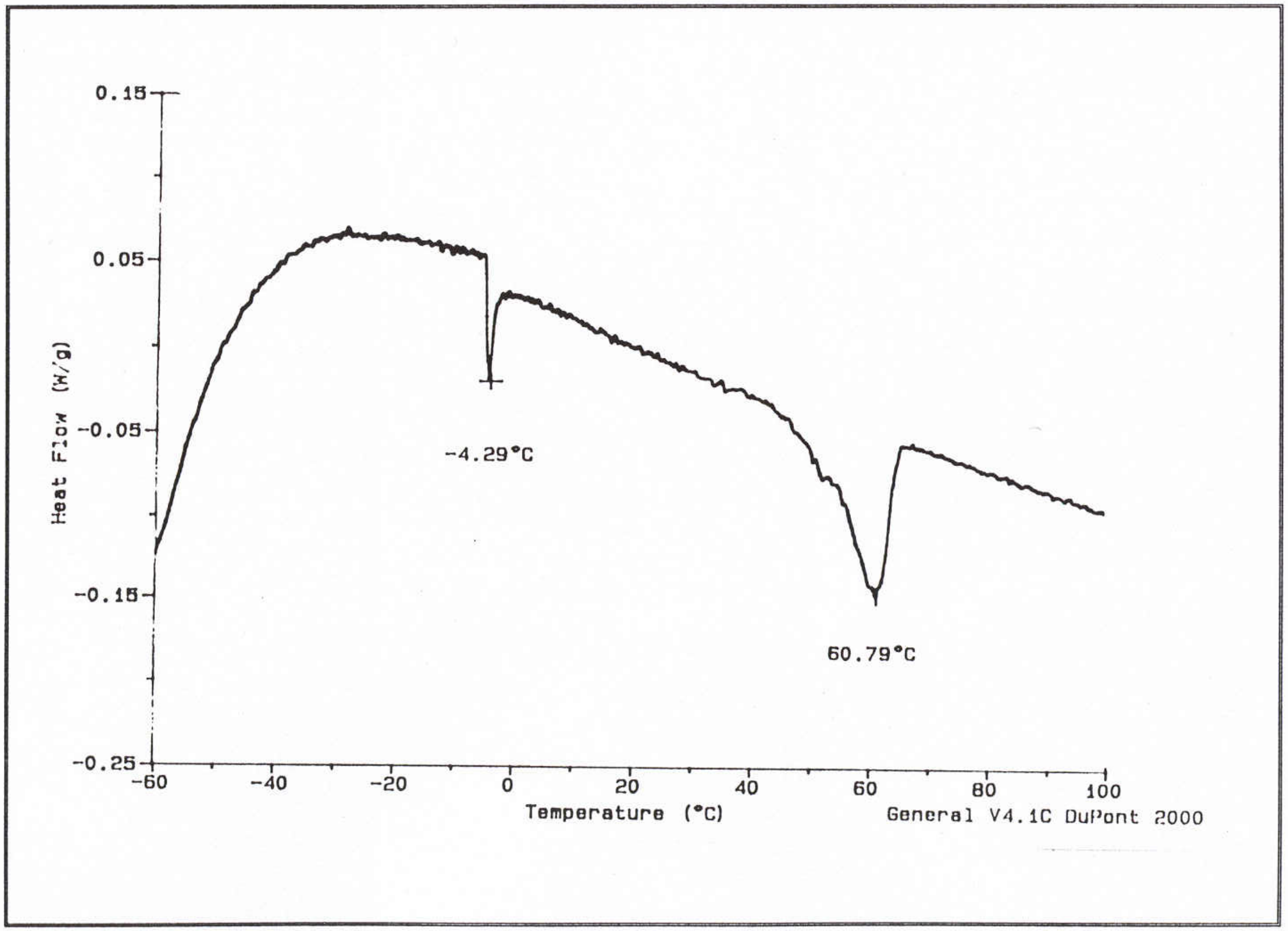
FigureB.1. % Conversion vs. Catalyst Concentration



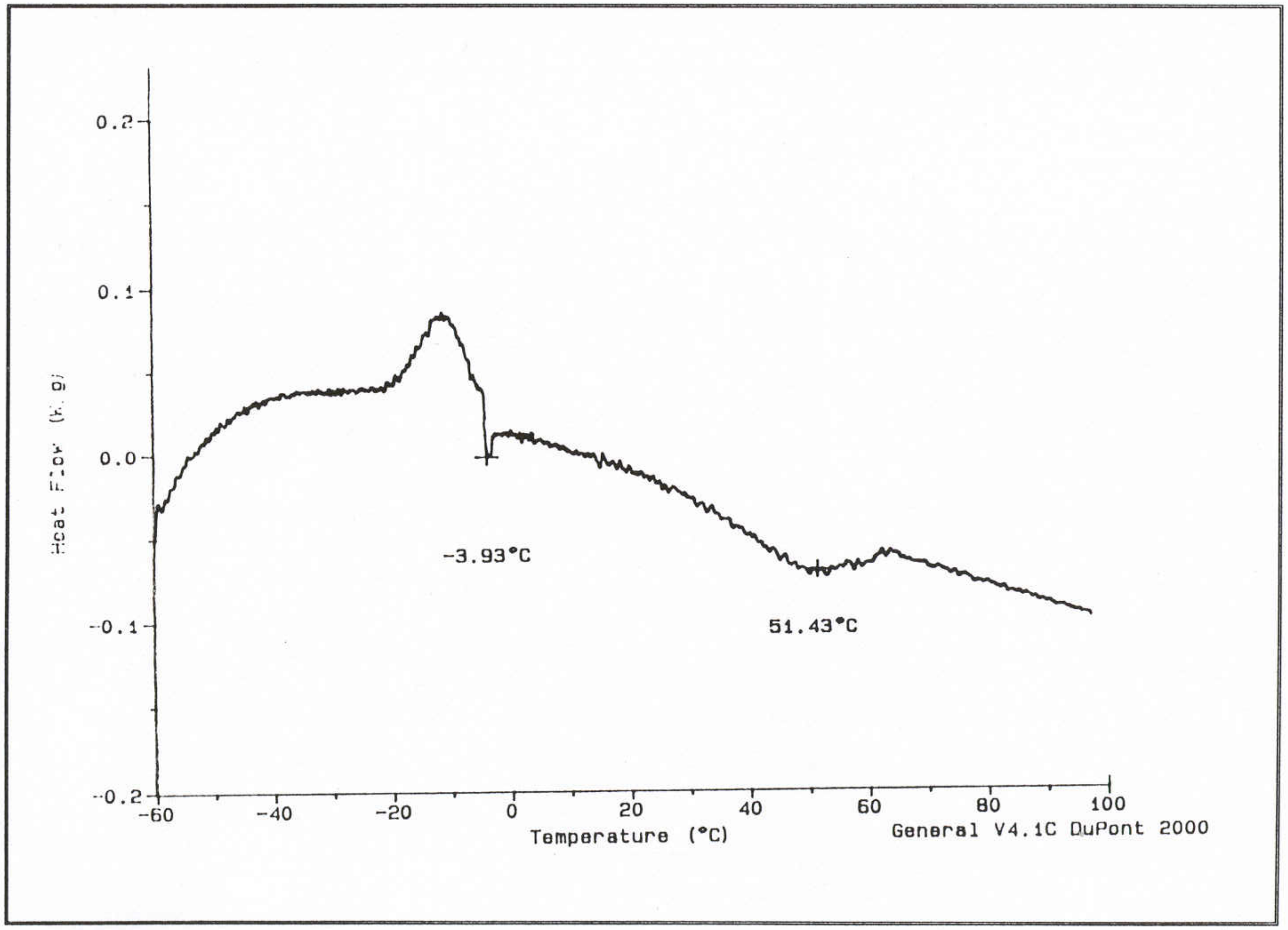
FigureB.2. % Conversion vs. Time



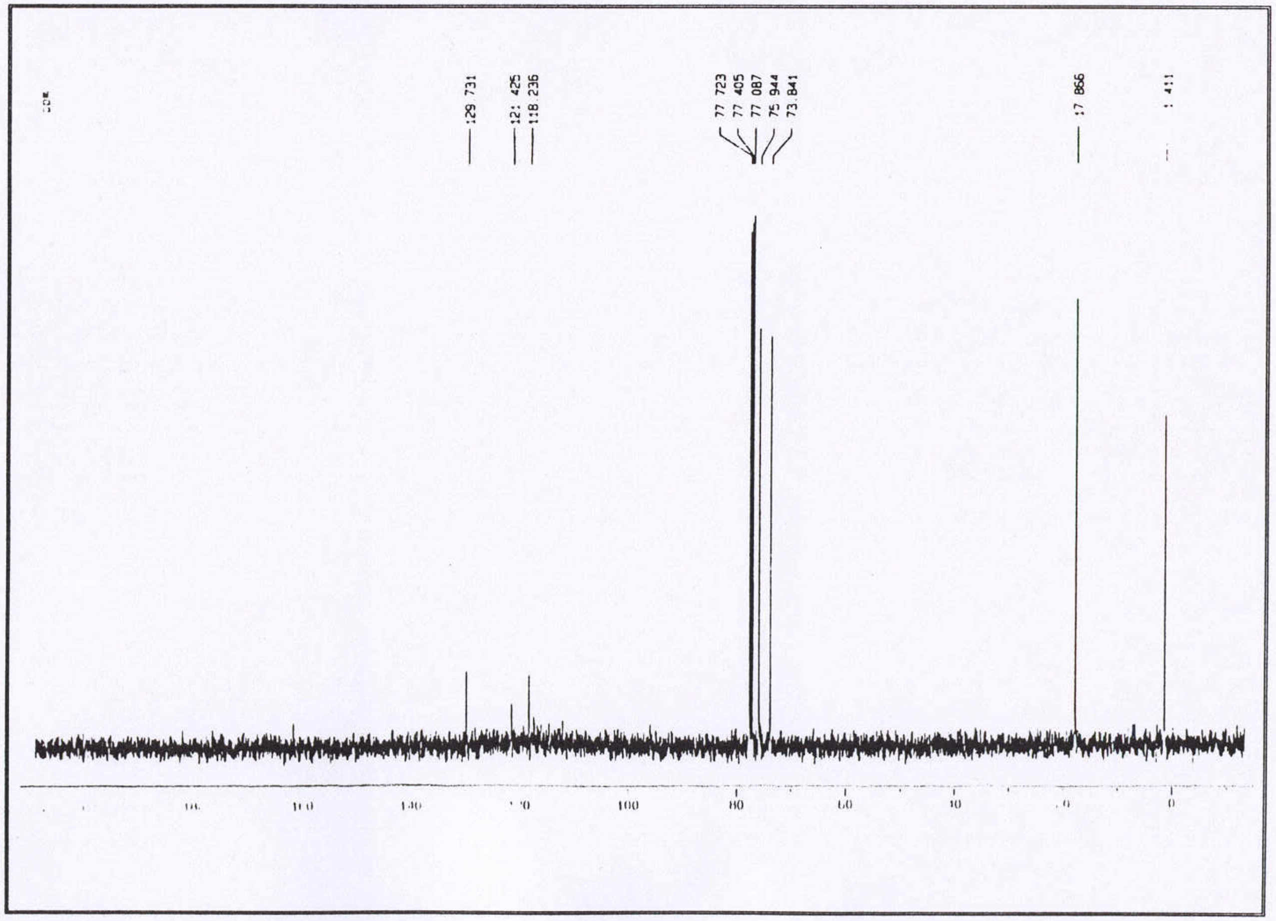
FigureB.3. IR Spectrum of D-polymer



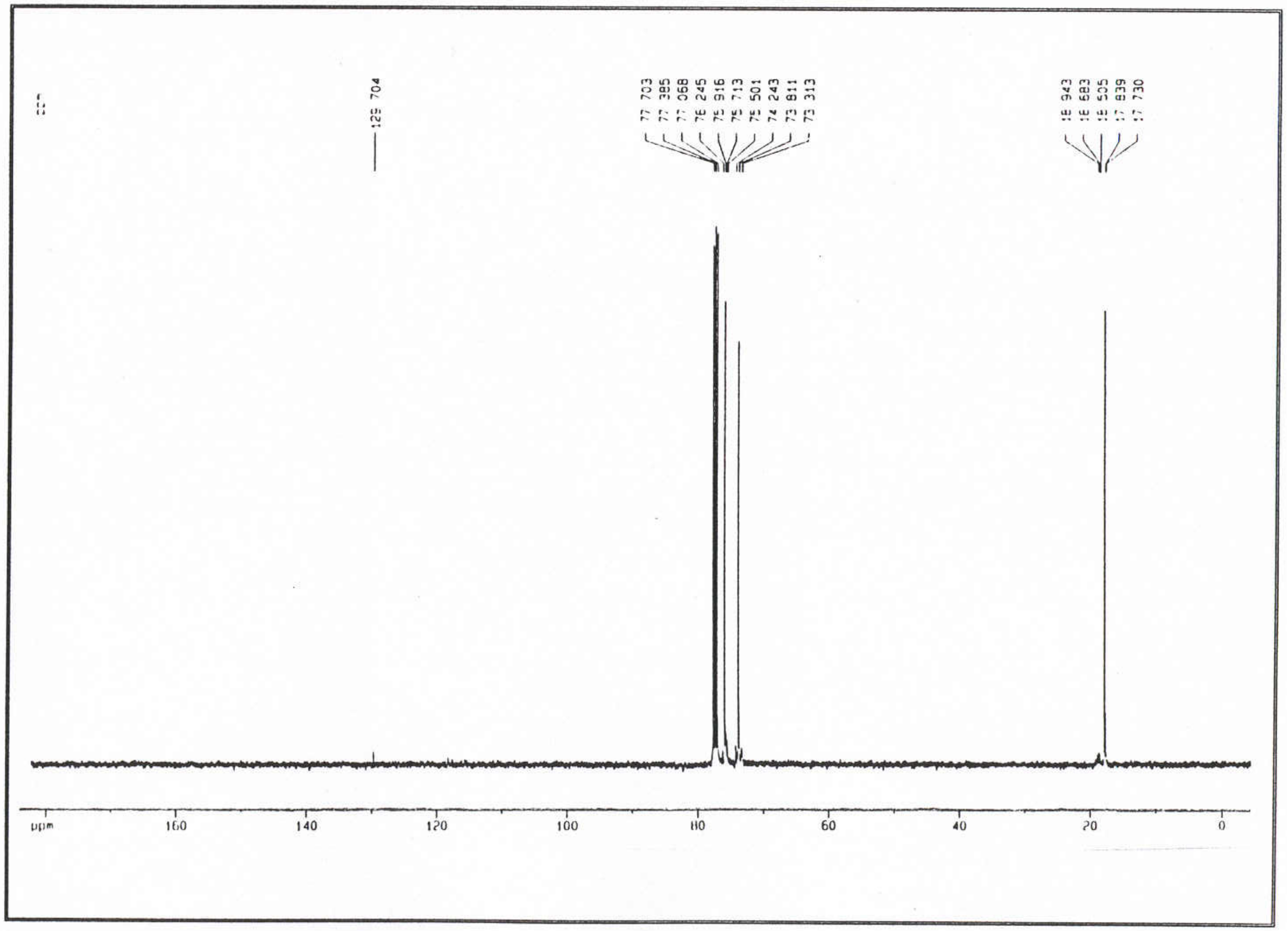
FigureB.4. DSC Spectrum of F_2



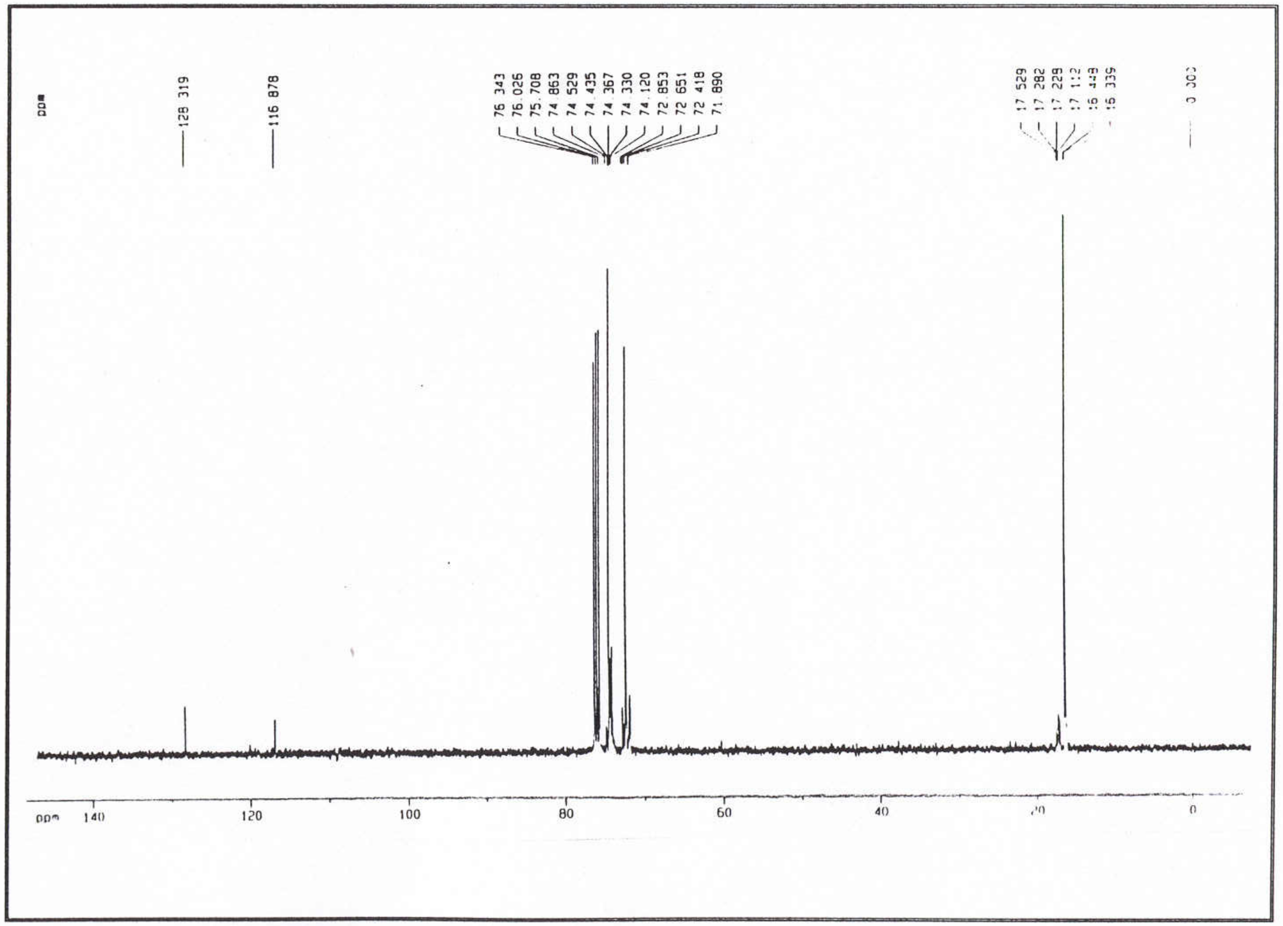
FigureB.5. DSC Spectrum of F_3



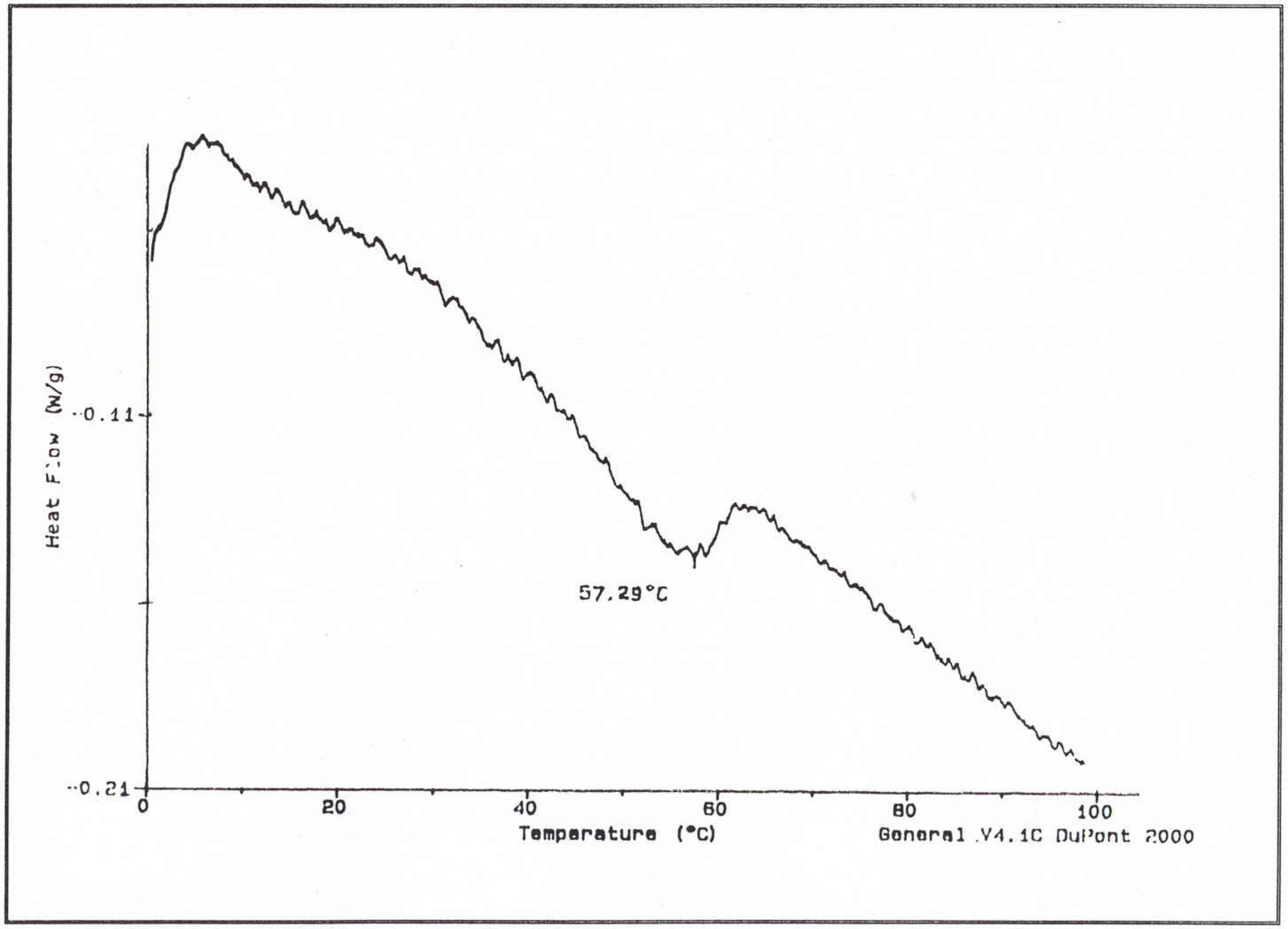
FigureB.6. ^{13}C NMR Spectrum of F_1



FigureB.7. ^{13}C NMR Spectrum of F_2



FigureB.8. ^{13}C NMR Spectrum of F_3



FigureB.9. DSC Spectrum of PPO Synthesized by Zinc Diethyl Dithiocarbamate