CHARACTERIZATION AND STUDY OF SOLUTION PROPERTIES OF POLY(PROPYLENE OXIDE) SYNTHESIZED BY METAL XANTHATE CATALYSTS

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ABSTRACT

CHARACTERIZATION AND STUDY OF SOLUTION PROPERTIES OF POLY(PROPYLENE OXIDE) SYNTHESIZED BY METAL XANTHATE CATALYSTS

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Zinc xanthates polymerize propylene oxide into high polymer (PPO) with coordination mechanism. The present work carried out to identify the structure and stereoisomerisms of this polymer. For this purpose PPO was subjected to thermal and column fractionation. Obtained fractions were characterized by end group analysis, cryoscopy, viscometry, IR and ^{13}C-NMR spectroscopy, melting temperature (both by hot-stage polarizing microscope and DSC). PPO is composed of a high molecular weight, stereoregular, crystallizable polymer (K-polymer) with low molecular weight (=500 g/mol) D-polymer. D-polymer has both double bond and hydroxyl terminals. Presence of double bonds was interpreted as the product of an anionic mechanism.

K-Polymers can be thermally fractionated on the base of their melting temperature T_m rather than molecular weight. It’s found that higher melting temperature fractions have lower molar mass, but they precipitate at higher temperatures then the fractions with higher molar mass but lower T_m.

In column fractionation, K-polymers were deposited on glass beads from isooctane solution in a narrow temperature interval. Then the precipitated samples were split into a number of fractions by using again isooctane but at a higher temperature than the precipitation temperature by increasing residence time of solvent from 5 minutes to several hours. It’s found that rate of solubility is not controlled by molecular weight at all, but it’s controlled only percentage crsytallinity and T_m.

Highest melting temperature polymers, with relatively higher molecular mass showed faster rate of solution than that of lower T_m, lower molar mass but higher percent crystalline fractions. This discrepancy was accounted by suggesting a stereo-block structure where tactic blocks are bound each other with non-crystallizable presumably atactic blocks.

On the basis of these results mechanism of polymerization was discussed in some detail.

Keywords: zinc xanthates, poly(propylene oxide), thermal fractionation, column fractionation, percent crystallinity, stereo-block structure

ÖZ

METAL KSENTAT KATALİZÖRÜ İLE SENTEZLENEN POLİ(PROPİLEN OKSİT)İN KARAKTERİZASYONU VE ÇÖZELTİ ÖZELLİKLERİNİN İNCELENMESİ

Tarkın, Eylem

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Eylül 2003, 89 sayfa

Çinko ksentatlar propilen oksiti, yüksek moleküler ağırlıklı polimere (PPO) koordinasyon mekanizması ile polimerleştirirler. Bu çalışma polimerin yapısını ve stereo-izomerizimini belirlemek için yapıldı. Bu amaçla, PPO kolon ve ısıl olarak fraksiyonlandırıldı. Elde edilen fraksiyonlar, uç grup analizi, donma noktası alçalması, viskometri, IR ve ^{13}C-NMR spektroskopi, erime sıcaklığı (hem polarize mikroskop hem DSC ile) ile karakterize edildi. PPO'nun yüksek moleküler ağırlıklı, stereoregüler, kristallendirilebilen polimer (K-polymer) ile düşük moleküler ağırlıklı (≅500g/mol), amorf D-polimerden oluştuğu saptandı. D-polimerin çifte bağ ve hidroksil terminalleri içerdiği gözlendi. Çifte bağ varlığı, D-polimerin anyonik mekanizma ürünü olduğu şeklinde yorumlandı.

K-polimerlerin ısıl fraksiyonlandırmada moleküler ağırlıklarına bağlı olarak değil, erime sıcaklıklarına bağlı olarak fraksiyonlandırıldığı gözlendi. Yüksek erime sıcaklığı olan fraksiyonların molar kütlesinin daha düşük olduğu, ve bu fraksiyonların yüksek molar kütle ve düşük erime sıcaklıklı fraksiyonlardan daha yüksek sıcaklıklarda çöktüğü saptandı.

Kolon fraksiyonlandırmada, K-polimerler izooktan çözeltisinden dar bir sıcaklık aralığı içerisinde cam boncuklar üzerine çöktürüldü. Sonra, çöken örnekler, yine izooktan kullanılarak, çöktürme sıcaklığından daha yüksek sıcaklıkta ve çözücünün bekletilme süresi 5 dakikadan birkaç saate kadar yükseltilerek birçok fraksiyona ayrıldı. Çözünürlük hızının moleküler ağırlıkla kontrol edilmediği ancak, sadece kristallenme yüzdesi ve erime sıcaklığı ile kontrol edildiği saptandı.

Molar kütlesi ve erime sıcaklığı yüksek olan fraksiyonların, daha düşük molar kütleli ve erime sıcaklıklı fakat daha yüksek kristallenme yüzdesi olan fraksiyonlardan daha hızlı çözündükleri gözlendi. Bu beklenilmeyen davranış taktik blokların kristallenemeyen ataktik bloklarla birbirine bağlı oldukları bir stereo-blok yapı önerilerek izah edildi.

Bu sonuçlara bağlı olarak polimerleşme mekanizması tartışıldı.

Anahtar Sözcükler: çinko ksentat, poli(propilen oksit), ısıl fraksiyonlandırma, kolon fraksiyonlandırma, kristallenme yüzdesi, stereo-blok yapı.

To M. Kemal ATATÜRK,

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INTRODUCTION

1.1. Historical Background

Epoxides give ring-opening polymerizations with anionic, cationic and coordination catalysts. Polymers obtained by cationic and anionic initiators are low molecular weight amorphous products. Those obtained by coordination catalysts are mixtures of high molecular weight stereoregular polymers with low molecular weight amorphous polymers in different proportions.

Fundamental studies on polymerization of epoxides began in 1930s with the work of Staudinger [1], while the earliest report of the polymerization of ethylene oxide was made by Wurtz [2] in 1863. In fact the interest racemic epoxide polymerization began in 1950s with the industrial production of different racemic epoxides. Pruitt and Baggett [3] who used the condensate resulting from reaction of ferric chloride with propylene oxide as the catalyst published the first report of the stereospecific polymerization of propylene oxide in 1955. The basic studies on this system were subsequently published by Price and his co-workers [4,5].

PO was the first cyclic ether to be polymerized in its optically active form by Price and Osgan [5] in 1956. D(+)-monomer was polymerized by using solid KOH and the product was optically active. It was also first monomer to be involved in an asymmetric selective or stereoelective polymerization in which a racemic monomer was polymerized by using an asymmetric catalyst [6].

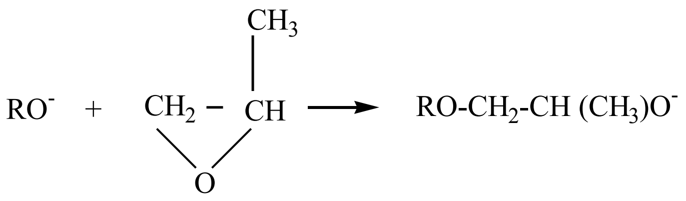
In 1957 it was found that the stereospecific polymerization of epoxides can be catalyzed by some organometallic compounds like $AlEt_3$, Et_2AlCl, $EtAlCl_2$, $Al(iBu)_3$, $ZnEt_2$, $MgEt_2$, $CdMe_2$ [7]. Later, it was found that they were catalytically inactive unless hydrolyzed or chelated [8]. Frukawa [9] showed that $ZnEt_2$ was effective as a stereospecific catalyst only when it was used with some compounds like O_2, H_2O and alcohol. Also it was proved that ferric chloride [10] and aluminum alkyls [11,12] were also inactive as a stereospecific catalyst in the absence of air and water.

The most extensively studied stereospecific initiators are modified forms of organometallic compounds. But only three catalytical systems and their derivatives were investigated in detail [13-18]. These are iron-propylene oxide, zinc alkyl-water and aluminum alkyl-water catalyst systems.

1.2. Simple Ionic Polymerization of Epoxides

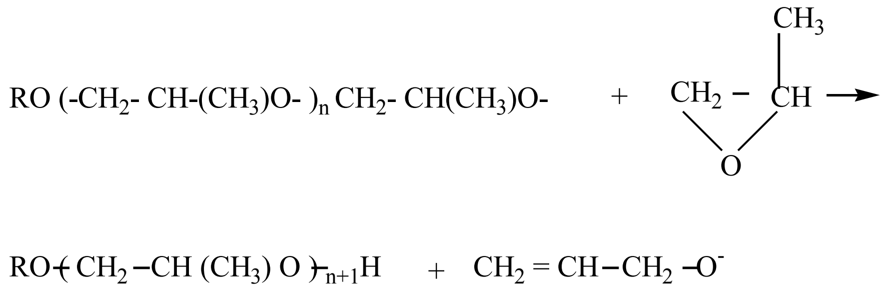
1.2.1. Simple Anionic Polymerization

Polymerization of PO and some other epoxides can be initiated by hydroxides, alkoxides and other bases [10-19]. Initiation is accomplished by the attack of a base to the primary carbon atom of the epoxide ring, followed by ring cleavage with the formation of an alkoxide anion.



Nucleophilic attack occurs almost exclusively at the primary carbon atom, at least hindered side of epoxide ring. Non-polymerization studies on the base catalyzed additions of small molecules such as water and alcohols across the epoxide ring support this idea and indicate that attack occurs almost at the primary carbon atom. Price and Osgan [5] showed that the polymerization of optically active D-propylene oxide catalyzed by solid KOH gave optically active polymer. They concluded that the absence of racemization was due to the protection of the substituted carbon atom against any nucleophilic attack.

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 [20,21], where the formed allyl oxide ion is also a strong nucleophile and can initiate a new chain.



$$RO(-CH_2-CH-(CH_3)O-)_n CH_2-CH(CH_3)O^- + \underset{O}{CH_2 - \overset{CH_3}{CH}} \longrightarrow$$

$$RO(CH_2-CH(CH_3)O)_{n+1}H + CH_2=CH-CH_2-O^-$$

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.

$$RO(-CH_2-CH(CH_3)O-)_n CH_2-CH(CH_3)O^- + ROH \longrightarrow$$

$$RO(-CH_2-CH(CH_3)O-)_{n+1}H + RO^-$$

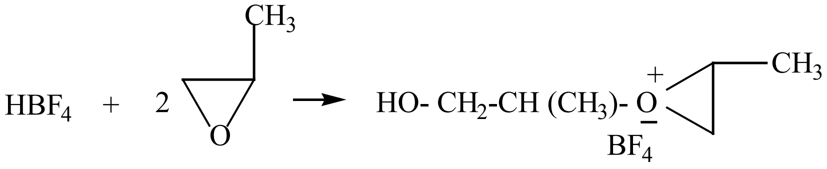
The existence of such transfer reactions in the simple anionic polymerization of PO, causes the formation of low molecular weight poly(propylene oxide) (5000-10000) as a viscous liquid.

PO can also be polymerized by alkali xanthate salts [22]. However with these catalyst systems, xanthate terminal groups on the growing chains give a condensation reaction with active centers resulting low molecular weight, sulfur containing cyclic polymers.

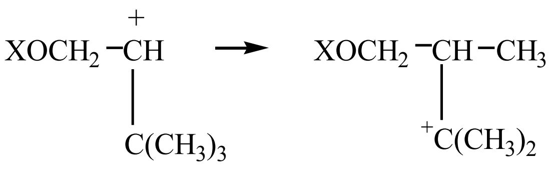
1.2.2. Simple Cationic Polymerization

Epoxides can also be polymerized to low molecular weight products by Friedel-Crafts type catalysts such as HBF_4, HBF_3OH, $HSbCl_3$ [23], $SnCl_4$ [24]. But most of the strong acids cannot be used as an initiator because their conjugates attack and combine with the propagating cations.

Polymerization starts with the formation of an oxonium ion [25], which is the active center in the propagation step.

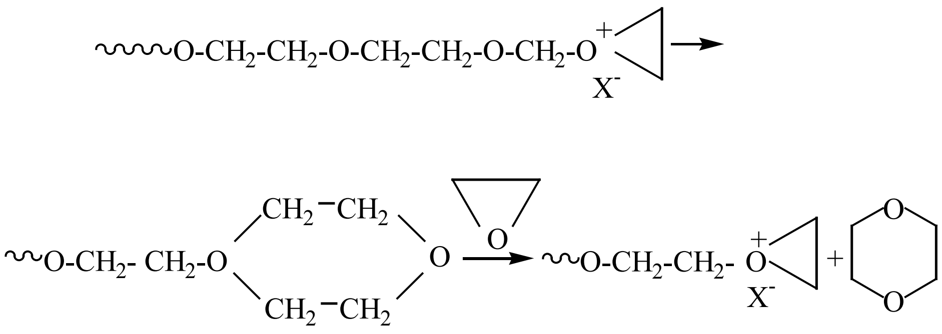


Worsfold and Estham [25] assumed the existence of equilibrium between oxonium and carbonium ions to explain some anomalous kinetic features of the reaction. However, this is now considered unlikely on energetic grounds and furthermore Bruce and Hurst [26] found no evidence (NMR spectroscopy) for methyl shift characteristic of carbonium ions in the cationic polymerization of t-butyl ethylene oxide,e.g.

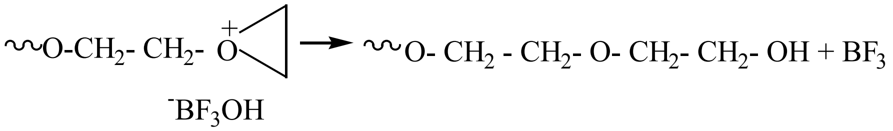


$$XOCH_2-\overset{+}{C}H\big(C(CH_3)_3\big) \longrightarrow XOCH_2-CH(CH_3)-{}^{+}C(CH_3)_2$$

Since the polyether chain also contains oxygen atoms capable of participating in oxonium ion with oxygen further back in the chain already formed. This leads to the formation of cyclic products. Cyclic product formation is one of the characteristics of the cationic polymerization of epoxides and the other cyclic ethers.



Consequently the molecular weight of the polymer cannot grow above a limiting value. Termination occurs by combination of the propagating oxonium ion with either the gegen-ion or, more likely with anionic fragment from the gegen-ion.



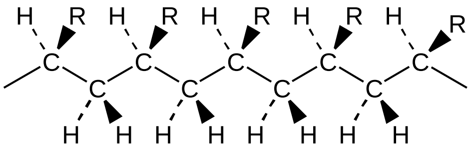
1.3. Stereospecific Polymerization of Epoxides

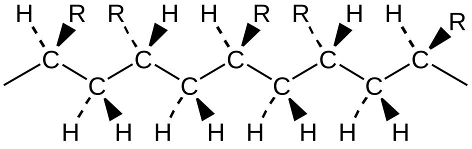
A stereoregular polymer, as described by the IUPAC commission on macromolecular nomenclature, is “a regular polymer whose molecules can be described by only one stereo-repeating unit in a single sequential arrangement”. A stereo-repeating unit is further defined as “a configurational repeating unit having defined configuration at all sites of stereo-isomerism in the main chain of a molecule”.

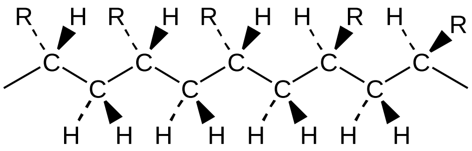
Although the definition of stereoregular polymer as given by the IUPAC commission refers to ideal structures, it may be applied to practical cases where deviations from ideality are not too large. In general, polymers having significant amount of steric and/or structural irregularities are called “partially stereoregular polymers”.

The concept of stereoregularity is most important in considering the substituted polymers. Mono or symmetrically disubstituted carbon atoms on the polymer backbone create sites of asymmetry in the chain. The regularity with which successive asymmetric centers show the same configuration determines the over all order of tacticity of the polymer chain. Tactic polymers are defined as “those, which exhibit a regular pattern of configurations for at least one type of stereoisomerisms sites in the main chain”.

There are three possible stereochemical arrangements for a substituted polymer chain. If each asymmetric carbon has the same configuration, it is called isotactic chain, if successive asymmetric centers have the opposite configuration, the chain is in syndiotactic structure. 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

Stereoregular polymers are in general produced under special conditions with the aid of special catalysts. Those catalysts producing stereoregular polymers are called “stereospecific catalysts”.

1.3.1. Stereospecific Catalysts

It was found in 1957 that some organometallic compounds polymerize epoxides [7]. Later the necessity of some modifiers, for an active catalyst and stereoregular product synthesis, was recognized. Some reagents as effective modifiers are; water, oxygen [24], hydrogen sulfide [27], alcohols [9,28], amines [29], dimethyl sulfoxide [30]. Among them the most used one is water. For example; Furukawa et al [9] claimed that the alcohols or oxygen can replace water as an effective additive in the zinc diethyl system, and $Zn(OR)_2$ had been suggested as the active species under these conditions. This was questioned by Colclough and Pratt [31] who prepared zinc dimethoxide by a method, which did not involve the use of zinc diethyl, and found to be insoluble in PO and inactive as a catalyst. Dimethyl sulfoxide was reported as a good modifier by Frukawa [30], but later Lees [32,33] and Alyürük [34] has found that the catalyst system $ZnEt_2$ + dimethyl sulfoxide (1:1) has no catalytical activity.

The function of such modifiers is to react with organometallic compounds to form new catalytical species, which are active in stereospecific polymerizations. Thus it is preferred to refer them a modifier instead of activator.

The most important and used modifier is water. It reacts immediately with metal alkyls to form a metal-alkyl hydroxide intermediate and an alkane.

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

The intermediate is not stable and may undergo either a self-condensation reaction or react with another metal alkyl to give alkyl metal oxides.

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

or

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

Further reaction up to a polymeric product consists of metal-oxygen linkages may take place. The formation and the degree of polymerization of such products depend on the nature of the used organometallic compound and on the preparation conditions.

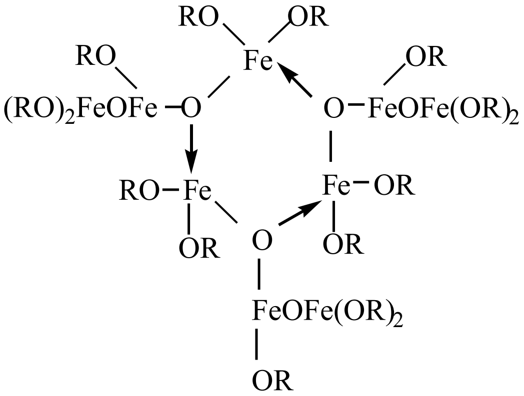
The formation of active catalysts by reacting organometallics with difunctional reagents such as water was explained as the formation of metal-oxygen-metal bonds [35]. In the stereospecific polymerization of epoxides mostly used catalysts are iron-propylene oxide, alkyl zinc-water and alkyl aluminum-water catalyst systems. In different works carried out with such systems, high molecular weight atactic products were obtained. The ratio of number of produced stereoregular chains per metal atom was found to be low, approximately 400-4000 [36].

All these may indicate that the catalyst systems are mixtures of different catalytical species. Some authors proposed that stereospecific sites catalyze stereoregular polymers and non-stereospecific sites in the catalyst mixture catalyze atactic polymers.

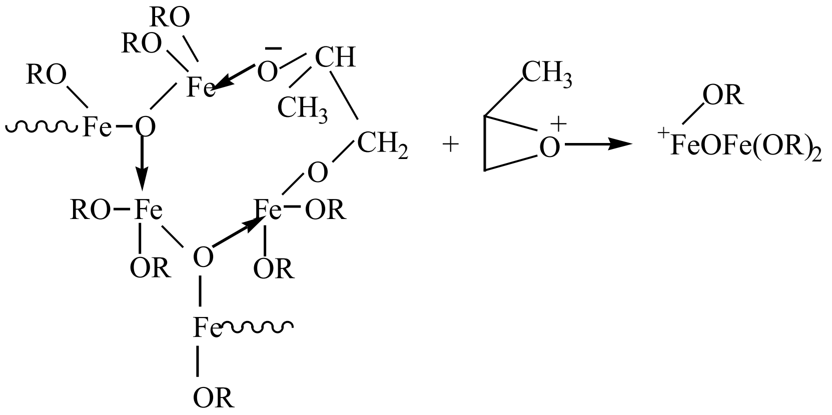
1.3.2. Pruitt-Baggett Catalyst System

The Pruitt-Baggett catalyst (PBC), as a catalyst for the stereoregular polymerization of propylene oxide (PO), attracted considerable interest in the 1960s. However, owing to imprecise terminology, where different authors referred to different compounds as PBC or ‘iron catalyst’; the chemical identity and physical properties of this catalyst have been described rather differently. Initially only $FeCl_3$ was known as PBC, then it was realized that stereoregular polymerization was only possible if $FeCl_3$ is partially hydrolyzed. Finally Çolak [37] showed that hydrolysis of $FeCl_3$ can be achieved in an etheric solvent in the absence of monomer. The activity of hydrolysate was maximum if the hydrolysis ratio ($H_2O/FeCl_3$ mole/mole) is 2/3. Aksoy et al. [38] showed that PBC as synthesized 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.

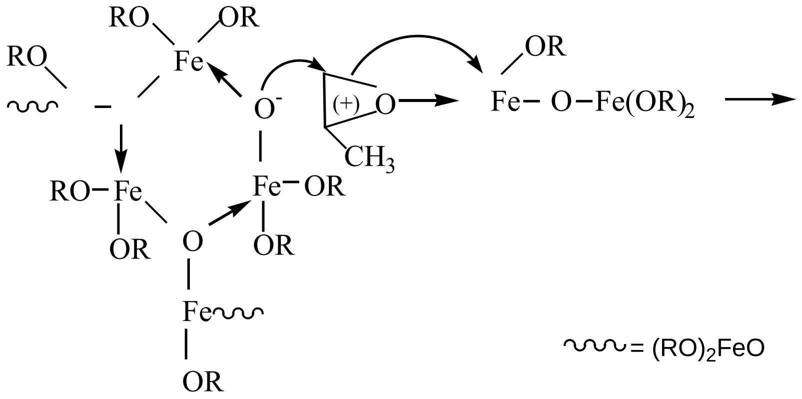
The structure of Pruitt-Baggett and the polymerization mechanism of PO were studied in some detail by Takrouri et al. [39]. Takrouri from the molecular weight measurements and electrolysis of PBC in acetonitrile in an Hitroff-cell showed that PBC ionizes in acetonitrile, to produce an anionic fragment composed of seven Fe atoms and a cationic fragment with two Fe atoms, where iron atoms bond each other with O atoms. 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 structure of PBC and the mechanism of K-polymer production are as follows;



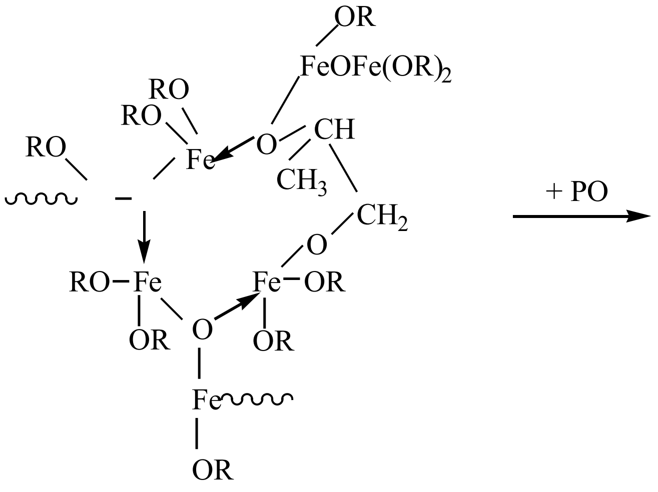
Structure of PBC



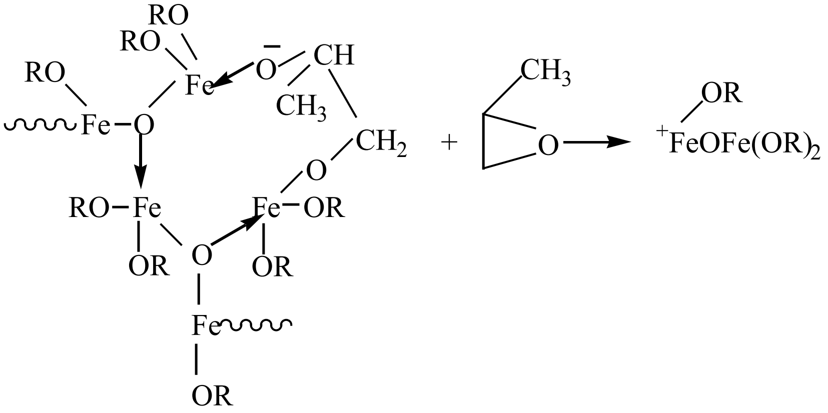
(1) Ionization and oxonium ion formation on the cationic fragment



(2) Formation of monomer-bound ion-pair and SN2 attack on the PO

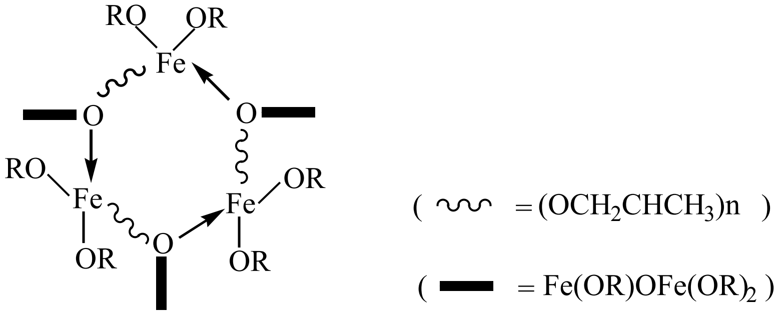


(3)



(4) Propagation

Ions in the above reaction reform the monomer-bound ion pairs followed by insertion of monomers to the growing K-polymer. Hence, in agreement with the experimental results, this mechanism is expected to produce K-polymers that are interconnected to each other with Fe atoms:



Aksoy et al. on the basis of kinetic evidence, conclude that oxonium ion formation of the PBC cation (with either diethylether or PO) occurs in a fast reaction. In agreement with this result, the gradual change of (2) to the above structure in the polymerization process would affect the overall reaction rate. Hence this mechanism also explains the observed acceleration period of polymerization. This is also consistent or, rather, does no contradict some of the other observed features of stereoregular polymerization, namely K-polymers contain considerable concentrations of structurally irregular repeating units and, the longer the K-polymer chains, the smaller their content of structurally irregular repeating units.

1.3.3. Zinc Alkyl-Water Catalyst System

The mostly used organozinc compound is diethyl zinc. Although it is not alone an active catalyst even for simple cationic polymerization, its hydrolysis products were found to be streospecific catalyst for stereoregular polymerization of epoxides.

The reaction between diethyl zinc and water first was studied by Sakata [40] and Frukawa et al. [41], where they formulated the hydrolysis reactions as follows;

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

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

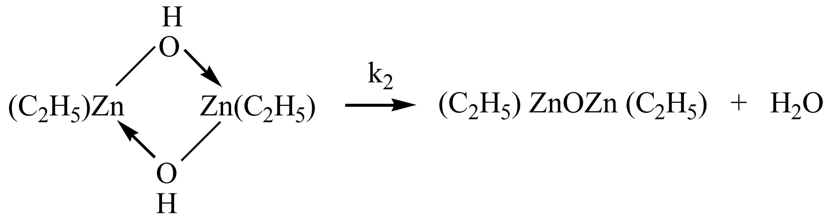
$$(C_2H_5)\,ZnOZn\,(C_2H_5) \;+\; H_2O \longrightarrow (C_2H_5)\,ZnOZnOH \;+\; C_2H_6$$

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

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

Later, the kinetics of the reaction was studied by Herald et al. [42]. They proposed;

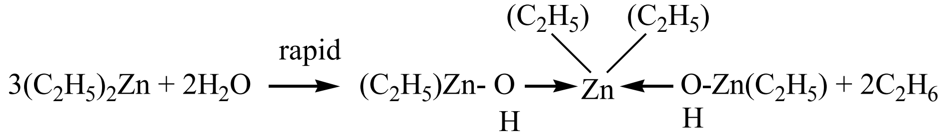
$$H_2O \;+\; Zn(C_2H_5)_2 \xrightarrow{k_1} (C_2H_5)\,ZnOH \;+\; C_2H_6$$



$$H_2O + (C_2H_5)\,ZnOZn\,(C_2H_5) \xrightarrow{k_3} (C_2H_5)\,ZnOZnOH + C_2H_6$$

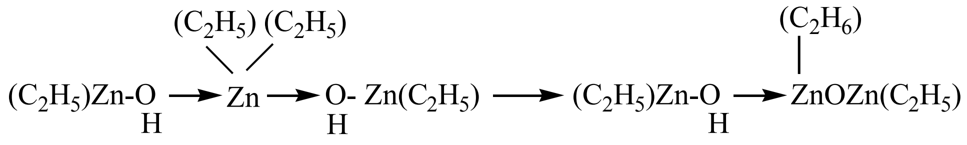
Where k₁ >> k₂ > k₃. The third step is the rate-determining step and the overall reaction is first order in [EtZnOH] and independent of the $ZnEt_2$ concentration.

It was found by Alyürük [43] that observed stoichiometry of the reaction and analysis formula of the resulting product were independent on the initial $H_2O/ZnEt_2$ ratio, when the ratio ≤ 0.66. He postulated the following mechanism;

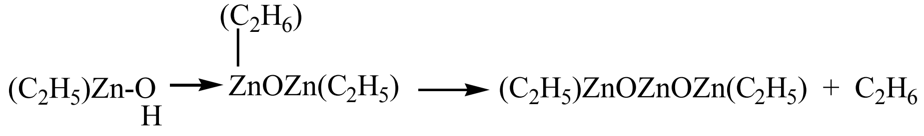


$$3(C_2H_5)_2Zn + 2H_2O \xrightarrow{\text{rapid}} (C_2H_5)Zn\text{-}\underset{H}{O} \rightarrow \overset{(C_2H_5)\ (C_2H_5)}{Zn} \leftarrow \underset{H}{O}\text{-}Zn(C_2H_5) + 2C_2H_6$$

It was suggested that the protons of the product are in Bronsted acid character and catalyze the decomposition in two stages.



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



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

1.3.4. Aluminum Alkyl-Water Catalyst System

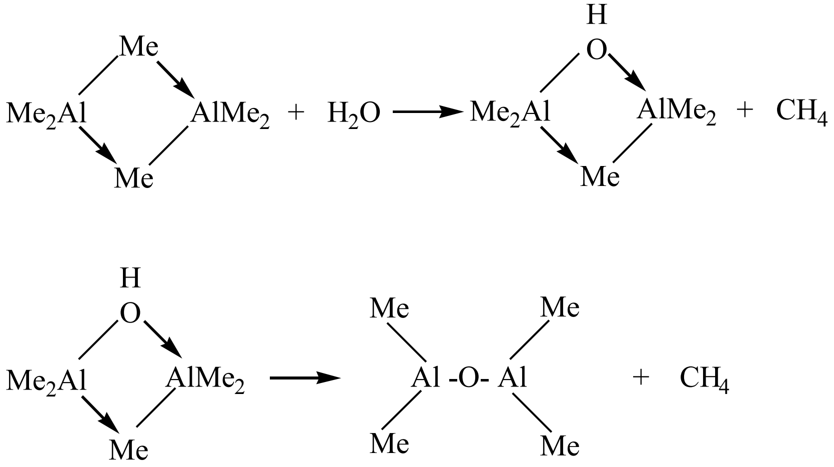
Alkyl aluminum-water catalyst system and its modified forms with reagents other than water show interesting catalytical characteristics for the stereoregular polymerization of epoxides and other many polar monomers. Most studied aluminum alkyls are $AlMe_3$, $AlEt_3$ and $Al(i\text{-}But)_3$. Beside the ease of preparation of this system, nature of the catalyst and its mechanism is complicated and could not be confirmed yet. Low stability of aluminum alkyls is one of the difficulties for this system. For example, $AlEt_3$ is known to decompose into diethyl aluminum hydride and ethylene [44] as;

$$(C_2H_5)_3Al \longrightarrow (C_2H_5)AlH + C_2H_4$$

Such decompositions may introduce different type of catalytical species into the hydrolysis product. But being mostly soluble in organic solvents and being homogeneous, are the advantages of this catalyst system over other metal alkyl-water catalyst systems.

The first aluminum alkyl used as a stereospecific catalyst was $AlEt_3$ [7]. In the absence of a modifier it gives only low molecular weight atactic polymers [45]. Also it was found that $AlMe_3$ produces low molecular weight atactic products in the absence of a modifier [11,46].

Kinetics of the hydrolysis of aluminum alkyls was studied first by Amdurski [47] and the presence of Al-O-Al linkages was predicted. Colclough et al. [11] studied the methane gas evolution in propylene oxide-trimethyl aluminum- water system where $H_2O/AlMe_3$ ratio was 0.5. They observed the rapid evolution of one mole of methane for each mole of water. Then the evolution was continued slowly to complete two moles of evolved methane for each mole of water in several hours. They formulated the hydrolyzation process as follows;



In the first step, water is reacted with trimethyl aluminum to form alkyl metal hydroxides and in the second step, by a slow intramolecular condensation a second mole of methane is eliminated. They concluded that bis-dimethyl aluminum oxide was not active for stereospecific polymerization and gave only atactic polymers through a cationic mechanism. However, it may go into inter or intra conversion to give stereospecific catalysts.

Ishia [48] and Saegusa et al. [49] suggested the reaction product to trimethylaluminum-water system might be,

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

They reported that n=1 predominates when $H_2O/AlEt_3$ molar ratio was 0.5. When ratio was between 0.5-1.0 predominating product or products were those with n > 1. They observed the precipitation of some product when the ratio was over two.

Later, Tani et al. [50] studied the hydrolysis of triethyl aluminum in etheral media.

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

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

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

$$\longrightarrow \quad \longrightarrow \quad \longrightarrow (C_2H_5)_2Al\,[-OAl(C_2H_5)-\,]_n\,OAl(C_2H_5)_2$$

On the contrary of previous work, it was suggested that water takes part through the hydrolysis reaction, not to disappear at the first step of hydrolysis. Although they assumed that water took place in each step of poly(alkyl aluminum oxide) formation, their assumption seems to be inadequate where such compounds can also be formed by thermal polycondensation of bis-dialkyl aluminum oxides [51] as;

$$n[\,(C_2H_5)_2Al]_2O \xrightarrow{150\text{ - }160^oC} n(C_2H_5)_3Al + [-(C_2H_5)AlO-\,]_n$$

Since the product was a mixture of catalytical species, they tried to prepare $Et_2AlOAlEt_2$ by the elimination of side reactions due to water. They reacted Et_2AlOLi with Et_2AlCl in equimolar [52] as,

$$(C_2H_5)_2AlOLi + (C_2H_5)_2AlCl \longrightarrow (C_2H_5)_2AlOAl(C_2H_5)_2 + LiCl\,(ppt)$$

But the product could not be considered as pure catalyst since aluminum alkyl chlorides disproportionate by producing [52,53];

$$2R_2AlCl \rightleftharpoons AlR_3 + AlRCl_2$$

$$2AlRCl_2 \rightleftharpoons AlR_2Cl + AlCl_3$$

Also disproportionation of $Et_2AlOAlEt_2$ into $AlEt_3$ and polymeric product, $(-OAlEt-)_n$ is possible.

In a series of work, which was carried out in this department [54-60], the most stable organoaluminum ($AlMe_3$) compound was studied under high vacuum conditions to minimize the contamination. In these studies, dilute solutions of $AlMe_3$ in dioxane was hydrolyzed with dilute dioxane solutions of water at low $H_2O/AlMe_3$ molar ratios. It was observed that one mole of methane was evolved instantaneously for every mole of water used initially, by indicating the consumption of all water. Then another mole of methane was formed slowly. Proposed reactions are as follows;

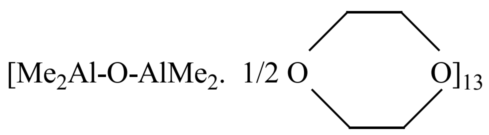
$$Al(CH_3)_3 + H_2O \xrightarrow{\text{very rapid}} (CH_3)_2AlOH + CH_4$$

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

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

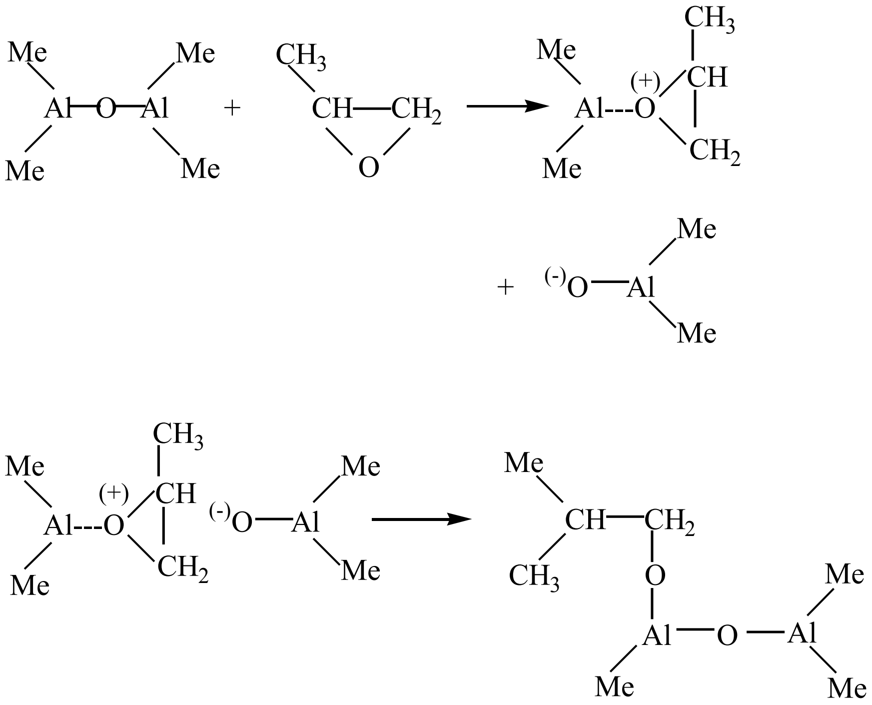
$$(CH_3)AlOAl(CH_3)OH + Al(CH_3)_3 \xrightarrow{k_3} (CH_3)_2AlOAl(CH_3)OAl(CH_3)_2 + CH_4$$

The obtained hydrolysis product was confirmed by analytical results to be a 13-mer form of bis dimethylaluminum oxide dioxane complex.



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.

Stereoregular polymerizations of propylene oxide by using polymethylaluminumoxide (PMAO) (the formula of PMAO is; $Me_2Al(OAlMe)_xMe_2$) and bis-dimethylaluminum oxide (BMAO) were studied by Öktem et al. [58,59]. Catalytic activities of several PMAO and BMAO samples with different degrees of polymerizations (DP) was investigated. Only a slight improvement of the stereoregular yield was observed by increasing the DP of the used catalyst. However, no significant difference in the catalytic activity between PMAO and BMAO with a variety of degree of polymerization. It was concluded that the methyl aluminum oxide repeating units are the active species in the stereoregular polymerization and catalytic activity cannot be ascribed either to the presence of an "undetected impurity" or an "unidentified unique structure of PMAO". The detailed description of the stereoregular polymerization of PO with BMAO and a greater understanding of the mechanism of the process were given [59]. The mechanism is as follows;



^{13}C-NMR study of thermally fractionated PPO samples showed that K-polymers (high molecular weight polymers) contain a considerable amount of configurational and structural irregularities. The amount of these irregularities increases as M_v of the fraction decreases, and it is maximized in D-polymers (low molecular weight polymers).

Polymerization of an other epoxide; styrene oxide with nickel ethyl xanthate, under air, nitrogen and vacuum conditions was studied by Kayatürk [61]. It was found that poly(styrene oxide) samples obtained under nitrogen and air atmosphere were partially crystalline having irregular head to head and regular head to tail sequence. It was also shown that the polymerization proceeded in cationic and/or coordinate cationic mechanism, which gives low molecular weight (Mv=850~1450) poly(styrene oxide).

In summary, coordination catalysts produce high molecular weight isotactic poly(propylene oxide). However;

i. They are very sensitive to moisture, air etc. Hence they are difficult to prepare and store and they are not well identified.

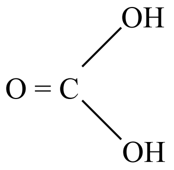
ii. Catalytical efficiency of these catalysts is usually very low 400-4000 metal atom can only produce one stereoregular chain.

iii. Together with high molecular weight tactic polymer, also rather large quantities of low molecular weight polymers are produced

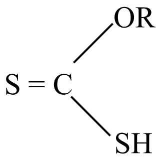
It appears that, this field of polymer chemistry requires a new coordination catalyst that is simpler in nature, more stable to atmospheric contaminations and produce higher molecular weight polymers with higher efficiency.

1.4. Polymerization of Propylene Oxide with Metal Xanthates

Xanthates are salts of xhantic acid, which is alkyl dithiocarbonic acid with two oxygen atoms in carbonic acid replaced by sulfur and one hydrogen atom replaced by an alkyl group [62]:



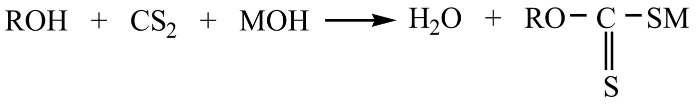
Carbonic acid



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. Xanthate were discovered by Zeise [62] 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.

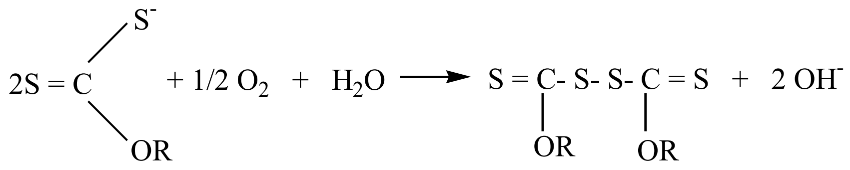
Xanthates are the reaction products of carbon disulfide with an alkoxide. They are formed by combination of the three reactants in the stoichiometric ratio 1:1:1, with the elimination of water. The general reaction is:



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

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 [63]. Many such catalysts are prepared by the reaction of alkyl metals (for instance dialkyl zinc, trialkyl aluminum) with active hydrogen compounds, oxygen or sulfur. Alkyl metals 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 [63]. 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 [64] studied metal xanthates as potential catalysts for stereoregular polymerization of propylene oxide. She used zinc isopropyl xanthate as the catalyst for polymerization of propylene oxide. In her M.Sc. thesis, she showed that these catalysts give high molecular weight poly(propylene oxide), and they are almost resistant to air and moisture. In characterization studies of formed polymers no spherulites were detected with polarized microscope. Also DSC and ^{13}C-NMR spectra of the products supported the microscopic results, therefore zinc isopropyl xanthate was reported as a unique catalyst to produce high molecular weight atactic PPO.

In 2001, catalytical activity of several transition metal xanthates in the coordination polymerization of propylene oxide was studied by Soysal [65]. Tin, copper and iron isopropyl xanthates were found to be catalytically active. In order to complete the work initiated by Bolat [64], zinc xanthate catalysts were examined in detail. The effect of alkyl group on the catalytical activity studied by synthesizing isopropyl, ethyl, 2-octyl xanthate catalysts. It was observed that as the alkyl groups become larger, stability of zinc xanthate catalysts against atmospheric impurities increase. Poly(propylene oxide), samples obtained with those catalysts were practically uncrystallizable. However, ^{13}C-NMR studies showed the presence of some partial stereoregularity on the polymer chains.

In summary, metal xanthate catalysts;

(i) produce high molecular weight, atactic poly(propylene oxide) with high percent conversion.

(ii) reduce polymerization time.

(iii) are stable, therefore can be used without high vacuum conditions which simplifies the polymerization conditions.

(iv) have high catalytical efficiency than organometallic catalysts

1.5. Fractionation of Partially Stereoregular Poly (propylene oxide)

1.5.1. Thermal Fractionation

A meaningful microstructural analysis of a partially stereoregular poly (propylene oxide) sample is only possible if a fractionation according to stereoregularity, in other words, separation of the whole sample into fractions of identical stereoregularity can be achieved to a reasonable extent.

For the case of poly(propylene oxide) Booth et al. [66], Çolak et al. [67] and Uğur et al. [68] observed some evidences for the possibility of such kind of fractionation from isooctane solution. Booth et al. [66] dissolved the high molecular weight polymer produced by zinc di-ethyl and water catalyst in isooctane at 60^{o}C and obtained phase separation by lowering the temperature incrementally to 0^{o}C. They observed that above 40^{o}C, high molecular weight polymers precipitated as solid phases. They were identical in average molecular weight but different in melting points. These results were interpreted as a separation of fractions according to difference in their ability to crystallize under given conditions. Below 40^{o}C, they obtained liquid-liquid phase separation with fractionation occurring on the basis of molecular weight. The fractions obtained were claimed as wholly amorphous that couldn’t be crystallized from solution.

Çolak et al. [67] applied the same procedure to poly(propylene oxide) prepared by bis-dimethyl aluminum oxide-dioxane catalyst. His results differed from Booths in two major points. He observed solid-liquid phase separation from 50^{o}C to 0^{o}C. The melting points of the fractions obtained decrease throughout this temperature range and average molecular weight of the precipitates decrease as well with decreasing separation temperature. He also noticed that the melting points of the fractions were identical with the fractions obtained at the same temperature in Booths study, although their molecular weights are extremely different. Because of these observations he claimed that the relation between precipitation temperature and molecular weight were not due to molecular weight control on precipitation. And he proposed that the precipitation occurred according to stereoregularity difference between the chains.

Poly(propylene oxide) samples obtained by using either bis-dimethyl aluminum oxide catalyst or Pruitt-Baggett catalyst, were separated into a succession of fractions differing in stereoregularity by Uğur et al. [68]. Each fraction was characterized by ^{13}C-NMR, DSC, GPC and viscometer techniques. ^{13}C-NMR examinations proved that the structural regularity of the polymers decrease with decreasing separation temperature. It was also observed that, the fractions obtained from different polymers (using different catalyst and polymerization conditions) at the same temperature and under similar separation conditions, have equivalent structural regularities. It should be also noted that the molecular weight of such fractions shows a remarkable difference. On the other hand, if a series of fractions from a given polymer was examined a tendency of decrease in molecular weights of fractions by lowering of separation temperature was observed. This observation can be explained by the fact that longer chains of poly(propylene oxide) tend to be more stereoregular than shorter ones.

These results were in agreement with a fractionation process where phase separation occurs on the basis of structural regularity rather than molecular weight. Therefore, it was concluded that it is possible to fractionate PPO into fractions with differing stereoregularity.

1.5.2. Column Fractionation

Column fractionation of poly (propylene oxide), synthesized by Pruitt-Baggett catalyst, was studied by Hartani et al. [69]. Owing to the necessity of using very dilute solutions in thermal fractionation and the fractions obtained were too small in amount to permit detailed characterization of these fractions, a column fractionation method was designed and applied to partially stereoregular poly(propylene oxide).

A column packed with glass beads was used to fractionate partially stereoregular poly(propylene oxide). PPO was first crystallized onto the glass beads from isooctane solution by stepwise lowering the column temperature. Each layer of PPO, which was deposited at different temperature ranges, was extracted by washing the beads with several columns full of isooctane. Thus several fractions differing in both stereoregularity and molecular weight were obtained by progressively increasing the extraction temperature and the solvent residence time in the column. It was concluded that by using the procedure described above, PPO could be fractionated on the basis of structural and steric regularity. The observed steady increase in the molecular weight of fractions with extraction temperature was interpreted as being due to the fact that the stereoregularity of chains increases with the molecular weight.

Thermal fractionation of PPO (K-polymer), synthesized by zinc ethyl xanthate catalyst, was achieved by applying the same procedure as described above by the author of this thesis in her undergraduate research project [70]. The fractions were characterized by viscosity measurements and ^{13}C-NMR studies. In contrast to Soysal’s conclusions it was found that molecular weight of the fractions did not decrease as the precipitation temperature was decreased. In fact, the second fraction precipitated at 37^{o}C had the lowest molecular weight among the others. It was thought that the reason of this unexpected result might due to an experimental error. In addition, ^{13}C-NMR studies showed the presence of some partial stereoregularity on the polymer chains according to order in the number of splitting of the fractions.

Table 1.1. Thermal Fractionation

1 **F**$^{(a)}$	**T**$_p^{(b)}$ **(^{o}C)**	**% w**$_i^{(c)}$	**M**$_v^{(d)}$ **x 10**$^{-6}$
F$_1$	42	6.83	----
F$_2$	37	14.08	0.014
F$_3$	32	9.02	2.300
F$_4$	25	13.69	0.290
F$_5$	0	56.37	----

(a) F = fractions (b) Tp = precipitation temperature (c) w_i = percent weight fraction (d) M_v = viscosity average molecular weight

1.6. Aim of This Work

Since Lal [63] did not characterize the metal xanthate synthesized PPO on the grounds of stereoregularity Bolat [64] and Soysal [65] had attempted to observe any signs of tacticity in the several zinc alkyl xanthate catalyzed PPO, by microscopy, DSC and ^{13}C-NMR techniques. Probably due to imprecise fractionation, samples those contained large quantities of amorphous material hence in the previous research product were wrongly identified as ‘atactic’. But the results of this author in her undergraduate research project apparently contradicted those conclusions. However, the results in the undergraduate research project were based only few samples and insufficient number of measurements.

Therefore present work was initiated with intention of:

a) Whether or not metal xanthate synthesized PPO is completely atactic

b) Whether or not metal xanthate synthesized PPO can be crystallized

c) If such synthesized PPO is partially tactic but uncrystalizable examine the anomalous solution properties of this polymer where at high temperatures lower molecular weight but at lower temperature higher molecular weight fractions separate out from the solution.

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.

2.1.2. Reagents

Diethyl ether, was supplied by Merck.

Acetone, was supplied by Merck.

Potassium hydroxide (Riedel-de.Haën),carbon disulfur (Merck), $ZnSO_4.7H_2O$ (Merck) was used without purification.

2-octanol, was supplied by Aldrich. It was distilled by fractionation column.

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

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 vacuum.
ii) Mixing the reagents in vacuum.

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

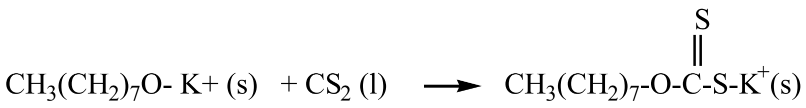
The dry N_2 box allows handling air sensitive reagents with gloves, under inert gas (N_2) atmosphere. Before using dry box, it was filled with N_2 gas and the interior moisture in the box, was dried by placing P_2O_5. Keeping the inside pressure of the box slightly higher than the atmospheric pressure 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 2-octyl Xanthate

Potassium 2-octyl xanthate was synthesized by following the procedure described by Vogel [71]. KOH and 2-octanol were refluxed for one hour. At the end of reflux, the warm solution was decanted. CS_2 was added drop wisely 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. Finally, 20 ml of dry diethyl ether was added and the resulting potassium 2-octyl 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:

$$KOH\ (s) + CH_3\text{-}(CH_2)_7\text{-}OH(l) \longrightarrow CH_3(CH_2)_7O\text{-}\ K^+\ (s) + H_2O\ (l)$$



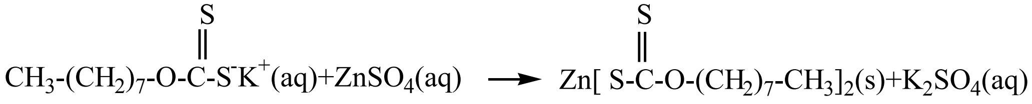
$$CH_3(CH_2)_7O\text{-}\ K+\ (s) + CS_2\ (l) \longrightarrow CH_3(CH_2)_7\text{-}O\text{-}\overset{\overset{S}{\|}}{C}\text{-}S\text{-}K^+(s)$$

potassium 2-octyl xanthate

2.3.2. Preparation of Zinc 2-octyl Xanthate

Metal xanthates are quite stable, but they would decompose in prolonged exposure to mist 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 Obtained potassium octyl xanthate was dissolved in degassed water and mixed with water solution of $ZnSO_4.7H_2O$. The reaction is as follows:



$$CH_3\text{-}(CH_2)_7\text{-}O\text{-}\overset{\overset{S}{\|}}{C}\text{-}S^-K^+(aq)+ZnSO_4(aq) \longrightarrow Zn[\ S\text{-}\overset{\overset{S}{\|}}{C}\text{-}O\text{-}(CH_2)_7\text{-}CH_3]_2(s)+K_2SO_4(aq)$$

zinc 2-octyl xanthate

The formed precipitate was sticky, non-crystalline mass that adhered strongly to glass. Hence, it could not be filtered. Therefore, it was washed with cold water to remove Zn^{2+} and SO_4^{2-} ions.

Since only very small amount of product formed, it was not further purified with recrystallization. Resulting Zinc 2-octyl xanthate was dried then dissolved in 100 ml benzene and stored in dry N_2 box.

2.3.3. Polymerization of Propylene Oxide with Zinc 2-octyl Xanthate

Polymerization experiments were carried out under high vacuum conditions. A defined amount of 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 propylene oxide was distilled on to the catalyst under vacuum by chilling the polymerization tube with liquid N_2. The polymerization tube was sealed off by flame and placed in a constant temperature bath at 82°C for a defined time. At the end of predetermined polymerization time, the polymerization tube was broken. Its content was dissolved in benzene, while heating and stirring, and transferred into a separatory funnel. Then, 1ml of 2M 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.

2.4. Fractionation of Polymer

The synthesized polymers were dissolved in 1.5 liters of isooctane at 70^{o}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. Both polymers, 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 (M_n) of the D-polymer was measured cryoscopically in recrystallised 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 2.1 below:

$$\Delta T = K_f\, m \tag{2.1}$$

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:

$$\Delta T/c = K / M_n + A_2c + A_3c^2 + \ldots\ldots \qquad (2.2)$$

$$\lim_{c\to 0} (\Delta T/c) = K / M_n \qquad (2.3)$$

$$1/M_n = [\ \lim_{c\to 0} [\ (\ \Delta T/c)/c\ ] \text{ x } \rho\ ] / 1000 \text{ x } K_f \qquad (2.4)$$

ρ : solvent density (g/cm^3)

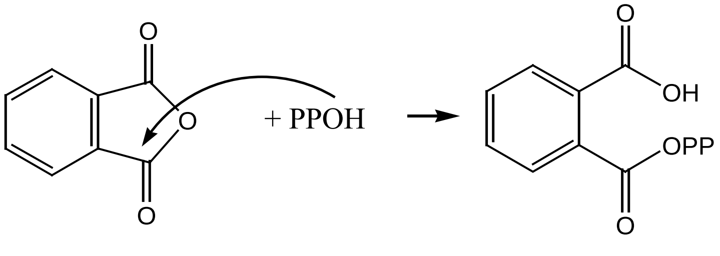
K_f : cryoscopic constant of solvent (^{o}C/ g cm^{-3})

c : solute concentration (g/cm^3)

M_n : number average molecular weight

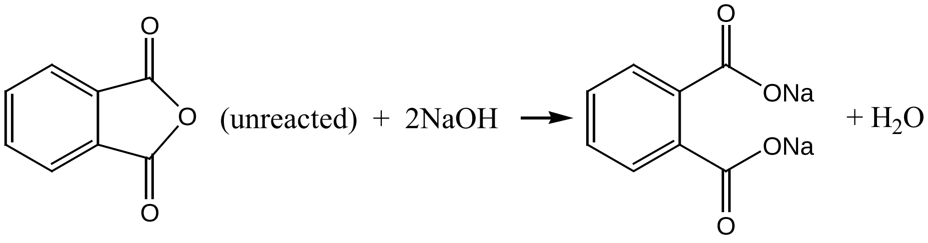
2.5.2. Determination of End-Group Functionality

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:

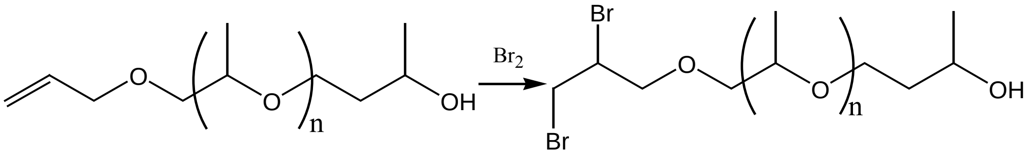


where PPOH indicates the hydroxyl end group of poly(propylene oxide)

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 cold 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;

$$M_n = 1\text{ g polymer} / (C_{OH} + C_{DB})/2 \qquad (2.5)$$

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

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

2.6. Fractionation of K-polymer

2.6.1. Thermal Fractionation

The procedure of Çolak et al. [66] was followed for fractionation of K-polymers. K-polymer was dissolved in 1.5 liters isooctane at 343K and put into a two necks flask in which a pear-shaped blister had been blown in the bottom (Figure A.2). The vessel was then placed in a constant temperature bath at 320K and the temperature of the system kept constant for 48 hours prior to isolation of polymer rich phase. The supernatant liquid was poured through a glass wool plug attached to the side neck into another fractionation vessel placed in a thermostat. The residues in the first flask and on the glass wool plug were dissolved in benzene and in order to prevent degradation diphenylamine was added as antioxidant. Benzene was removed by freeze-drying. Successive fractions were obtained by lowering the temperature in about 5 decrements and by applying the above procedure at each precipitation step

2.6.2. Column Fractionation

Column fractionation was carried out as described by Hartani et al. [69]. A column packed with glass beads (Figure A.3.) were used to fractionate K-polymer. K-polymer was first crystallized onto glass beads from an isooctane solution by lowering the temperature (Tp). At the end of precipitation time the solution was discharged off and stored for future use. The precipitate (deposited at temperature range) on the glass beads was partially dissolved with isooctane, for an allowed residence time, at constant solution temperature (Ts) where Ts= Tp + 5K. At the end of residence time the solution was discharged and dissolved polymer was isolated by evaporation of the solvent. The same procedure was repeated until the depletion of the polymer in the column by increasing solving residence time at the same Ts. The previously stored solution was charged into the column and above procedure was applied by decreasing the precipitation temperature. Thus, several fractions were obtained by progressively decreasing temperature and by increasing the solvent residence time in the column.

The fractionation column figure consists of mainly four parts.

i) The column: The column was made by a 1m length, 3 cm. diameter glass tube, which was filled with 0.5-1.0 mm glass beads. Glass beads used allowed about 300 cm^3 free volume in the column.

ii) The column tap: A rotaflo tap was used to charge or discharge the column. In order to avoid the flow of glass beads from the tap, 4.5 mm diameter lead spheres were placed between glass beads and the plug of the tap (Figure A.3).

iii) The constant temperature jacket: The temperature of whole column can be controlled within 0.5^oC by using a water jacket (Figure A.3). Water supply from a constant temperature bath was circulated through the column jacket.

iv) Column charging and discharging unit: To charge the column, a siphon tube S, connected to column tap was used. The polymer solution (g/l) was put into the siphoned tube and, the solution was driven into the pre-heated column applying pressurized air into the inlet A (Figure A.4). Using the same siphoned tube, pure solvent can be charged into the column as well. The column was discharged and contents of column were collected in the S-tube by applying pressurized air from inlet T, (Figure A.3).

The sticking property of poly(propylene oxide) to the glass beads was quite satisfactory. Although no filter was used in the column tap the discharged solutions appeared to be clear and homogeneous. The operation programmed on the fractionation column is described in Chapter III in detail.

2.6.3. Determination of Percent Degradation during Column Fractionation

In order to investigate whether there is degradation during column fractionation process, a definite amount of K-polymer with measured viscosity average molecular weight (M_v) was fractionated at 318K with different residence time. All fractions were collected together and final molecular weight (M_v) and mass were determined.

2.7. Characterization of Fractions

2.7.1 Determination of Molecular Weight

Viscosity average molecular weights were calculated form intrinsic viscosities measured with Ubbelohde viscometer in toluene at 25°C using Mark-Houwink Equation [72]:

$$[\eta] = K\, M^{a} \tag{2.6}$$

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

2.7.2 Determination of Melting Temperature

Benzene solution of fractions (about 0.003g/ml) were put drop wisely 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°C. The temperature of the oven was decreased gradually to room temperature in at least 12 hours. Such treated samples were found to be 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°C/min. The temperature at which spherulites were completely disappeared was noted as the melting point.

2.7.3. DSC Measurements

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°C to 100°C at heating rate of 2°C/min and then cooled to –60°C at cooling rate 2°C/min.

2.7.4. ^{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.

2.7.5. 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.

CHAPTER III

RESULTS and DISCUSSIONS

3.1. Polymer Samples

Soysal [65] has claimed that zinc 2-octyl xanthate polymerize PO into high molecular weight PPO with high efficiency and it was more stable than Zn(isoPr)Xt and ZnEtXt against atmospheric agents. Therefore, ZnOcXt was used for polymerization of PO in this work.

Synthesized zinc 2-octyl xanthate was a sticky viscose mass. It was washed with degassed water in order to remove water-soluble salts (K_2SO_4 and $ZnSO_4$) and residual water was evaporated under reduced pressure. Zinc 2-octyl xanthate gave colorless to pale yellow and perfectly clear solution in benzene. The solution was stable, no precipitation or turbidity developed during prolonged storage in dry N_2 box. Polymerizations were carried out by mixing ZnOcXt with propylene oxide in 1/1000 (mole/mole) ratio.

In order to investigate the solution properties and characterize PPO, two polymer samples were synthesized by using the same catalyst solution. Polymerization conditions are given in Table 3.1.

Table 3.1. Polymerization Conditions

	Moles of monomer	**Moles of catalyst (x 10^3)**	**Polymerization time (h)**	**Polymerization temperature (^{o}C)**	**% conversion**
P_1	0.143	0.128	52	82	46
P_2	0.286	0.256	52	82	55

Polymer samples were fractionated from a dilute isooctane solution into two contrastingly different fractions: D-polymer and K-polymer. The former constituted the minor part (~24%) and it was pale yellow in color and oily polymer. The latter was high molecular weight, white and elastic polymer. Table 3.2. shows the amounts and percent weight fractions of D-polymer and K-polymer fractionated from P_1 and P_2 respectively. As, it was concluded by earlier authors [64,65] the ratio of high molecular weight fractions to low molecular weight fractions was higher than the polymer synthesized by organometallic catalysts.

Table 3.2. D-polymers and K-polymers in P_1 and P_2

Sample	**Amount of polymer (g)**	**Amount of D-polymer (g)**	**% $w_i$$^{(a)}$ D-polymer**	**Amount of K-polymer (g)**	**% $w_i$$^{(a)}$ K-polymer**
P_1	3.8	0.9	23	2.9	77
P_2	8.9	2.3	25	6.6	75

(a) % w_i : percent weight fraction

3.2. Characterization of D-polymer

D-polymer of P_1 was characterized by determination of number average molecular weight, IR and ^{13}C-NMR studies. With the purpose of comparison same characterization was also carried out for the PPO synthesized via anionic polymerization by using KOH. As explained in the introduction part it is known that anionic polymerization of PO yield PPO with double bonds and hydroxyl groups at the chain terminals.

Number average molecular weights of the polymers were measured with both cryoscopy and end group determination methods. Empirical 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. Hydroxyl and double bond terminals were measured by determination of end group functionalities of the polymers. The amount of end groups in 1-gram polymer and molecular weight of the polymer were calculated. The results are given in Table 3.3.

Table 3.3. The Determination of Number Average Molecular Weight

SAMPLE	**$M_{n(I)}^{(a)}$**	**$C_{OH}^{(b)}$ (mmoles)**	**$C_{DB}^{(c)}$ (mmoles)**	**$M_{n(II)}^{(d)}$**
D-polymer	528	0.132	4.159	466
PPO (anionic polym)	1506	1.775	0.131	1050

(a) $M_{n(I)}$: Number average molecular weight determined by cryoscopy (b) C_{OH}: OH functionality in 1-gram polymer (c) C_{DB}: Double bond functionality in 1-gram polymer (d) $M_{n(II)}$: Number average molecular weight determined by end group analysis

It is well known that in a typical anionic polymerization of epoxides chain transfer process causes the simultaneous formation of hydroxyl and double bounds like C=C. End group determination shows that D-polymer has both double bond and hydroxyl terminals. D-polymer was also examined spectroscopically to establish the nature of the end groups. The IR spectra of the D-polymer showed a low –OH stretching absorption peak at 3340cm^{-1} (Figure B.1). Also C-O-C peak at 1107 cm^{-1}, C-H stretching peak at 1455cm^{-1}, -CH_3 peak at 2871 and –CH_2- peak at 2972cm^{-1} were observed in the spectra. Some other peaks were observed may be due to impurities or degradation products, such as the peaks at 1739cm^{-1}, 2360cm^{-1} or 1374 cm^{-1}. The presence of unsaturated end groups was detected by ^{13}C-NMR study, and the spectrum was showed a sharp characteristic C=C peak at 128 ppm (Figure B.2). The presence of both double bond and hydroxyl end groups may indicate an anionic polymerization. If D and K-polymers are both formed in the same process, the mechanism of polymerization can be identified as coordinate-anionic polymerization, since simple ionic mechanism can only produce low molar mass atactic polymer.

3.3. Thermal Fractionation of K-polymer

K-polymer obtained from P_1 was fractionally precipitated from a dilute isooctane solution as described in Chapter II. Precipitation temperature, T_p, viscosity average molecular weight, M_v, weight fraction values, w_i, (calculated by dividing the weight of each fraction by total weight of the fractions), and melting temperatures, T_m, are given in Table 3.4.

Table 3.4. Thermal Fractionation of K-polymer

	$T_P^{(a)}$ (K)	$m_i^{(b)}$	$w_i^{(c)}$	$M_V^{(d)} \times 10^{-6}$	$T_m^{(e)}$ (K)
F_1	320	0.01545	0.00521	0.01	-
F_2	314	0.0012	0.00040	1.34	329
F_3	310	0.11736	0.03396	2.28	327.5
F_4	304	0.29388	0.09913	2.99	318
F_5	299	0.56245	0.18972	2.38	314
F_6	293	0.46047	0.15532	0.70	-
F_7	285	0.77374	0.26099	0.24	309.5
F_8	277	0.24154	0.08147	0.09	-
F_9	273	0.49853	0.16816	0.04	-

(a) T_p : precipitation temperature (b) m_i : mass of fractions (c) w_i : weight fractions (d) M_v : viscosity average molecular weight (e) T_m : melting point (measured by hot-stage polarizing microscope)

3.4. Characterization of Fractions

All the fractions obtained were analyzed for molecular weight with intrinsic viscosity measurements, for melting behavior with hot stage polarizing microscope and DSC, for microstructure with ^{13}C-NMR. The results of these analyses will be given separately.

3.4.1. Molecular Weight

In the lights of Uğur's [68] results the first fraction precipitated at 320K was expected to have the highest molecular weight. However, results (Table 3.4) show that the first fraction has the lowest molecular weight among the other fractions and this fraction did not crystallize at all. The exceptional behavior of this fraction will be discussed later in this chapter. In fact, there appears no relationship between the molecular weight of the fractions and precipitation temperature in the range of T_p=320-299K. Only a trend appears that below T_p= 299K, where molecular weight decreases with decreasing T_p. The variation of molecular weights supports the results of author's undergraduate research project [71] and Çolak's [67] results. This variation indicates that the phase equilibrium in thermal fractionation in the range of 320-299K T_p is not controlled at all with the molecular weight of the species. In order to provide further support for these results column fractionation of K-polymers was also carried out in this work.

3.4.2. Melting Behavior

In characterization studies of poly(propylene oxide) synthesized by metal xanthate catalyst, Bolat [64] and Soysal [65] could not detect spherulites with polarized microscope and melting points in DSC measurements. Only, PPO fractionated at $40^{o}C$ from dilute isooctane solution in Soysal's study, gave a characteristic singlet methyl peak at 17.8 ppm in ^{13}C-NMR spectrum and the splitting increased in the spectra of fractions precipitated at $25^{o}C$ and $0^{o}C$. This shows the polymer had partially stereoregular structure. Finally, they concluded that PPO synthesized with metal xanthates is atactic; hence uncrystallisable.

In this work, during the microscopic studies, the spherulites were detected and melting points of the fractions were measured with microscope and DSC. This observations show that poly(propylene oxide) synthesized by metal xanthate catalysts is crystallizable; hence has partial stereoregularity. Because stereoregular polymers are usually crystalline materials; whereas stereoirregular polymers are amorphous, stereoregularity and crystallinity are used synonymously in many cases. The shape (Maltese Cross) of the crystals is given in Figure 3.1. Also Figure B.3 shows DSC spectrum of F_3.

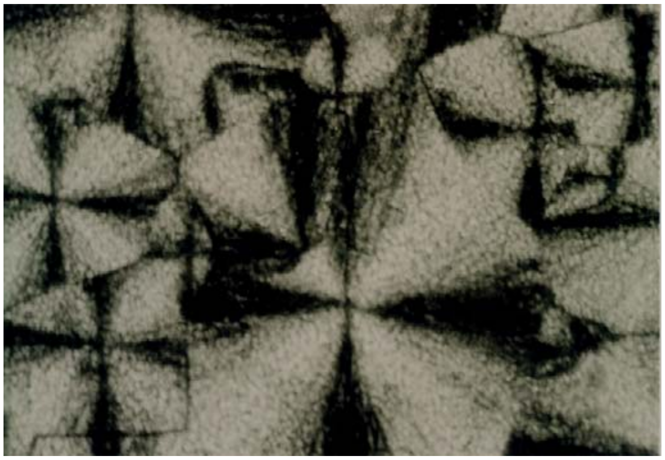
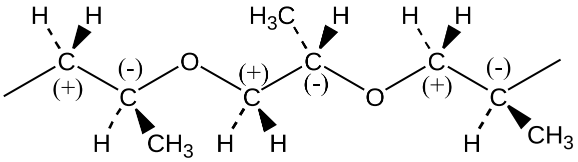


Figure 3.1. Photograph of Crystals

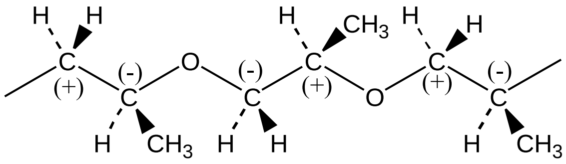
The melting point results (Table 3.4) show that T_m values of fractions, stereoregularity, decrease with decreasing precipitation temperatures. The results are in accordance with Çolak et al. [67] who concluded that stepwise thermal precipitation from dilute isooctane solution of K-polymers yielded a succession of fractions, which differed in melting point.

3.4.3. Structural Regularity

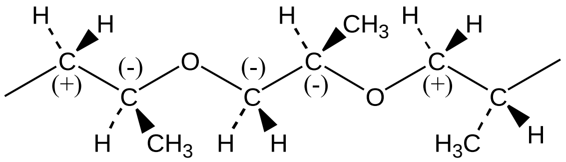
^{13}C-NMR spectroscopy was used to determine the degree of stereoregularity and the distribution of the steric irregularities possibly present in the fractions. Fischer projection of three possible stereochemical arrangements for poly(propylene oxide) are given below;



isotactic poly(propylene oxide)



syndiotactic poly(propylene oxide)



atactic poly(propylene oxide)

^{13}C NMR investigation of poly(propylene oxide) was studied by various authors [73-77] and their assignments can be summarized as follows:

i) The spectrum of isotactic poly(propylene oxide) has three single peaks of almost equal intensity. The up field 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.

ii) For the partially crystalline and amorphous polymer containing no head-to-head, tail-to-tail linkage, there are three peaks in the methine carbon and two peaks in the methylene carbon. Since the samples contain no abnormal linkages, these splitting arise from different configurational isomeric units. In comparison with the spectrum of isotactic polymer the two peaks in methylene carbon at 73.9 and 73.7 ppm were assigned to isotactic and syndiotactic dyads. And the three methine carbon peaks (at 75.9, 75.8, and 75.7 ppm) were assigned to isotactic, hetero tactic and syndiotactic triads.

According to these assignments, when we look at NMR spectra of fractions three characteristic methine carbon peaks and two methylene peaks are seen at the ppm values mentioned above. The peaks at 73.9 ppm (isotactic methylene) and 75.9

ppm (isotactic methine) have higher intensities than the other peaks. These results show that poly(propylene oxide) synthesized by metal xanthate catalysts is partially stereoregular. The spectra of F_3, F_5 and F_7 are given below;

i) The spectrum of F_3 (precipitation temperature is 310K; melting temperature is 327.5K) is shown in Figure 3.2.

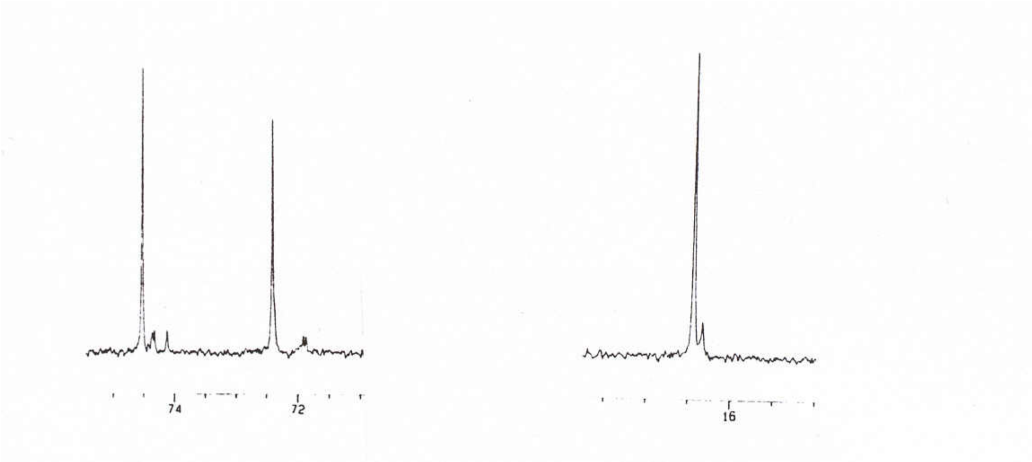


Figure 3.2 ^{13}C-NMR Spectrum of F_3

In this spectrum there are three methine peaks at 75.8 (isotactic), 75.6 (atactic) and 75.4 (syndiotactic) ppm and two methylene peaks at 73.7 (isotactic) and 73.2 (syndiotactic) ppm. The intensities of isotactic peaks are higher than the other peaks. It is also observed that methyl peak split into two peaks at 17.7 and 17.6 ppm. Uğur et al. observed the same splitting in some spectra of fractions and proposed that the up field peak refers to isotactic dyads and the other is possibly due to syndiotactic dyads.

ii) The spectrum of F_5 (precipitation temperature is 299K; melting temperature is 314K) is shown in Figure 3.3.

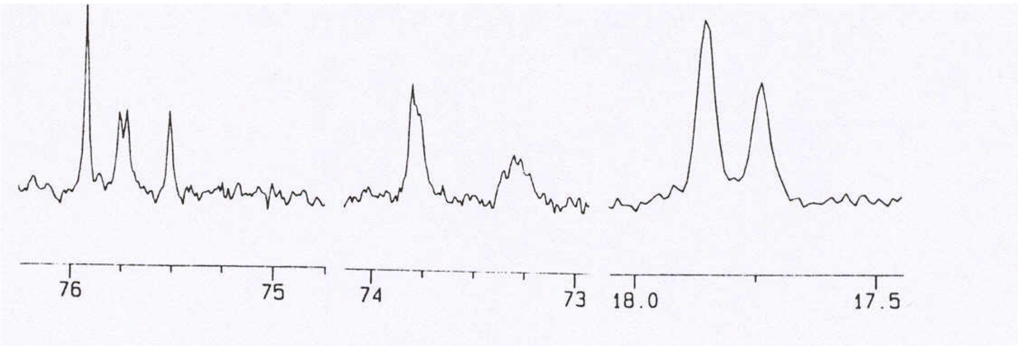


Figure 3.3 ^{13}C-NMR Spectrum of F_5

Three methine peaks at 75.9 (isotactic), 75.7 (atactic), 75.5 (syndiotactic) ppm, two methylene peaks at 73.8 (isotactic), 73.3 (syndiotactic) ppm and two methyl peaks at 17.8 (isotactic), 17.7 (syndiotactic) ppm are observed. However, the intensities of isotactic peaks decreased and the number of splitting increased.

iii) The spectrum of F_7 (precipitation temperature is 285K; melting temperature is 309.5K) is shown in Figure 3.4.

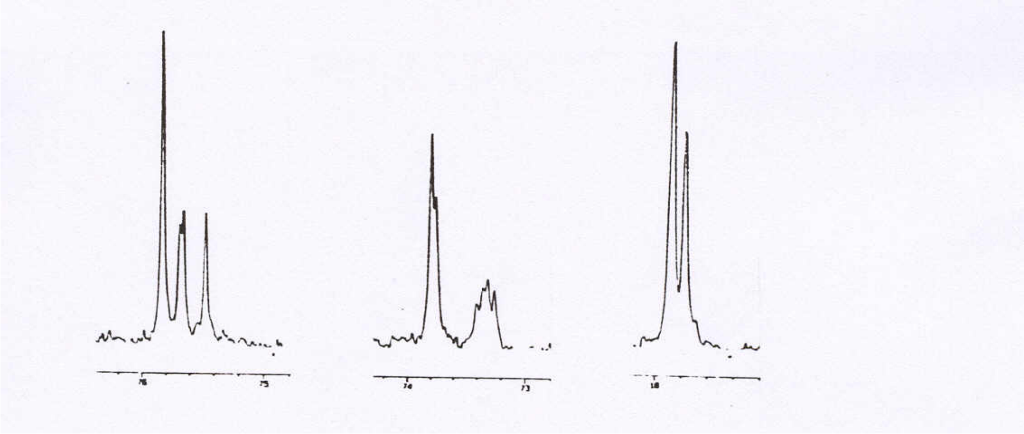


Figure 3.4 ^{13}C-NMR Spectrum of F_7

As seen in the spectrum the characteristic methine, methylene and methyl peaks are observed again. The number of splitting in the peaks is higher than that of the other fractions mentioned above which shows that the stereoregularity of the fraction decreased.

According to spectra of fractions it is observed that when the precipitation temperature and melting points of fractions decrease, the intensities of isotactic peaks decrease and number of splitting increases. These results support the idea that the stereoregularity of the fractions decreases as the melting point and the precipitation temperature decreases. It can be claimed that, by stepwise thermal precipitation of K-polymers, fractions can be obtained with differing in melting point and stereoregularity.

3.5. Column Fractionation of K-polymer

In this method, the glass beads were coated (or deposited) with only one layer of polymer film. To achieve this, column was charged with an isooctane solution of poly(propylene oxide), (in this attempt K-polymer obtained from P_2 was used). 5.7g/300ml at 343K. The temperature of the column was adjusted to T_p = 323K (precipitation temperature) and kept constant for 36 hours for complete precipitation of the polymer. At the end of this time, the solution was driven out of the column, the column was washed with cold isooctane and the solution was stored for future use.

The column was filled with isooctane at T_s= 343K (solving temperature) and after an allowed time (t_r, residence time), the solution in the column was discharged and the polymer fraction obtained by evaporating isooctane and freeze-drying the residue from benzene. Because of the tendency of poly(propylene oxide) toward oxidative degradation diphenylamine was added (0.01 wt%) to each fraction. The above procedure was repeated by increasing t_r, at each time, until the solution rate of the polymer become vanishingly small. The stored residue of the original solution was warmed until the clearness and, charged into the column and then, the precipitation temperature was adjusted to T_p = 316K. After 36 hours of precipitation time, the solution was discharged and again stored for future use. The obtained coat on the glass beads was fractionated as described above. The same procedure was repeated to the stored solution until T_p = 279K was reached.

3.6. Characterization of Fractions

All fractions were characterized by the methods that were applied for fractions obtained by thermal precipitation. The characterization results within the temperature ranges are given in the tables below. Discussions according to viscosity average molecular weights (M_v), melting behavior (T_m) and microstructure (^{13}C-NMR) will be given separately.

Table 3.5. Temperature Range 348-323K

Total weight of fractions Σw_i = 0.1001g, precipitation temperature T_p=323K, solving temperature T_s= 348K.

	$t_r^{(a)}$	$m_i^{(b)}$	$w_i^{(c)}$	$[\eta_i]^{(d)}$	$M_v x10^{-6(e)}$	$[\eta_i]xw_i$	$T_m^{(f)}$ (K)
P_1	5min	0.0387	0.0069	4.7782	1.23	0.0328	-
P_2	30min	0.0256	0.0045	4.3210	1.08	0.0197	330.3
P_3	180min	0.0252	0.0045	3.7956	0.91	0.0170	-
P_4	24hours	0.0431	0.0765	0.8348	0.13	0.0689	-
P_5	36hours	0.0432	0.0077	0.8344	0.12	0.0064	-
$P_{50}^{(g)}$	-	0.3561	0.0632	3.3718	0.88	0.2132	-

(a) t_r: residence time (b) m_i: mass of fractions (c) w_i: weight fractions (d) $[\eta_i]$: intrinsic viscosity (e) M_v: viscosity average molecular weight (f) T_m: melting point measured by DSC, - :no spherulites were observed under microscope and could not measured with DSC due to not enough amount of polymer for measurement (g) P_{50}:the residual part obtained during precipitation

Table 3.6. Temperature Range 323-316K

Total weight of fractions Σw_i = 0.05066g, precipitation temperature T_p=316K, solving temperature T_s=328K (solving temperature of P_{65} is 338K)

	t_r	m_i	w_i	$[\eta_I]$	$M_v x10^{-6}$	$[\eta_i] x w_i$	$T_m^{(a)}$ (K)	$T_m^{(b)}$ (K)
P_6	5min	0.0260	0.0046	3.940	0.96	0.0182	338	-
P_7	15min	0.0498	0.0088	3.474	0.81	0.0307	336	-
P_8	30min	0.0298	0.0053	3.142	0.68	0.0166	335	334.5
P_9	90min	0.0189	0.0034	2.038	0.39	0.0069	332	-
P_{10}	24hour	0.1103	0.0196	2.223	0.45	0.0435	331	-
P_{65}	24hour	0.0504	0.0089	3.307	0.76	0.0296	336	-

(a) T_m measured by hot-stage polarizing microscope (b) T_m measured by DSC, -: T_m could not be measured due to not enough amount of polymer

Table 3.7. Temperature range 316-309K

Total weight of fractions Σw_i = 0.07371g, precipitation temperature T_p=309K, solving temperature T_s=321K (solving temperature of P_{55} is 328K)

	t_r	m_i	w_i	$[\eta_i]$	$M_v x10^{-6}$	$[\eta_i] x w_i$	$T_m^{(a)}$ (K)	$T_m^{(b)}$ (K)
P_{11}	5min	0.0797	0.0141	9.8594	3.24	0.1395	321	321.1
P_{12}	15min	0.0457	0.0081	7.3176	2.18	0.0594	323	324.7
P_{13}	30min	0.0629	0.0117	5.5913	1.52	0.0624	322	322.2
P_{14}	180min	0.0608	0.0108	4.9624	1.29	0.0536	321	-
P_{15}	24hour	0.0894	0.0159	3.3236	0.76	0.0527	320	-
P_{55}	24hour	0.0738	0.0131	1.9011	0.36	0.0249	331	-

(a)T_m measured by microscope (b) T_m measured by DSC, -: T_m could not be measured with DSC due to not enough amount of polymer

Table 3.8. Temperature Range 309-302K

Total weight of fractions Σw_i = 0.20215g, precipitation temperature T_p=302K, solving temperature T_s=314K (solving temperature of P_{45} is 318K)

	t_r	m_i	w_i	$[\eta_i]$	$M_v x 10^{-6}$	$[\eta_i] x w_i$	T_m [(a)] (K)
P_{16}	5 min	0.3335	0.0592	7.4451	2.23	0.4409	-
P_{17}	30 min	0.3806	0.0676	6.9161	2.02	0.4674	-
P_{18}	180 min	0.2346	0.0416	5.4990	1.46	0.2290	-
P_{19}	24 hours	0.1443	0.0256	4.3670	1.09	0.1119	-
P_{20}	36 hours	0.0331	0.0059	0.3437	0.04	0.0020	-
P_{45}	24 hours	0.0124	0.0022	2.5617	0.54	0.0056	317

(a) T_m measured by microscope, -: no spherulites were observed under microscope and could not be measured with DSC due to not enough amount of polymer

Table 3.9. Temperature Range 302-293K

Total weight of fractions Σw_i = 0.20302g, precipitation temperature T_p=293K, solving temperature T_s=307K (solving temperature of P_{40} is 313K). T_m values are not given because no spherulites were detected under microscope and the amount of fractions for DSC measurements were not enough.

	t_r	m_i	w_i	$[\eta_i]$	$M_v x 10^{-6}$	$[\eta_i]$ x w_I
P_{21}	5 min	0.55266	0.09813	2.4481	0.51	0.24023
P_{22}	30 min	0.34700	0.06161	2.4411	0.50	0.15040
P_{23}	90 min	0.11400	0.02024	1.7310	0.32	0.03504
P_{24}	24hours	0.08795	0.01562	1.2094	0.19	0.01889
P_{40}	24hours	0.04180	0.00742	0.4788	0.06	0.00355

Table 3.10. Temperature Range 293-286K

Total weight of fractions Σw_i = 0.10892g, precipitation temperature T_p=286K, solving temperature T_s=298K (solving temperature of P_{30} is 303K). T_m values of fractions are not given because no spherulites were detected with microscope and DSC.

	t_r	m_i	w_i	$[\eta_i]$	M_v x10^{-6}	$[\eta_i]$ x w_I
P_{25}	5 min	0.19410	0.03446	0.6113	0.08	0.02107
P_{26}	30 min	0.20645	0.03666	1.4546	0.25	0.05332
P_{27}	180 min	0.14220	0.02525	1.3335	0.23	0.03367
P_{28}	24 hours	0.04974	0.00883	0.8490	0.12	0.0075
P_{30}	24 hours	0.02096	0.00372	0.4554	0.05	0.00169

Table 3.11. Temperature Range 286-279K

Total weight of fractions Σw_i = 0.1251g, precipitation temperature T_p=279K, solving temperature T_s=291K (solving temperature of P_{25} is 298K). T_m values of fractions are not given because they could not detected with microscope and DSC measurements.

	t_r	m_i	w_i	$[\eta_i]$	M_v x10^{-6}	$[\eta_i]$ x w_i
P_{29}	5 min	0.2552	0.04531	0.5641	0.072	0.02556
P_{30}	30 min	0.11765	0.02089	0.5480	0.069	0.01145
P_{31}	180 min	0.1095	0.01944	0.5793	0.074	0.01126
P_{32}	24 hours	0.11025	0.01958	0.7790	1.09	0.01525
P_{25}	24 hours	0.11195	0.01988	0.9984	1.53	0.01985

Table 3.12. Temperature Range 279-273K

	m_i	**w_i**	**$[\eta_i]$**	**M_v x10^{-6}**	**$[\eta_i]$ x w_i**
P_{33}	0.8024	0.14247	03573	0.039	0.05091

This fraction was obtained by discharging off polymeric solution from the column at 273K and evaporating isooctane.

3.6.1. Molecular Weight

In the previous work done by Hartani [69], it was observed that molecular weight of the fractions increase with increasing dissolving temperature. However, in the present work an opposite relationship was observed between the molecular weight and residence time. That is, fractions with higher Tm and higher molar mass surprisingly dissolve faster among the others. On the other hand fractions precipitated at T_p=318 and 309K contained some fractions those can only be redissolved at higher T_s (i.e. 338K instead of 328K and 328K instead of 321K). These fractions apparently have higher M_v than others. It appears that rate of solution is not only controlled by M_v and T_m of the polymers.

It is also observed in the tables above the molecular weight of fractions increase with increasing T_m of the fractions. This behavior will be discussed later in this chapter.

The viscosity average molecular weight of K-polymer was measured before the application of column fractionation. Intrinsic viscosity $[\eta]$ was found as 6.49 and molecular weight was found as M_v= 1.86 x 10^6. 5.7 gram polymer was used for fractionation and 5.6 gram was obtained after fractionation. After fractionation intrinsic viscosities of the fractions were multiplied by their weight fractions and the sum of these multiplications was calculated (Equation 3.1). This value is expected to be approximately equal to intrinsic viscosity of unfractionated polymer. However, intrinsic viscosity was found as 2.85, instead of 6.49.

$$\sum w_i \times [\eta_i] = 2.85 \tag{3.1}$$

This result shows that during column fractionation extensive degradation of polymers has taken place. To confirm this conclusion following experiment was carried out. K-polymer with known weight and molecular weight was fractionated as described above. The total weight of fractionated polymer was found exactly same to that of unfractionated polymer. However, molecular weight of the fractionated polymer was markedly lower than that of unfractionated polymer, showing the existence of a degradation during the fractionation process.

$W_i = 0.82$ gram $M_{vi} = 1.86 \times 10^6$
$W_f = 0.82$ gram $M_{vf} = 1.26 \times 10^6$

However this result cannot explain the observation that decreasing in molecular weight of fractions with increasing residence time during column fractionation. For example in Table 3.6, fraction P_6 is recovered in 5 minute t_r with $M_v = 9.6\text{x}10^5$ whereas P_8 obtained after 30 minute residence, with M_v=$6.8\text{x}10^5$. If degradation were this fast after 24 hours time M_v is expected to be much lower than $4.5\text{x}10^5$ (compare for P_{10}).

3.6.2. Melting Behavior

Melting points of several fractions were determined by hot-stage polarizing microscope and DSC measurements. The melting points of the fractions are given in the tables above.

In order to compare percent crystallinities of P_{11}, P_{12}, and P_{13}, heats of fusion (j/g) for fractions were found by comparing their transition peak area in DSC curves with that of standard with known weight and known heat of fusion. To obtain the crystallinity data, the heat of fusion of the sample must be compared with the heat of fusion of the theoretically 100% crystalline poly(propylene oxide). ΔH^o was known as 143.94 j/g [78]. By using the following formula heats of fusion and % crystallinities so calculated for P_{11}, P_{12}, and P_{13} given in Table 3.12. DSC spectra of fractions are given in Figure B.4, B.5, and B.6.

$$\% \text{ Crystallinity} = \frac{\Delta H \text{ sample}}{\Delta H^o} \times 100$$

Table 3.13. % Crystallinity

	T_m (K)	ΔH sample	% crystallinity
P_{11} (5 min)	321.11	3.069	2.13
P_{12} (15 min)	324.64	6.510	4.52
P_{13} (30 min)	322.27	6.934	4.82

The results show that % crystallinity of fractions increase with increasing residence time. In other words rate of solubility also decrease with increasing % crystallinity. Higher T_m of the fractions have not necessarily higher % of crystallinity can be explained by stereo-block character of the polymer where a number of atactic and tactic blocks with differing segmental lengths are combined in a chain. T_m is related with the average length of the tactic blocks, where segment terminals act as impurity decreasing the T_m. On the other hand the amount of atactic segments in the chains control the % crystallinity. These results can be explained by assuming following composition of the ZnOcXt polymerized PPO in Table 3.14.

Table 3.14. Hypothetical Composition of ZnOcXt polymerized PPO

C(a)	Structure	Properties
I	Few tactic blocks with high segmental length distributed among large quantities of atactic material.	High T_m, low % crystalinity, high Mwt, higher rate of solubility
II	Higher mass percentage of tactic blocks with differing average segmental length	Higher % crystalinity with lower rate of solubility. As the Mwt. decreases also length of tactic segmental blocks decrease
III	Almost completely atactic blocks; some tacticity may present but not enough for crystalinity.	Almost amorphous material with low T_p and T_s values

(a) composition

Thus at high temperatures Component I dissolves first, then Component II dissolves. Component III precipitate only at lower temperatures.

3.6.3. Structural Regularity

^{13}C-NMR spectra of several fractions with decreasing precipitation temperature and same residence time show almost the same results in thermal fractionation (Figure B.7, B.8, B.9, B.10, B.11, B.12, B.13). As the precipitation temperature decreases, the number of splitting increases and the intensities of isotactic peaks decrease. In the spectrum of P_9 Figure B.8. (T_p= 316K, T_s= 338K, t_r =90 min, T_m=333K) there are three main peaks at 75.9, 73.8 and 17.8 ppm of almost equal intensity. The up field peak at 17.8 ppm can be assigned to the methyl carbon, the peak at 73.8 ppm to the methylene carbon and the peak at 75.9 ppm to the methine carbon. Following the assignments given previously, these unsplitted absorption peaks are ascribed as regular isotactic structure. Therefore, it is concluded that P_9 is highly isotactic.

A series of fractions obtained in the temperature range (316-309K) were also analyzed for stereoregularity with ^{13}C NMR (Figure B.14, B.15, B.16, B.17, B.18, B.19). Three methine peaks, two methylene peaks and two methyl peaks are seen in all spectra of fractions. The number of splitting and the intensities of isotactic peaks increase, as the residence time of fractions increases (as in the case of % crystallinity). In fact, the spectrum of P_{55} (Figure 3.5) the fraction that is obtained by solving at 328K (has the highest melting point in this series of fractions, T_m=331K) shows three main peaks at 75.9 ppm (isotactic methine peak), 73.8 ppm (isotactic methylene peak) and 17.8 ppm (isotactic methyl peak). Therefore, P_{55} is concluded as highly isotactic fraction.

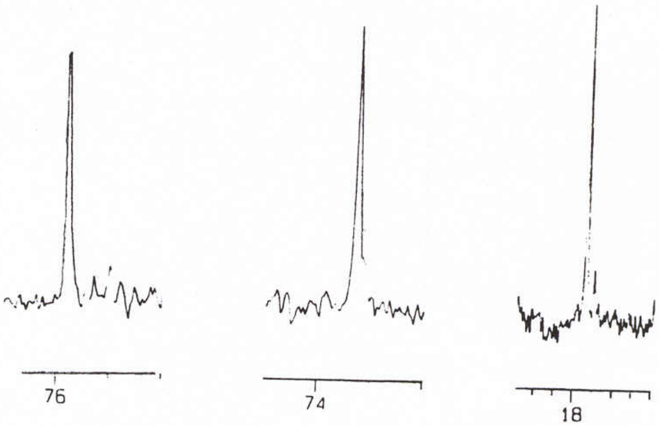


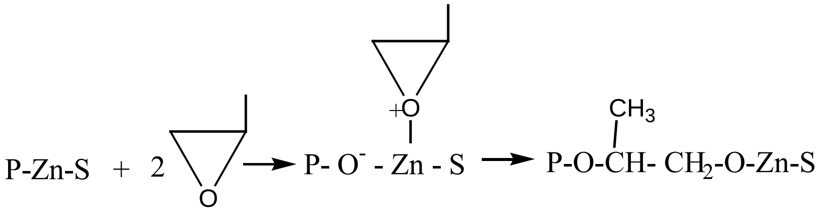
Figure 3.5. ^{13}C-NMR Spectrum of P_{55}

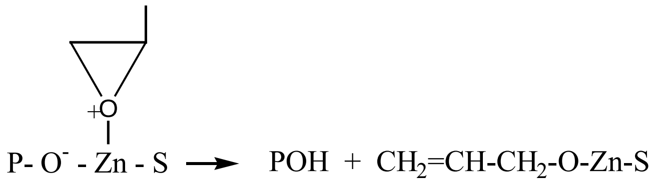
In summary, ^{13}C-NMR studies show that, column fractionation of K-polymers yielded a succession of fractions, which differed in melting points and stereoregularity.

3.7. A Tentative Comparison of Catalytic Activity of ZnOcXt with that of Pruitt-Baggett and Metal Alkyl-Water Systems

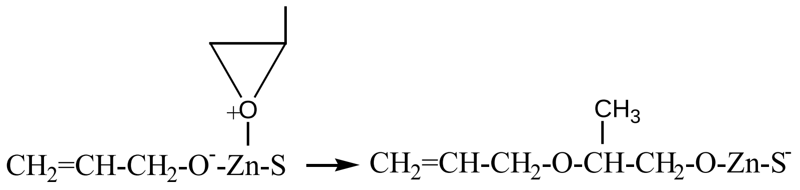
In this paragraph in spite of limited experimental evidences obtained in the present work, a tentative comparison of classical systems with ZnOcXt system will be attempted. The aim of this attempt is to provide some inspiration for the future researchers for designing new experiments. As explained in introduction section both Pruitt–Baggett systems and Metal Alkyl-Water systems produce D-polymers with only hydroxyl terminals together with some cyclic molecules. Although Takrouri [39] by Hittorf electrolysis showed that streoregular polymers grew on the anionic fragment of the catalyst, argued that the anion was not free to give a simple anionic polymerization, but it can only attack on the correctly coordinated and oriented monomer that is activated by the cationic fragment of the monomer bound ion pairs. However in ZnOcXt system D-polymers containing both hydroxyl and double bond terminals were present. This may indicate that the anionic fragment are comparatively free, to abstract protons from monomer to form allyl alcohols. In fact, Steiner-Pelletier [79] has shown that under anionic conditions, a methyl proton can be abstracted by an alkoxide group.

According to this mechanism Bolat [64] has suggested the reactions below where P donates poly(propylene oxide):





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



If, monomer bound ion pairs are looser the stereo-chemical control of ZnOcXt catalyst would be weaker. This can explain why observed tacticity of PPO obtained with this system is much lower than that of classical systems. For example in Pruitt-Baggett systems some fractions observed with T_m 342K but in this system the highest T_m was only 338K

Classical systems produce stereoregular PPO with tactic chain segments combined each other with head to head (or tail to tail) units. Presences of these irregular units which act as impurity, decrease the T_m of polymer. However ZnOcXt system there is significant amount amorphous material and the chains have stereo-block structures where tactic chains are combined with each other by atactic blocks. This structural difference can also be ascribed the looseness of ion pairs in the ZnOcXt system. In Pruitt-Baggett system a wrong monomer addition results to head to head (or tail to tail) linkage, blocking the active center into the dormant state. Owing to the tightness of the ion-pair re-activation of the system is difficult but once its activated produces isotactic blocks again. However in ZnOcXt system chain carrying anionic fragment is free enough to produce occasional atactic blocks.

Takrouri [39] measured intrinsic viscosity of freshly prepared Pruitt-Baggett catalyzed PPO. With the purpose of removing any Fe in the polymer washed this PPO with 0.1M HCl solution and measured the intrinsic viscosity again and found that molecular weight of PPO decreased by 1/3 factor. To make sure that this drop in molecular weight is not due to degradation, rewashed the already washed sample again with HCl solution and found no change in the molecular weight. Thus he claimed that freshly prepared PPO is consisting of PPO blocks joined to each other by Fe atoms. PPO obtained by ZnOcXt catalyst has also Zn atoms bound to polymer chains. The Zn atoms cannot be easily removed by HCl washing. The residual Zn usually separates as a precipitate during fractionation at high temperatures. Thus F_1 in Table 3.4 is presumably mainly Zn residue with some adsorbed polymer.

3.7.1. Future Research

In the light of present work following future researches may be suggested:

1. The weakest point in the present research is the degradation of the samples. Degradation probably occurred in distillation of large quantities of isooctane in order to isolate fractions. Since rotary evaporator was used for distillation was not in order distillations carried out at high temperatures and last about 30 minutes Therefore during the distillation at high temperatures extensive degradation is probable. Therefore in future in order to avoid degradation, fractions can be isolated by cooling the isooctane solution at low temperatures.

2. Electrical conductivity of ZnOcXt in etheric solutions might be studied.

3. Mechanical tests to PPO obtained either by Pruitt-Baggett system and ZnOcXt system may be studied to find out if there is a structural difference (i.e. stereo block or not) between them.

4. Some experiments can be designed (like Takrouri has done) to observe if there are any Zn metal combined PPO blocks.

5. % Crystallinity of each fraction might be determined by DSC.

CHAPTER IV

CONCLUSIONS

On the base of presented experimental data followings are concluded:

1. ZnOcXt catalyst polymerizes PO to high molecular weight, stereoregular, crystallizable polymer (K polymer) together with low molecular weight (=500 g/mol) D-polymer.

2. D-Polymer has double bond as well as hydroxyl terminals.

3. Presence of double bonds indicates an anionic coordinate mechanism.

4. K-polymers crystallize forming spherulites in the shape of Malta’s Cross.

5. K-polymers can be thermally fractionated on the basis of their melting temperature rather than molecular weight.

6. In column fractionation K-polymers were deposited on glass beads from isooctane solution in a narrow temperature interval. Then the precipitated samples were split into a number of fractions, by using isooctane at a higher temperature than the precipitation temperature, by increasing residence time of solvent from 5 minutes to several hours. It’s found that rate of solubility

is not controlled by molecular weight at all but it's controlled only percentage crsytallinity and melting temperature.

7. Highest melting temperature polymers, with relatively higher molecular mass showed faster rate of solution than that of lower T_m, lower molar mass but higher percent crystalline fractions. This discrepancy was accounted by suggesting a stereo-block structure where tactic blocks are bound each other with non-crystallizable presumably atactic blocks.

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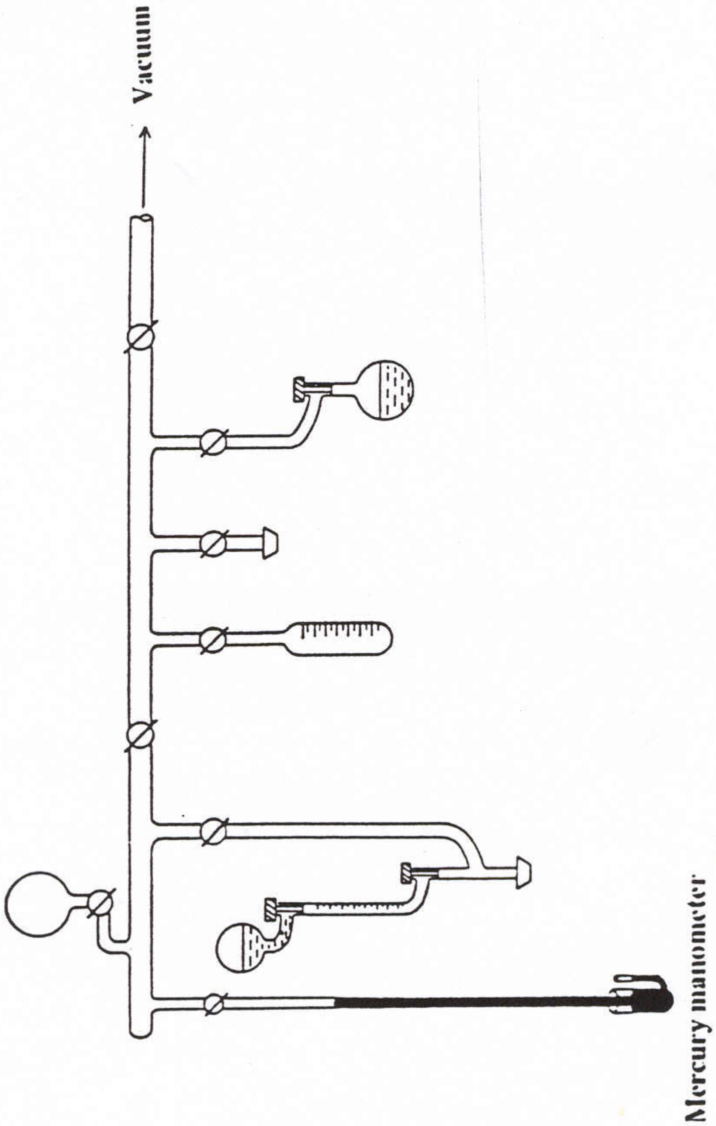
APPENDIX

A. APPARATUS



FigureA.1. Vacuum-Line

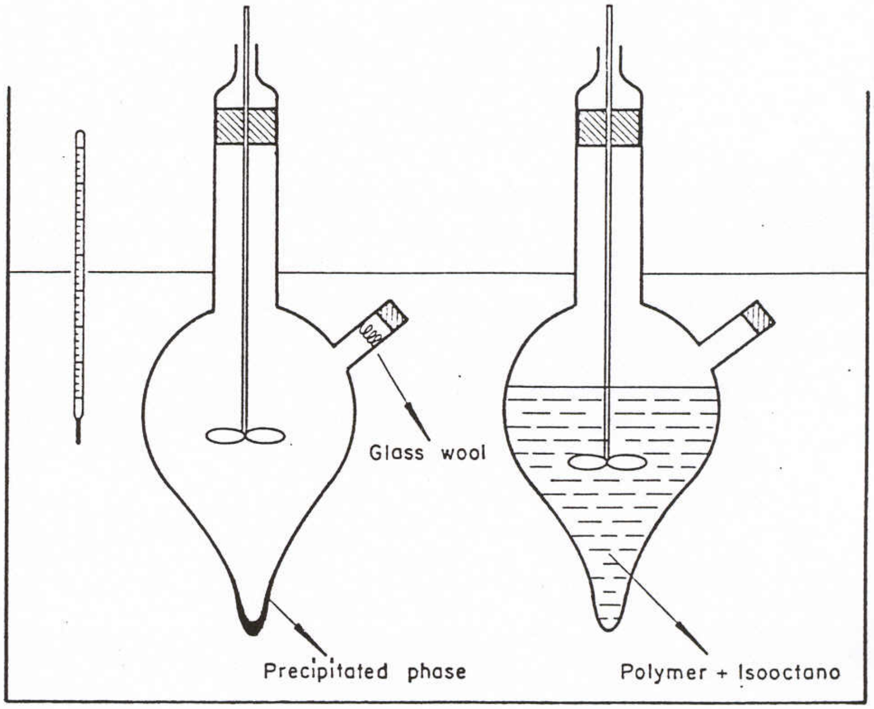


Figure A.2. Thermal Fractionation System

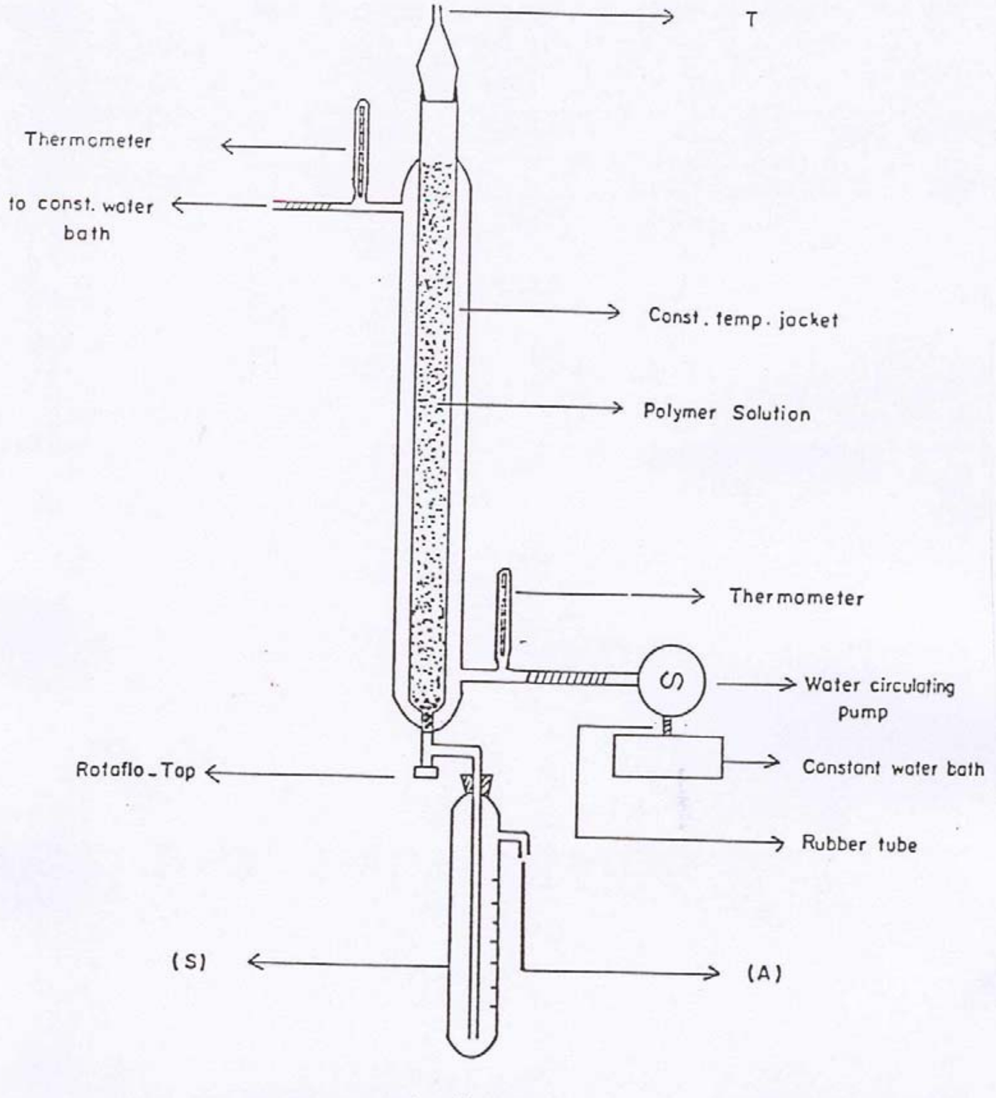


Figure A.3. Column Fractionation System

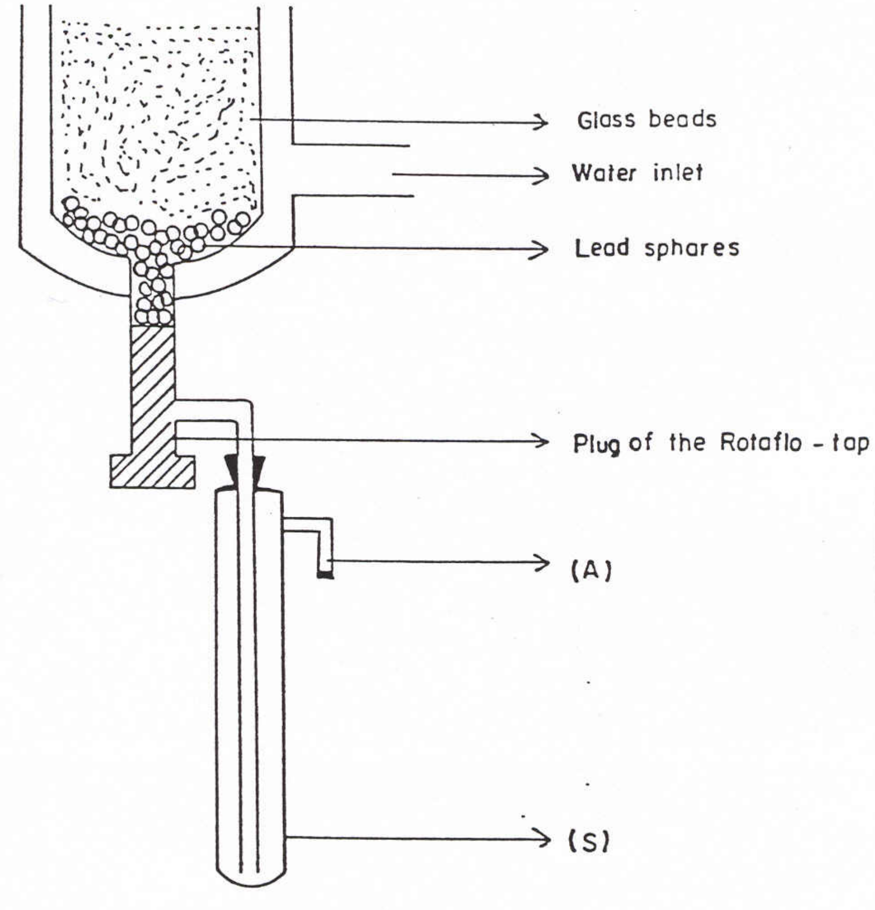


Figure A.4. Charging and Discharging Unit

APPENDIX B

SPECTRA AND GRAPHICS

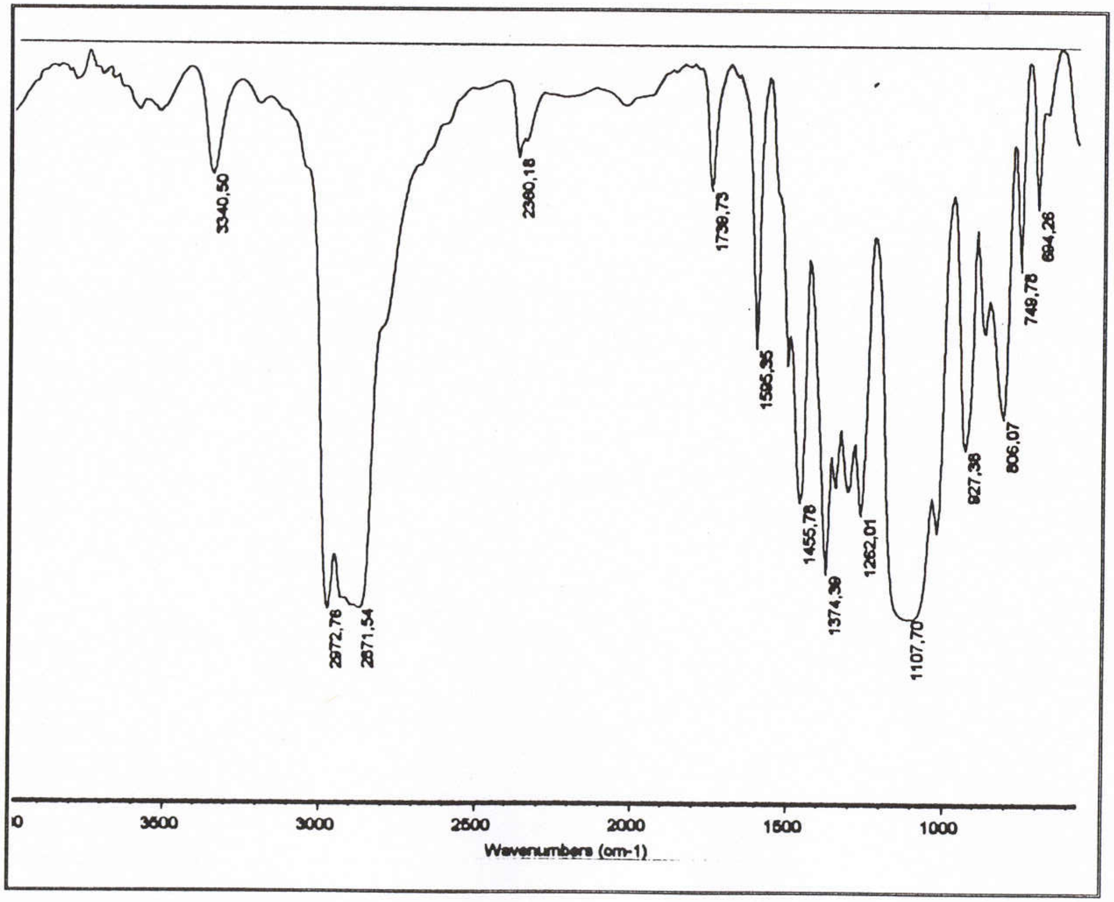


Figure B.1. IR Spectrum of D-polymer

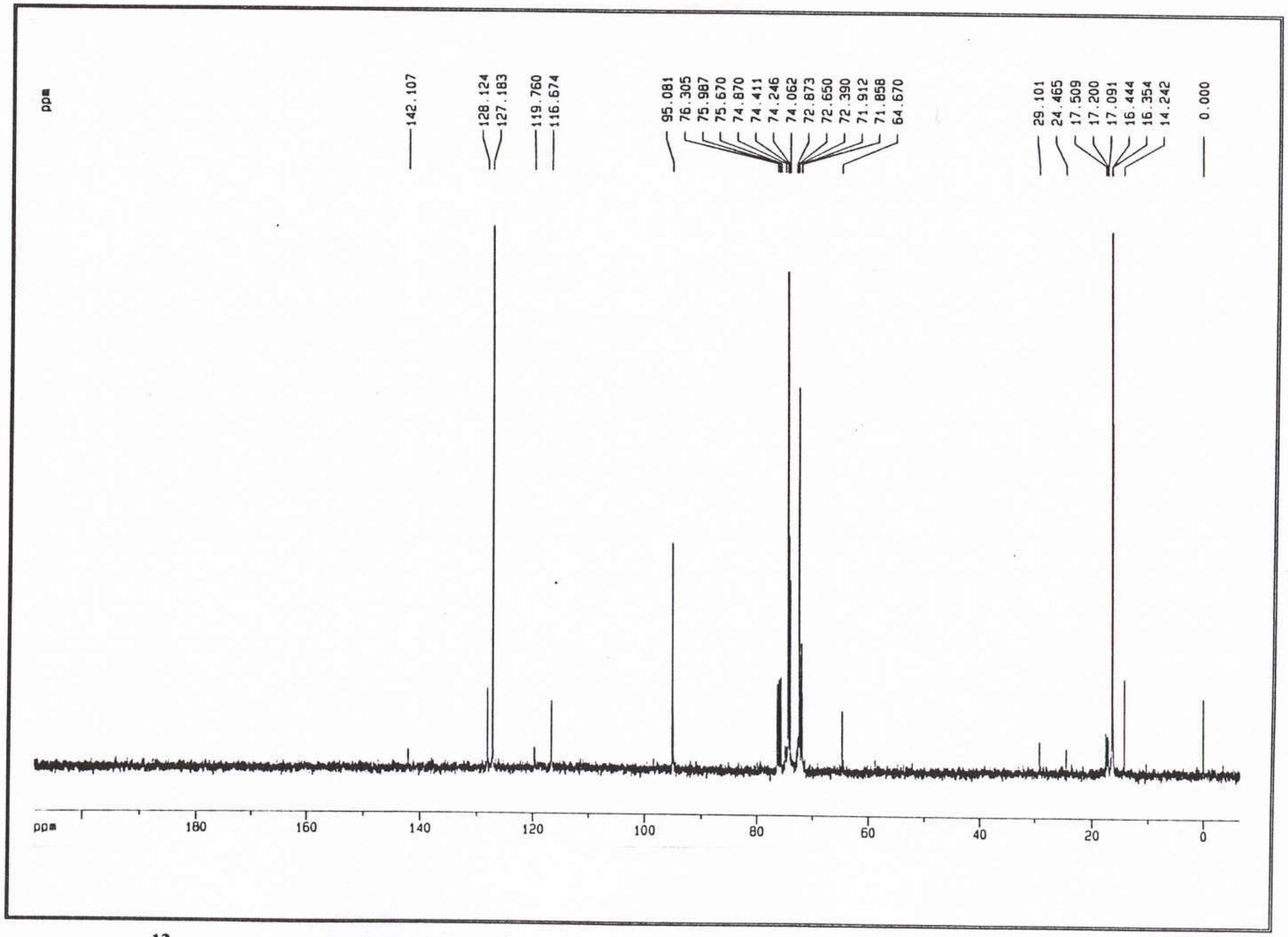


Figure B.2. ^{13}C NMR Spectrum of D-polymer

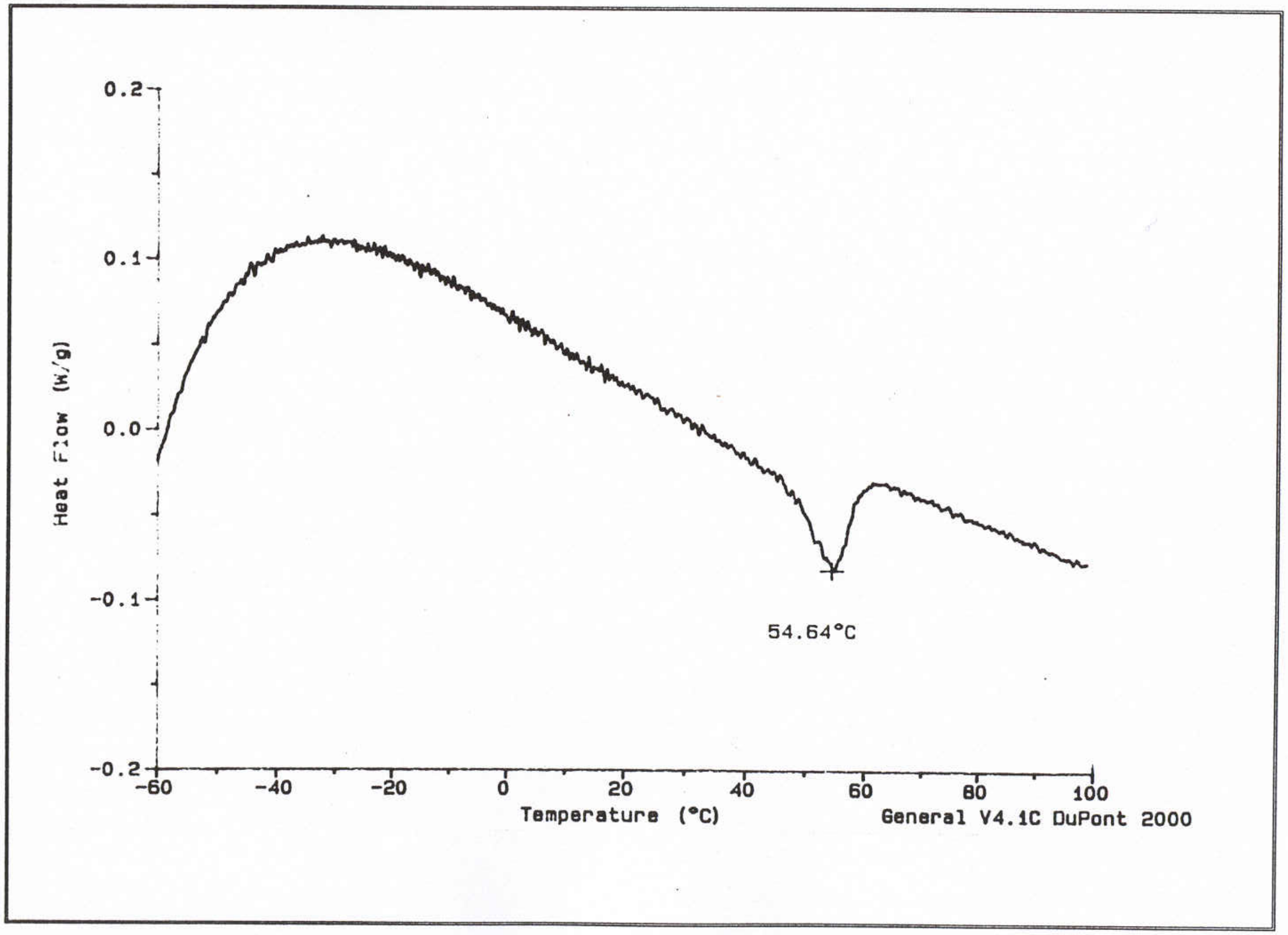


Figure B.3. DSC Spectrum of F_3

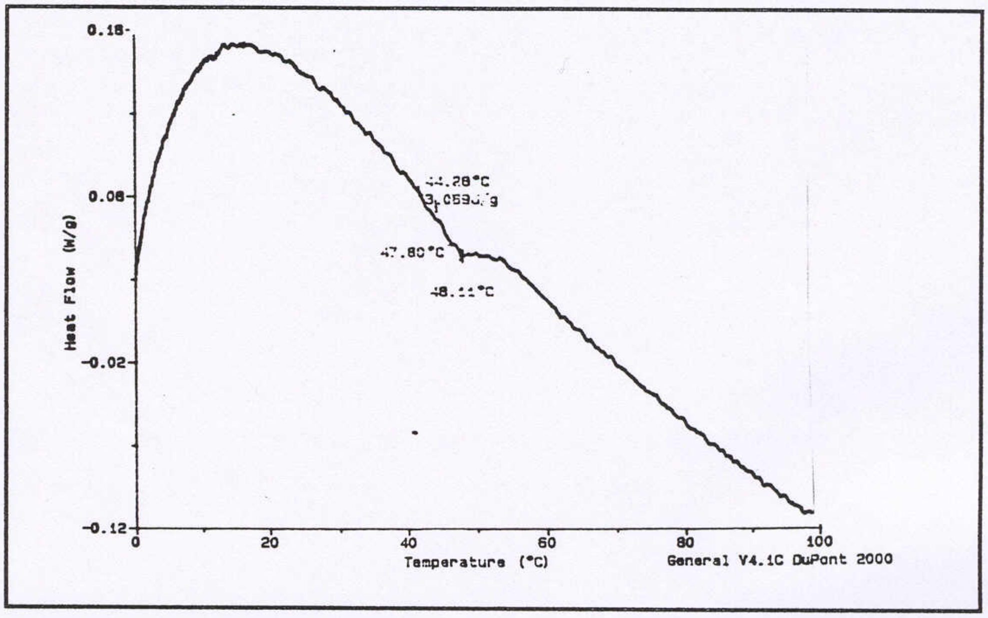


Figure B.4. DSC Spectrum of P_{11}

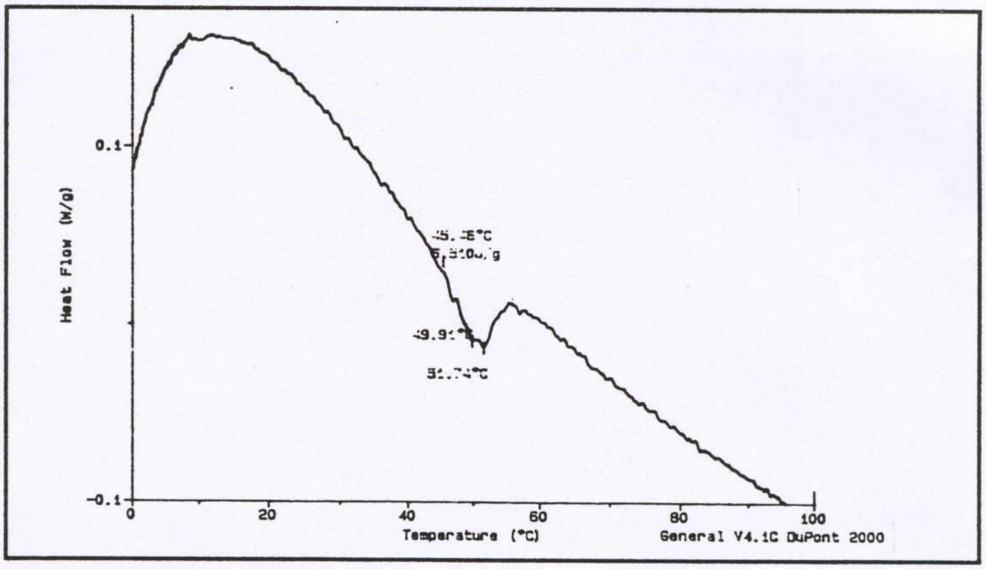


Figure B.5. DSC Spectrum of P_{12}

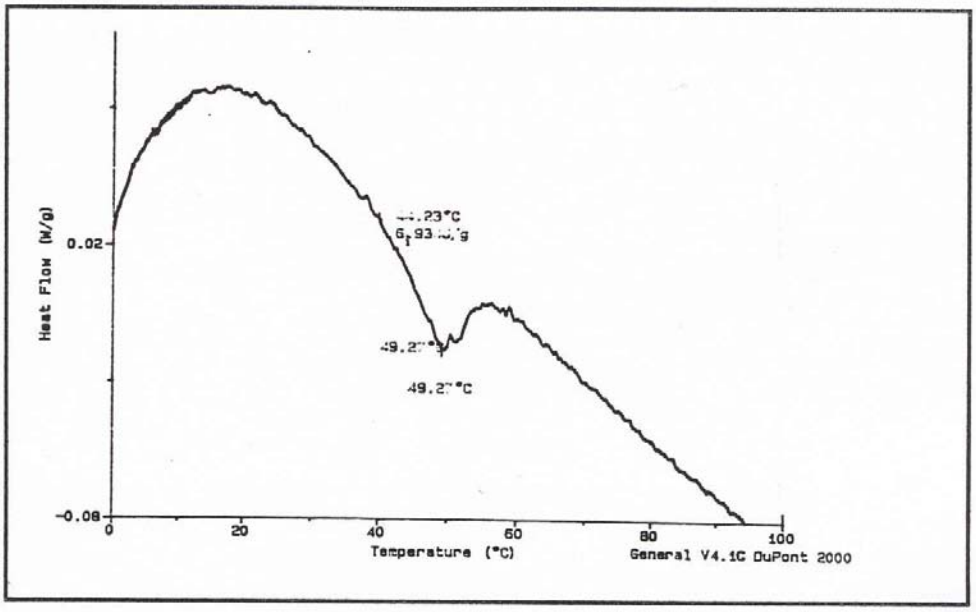


Figure B.6. DSC Spectrum of P_{13}

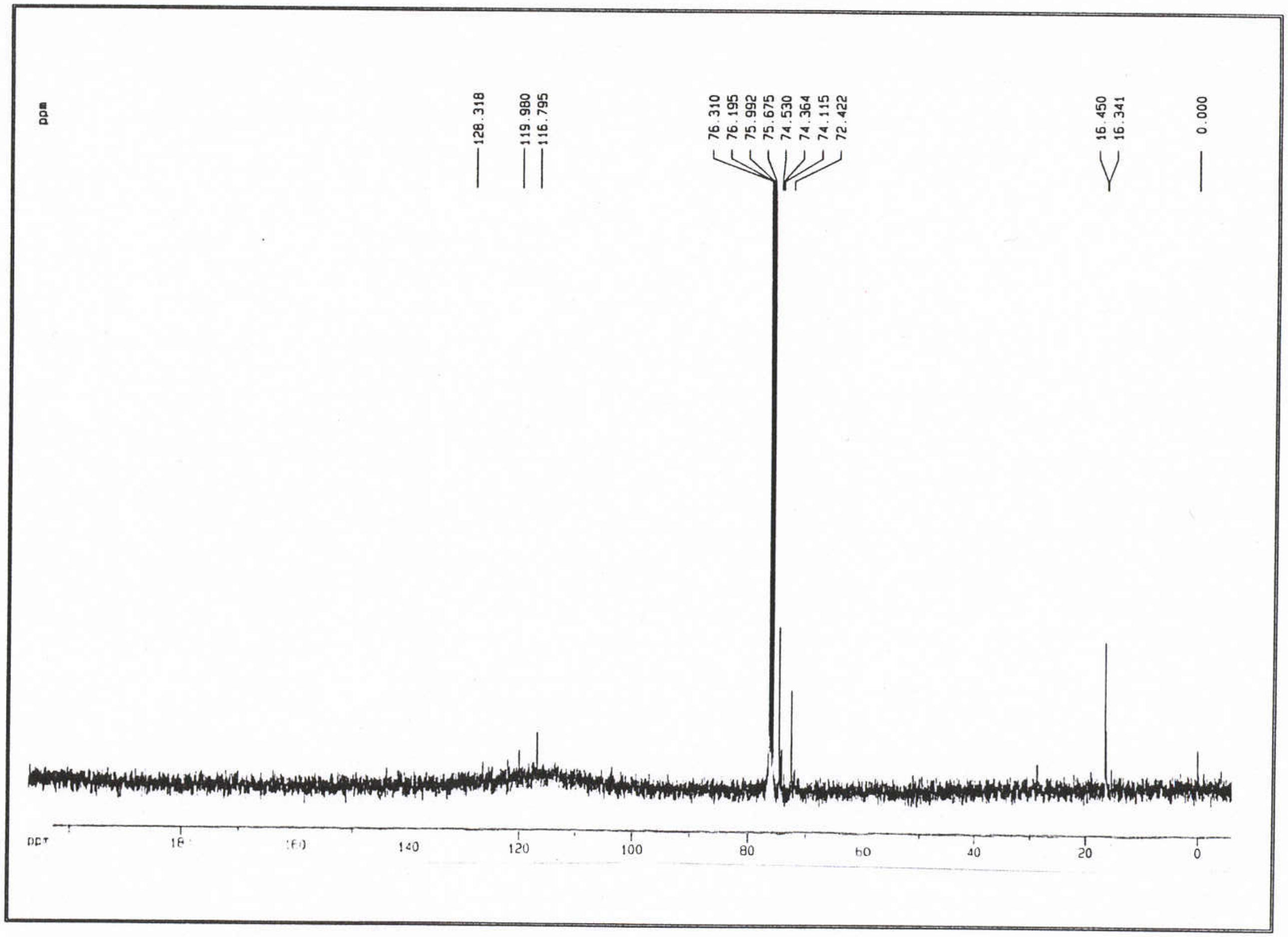


Figure B.7. ^{13}C NMR Spectrum of P_3

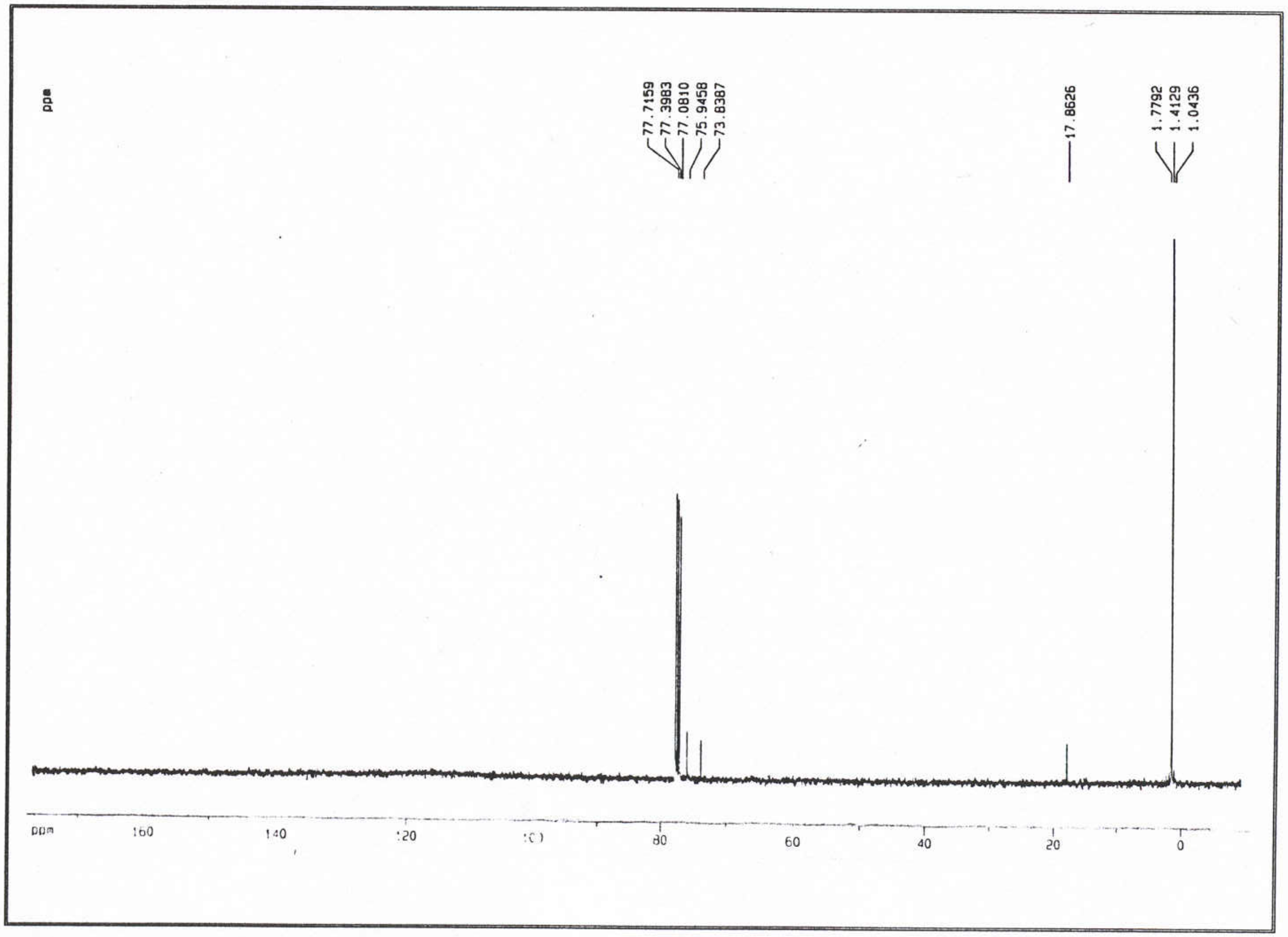


Figure B.8. ^{13}C NMR Spectrum of P_9

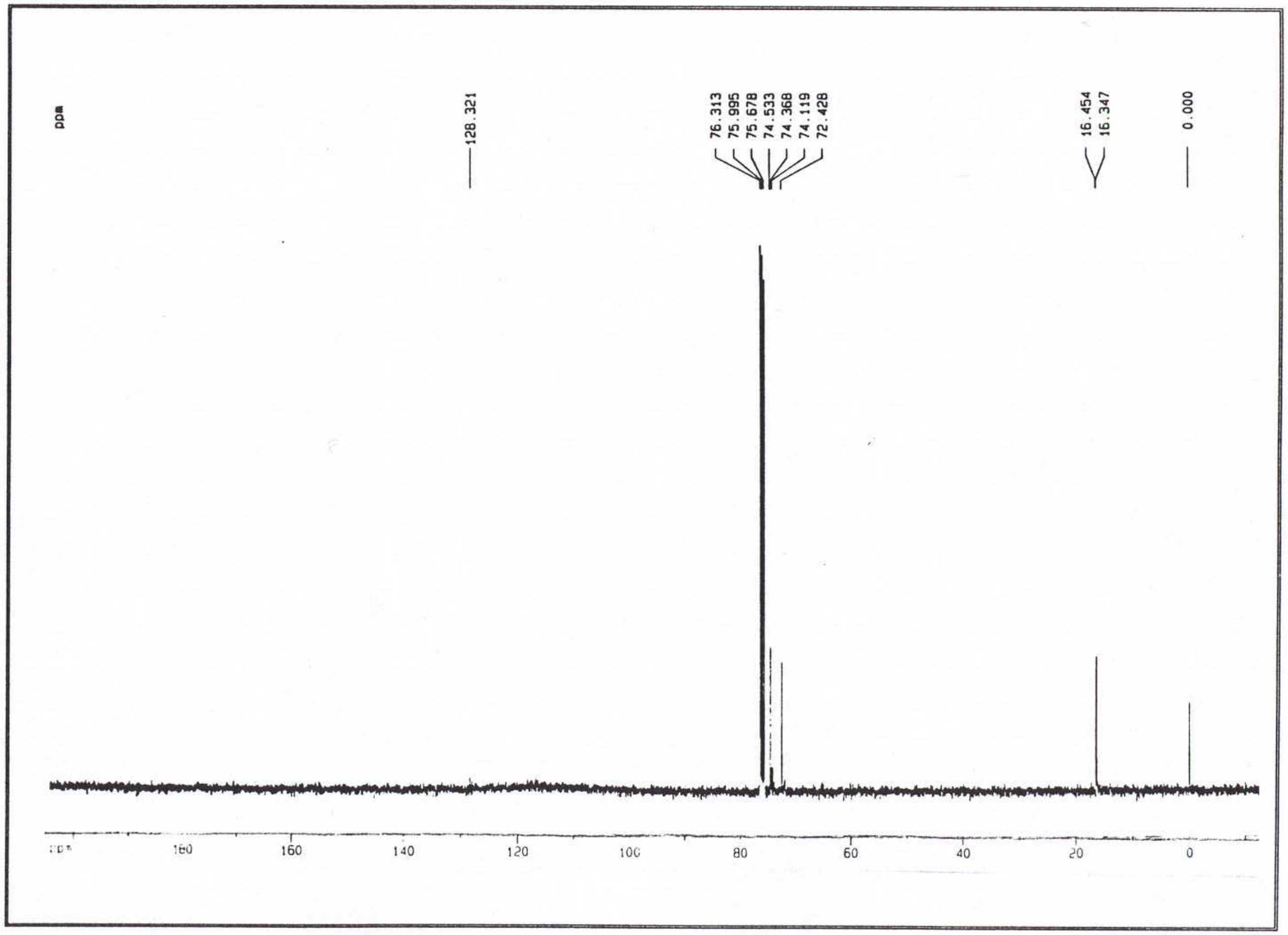


Figure B.9. ^{13}C NMR Spectrum of P_{14}

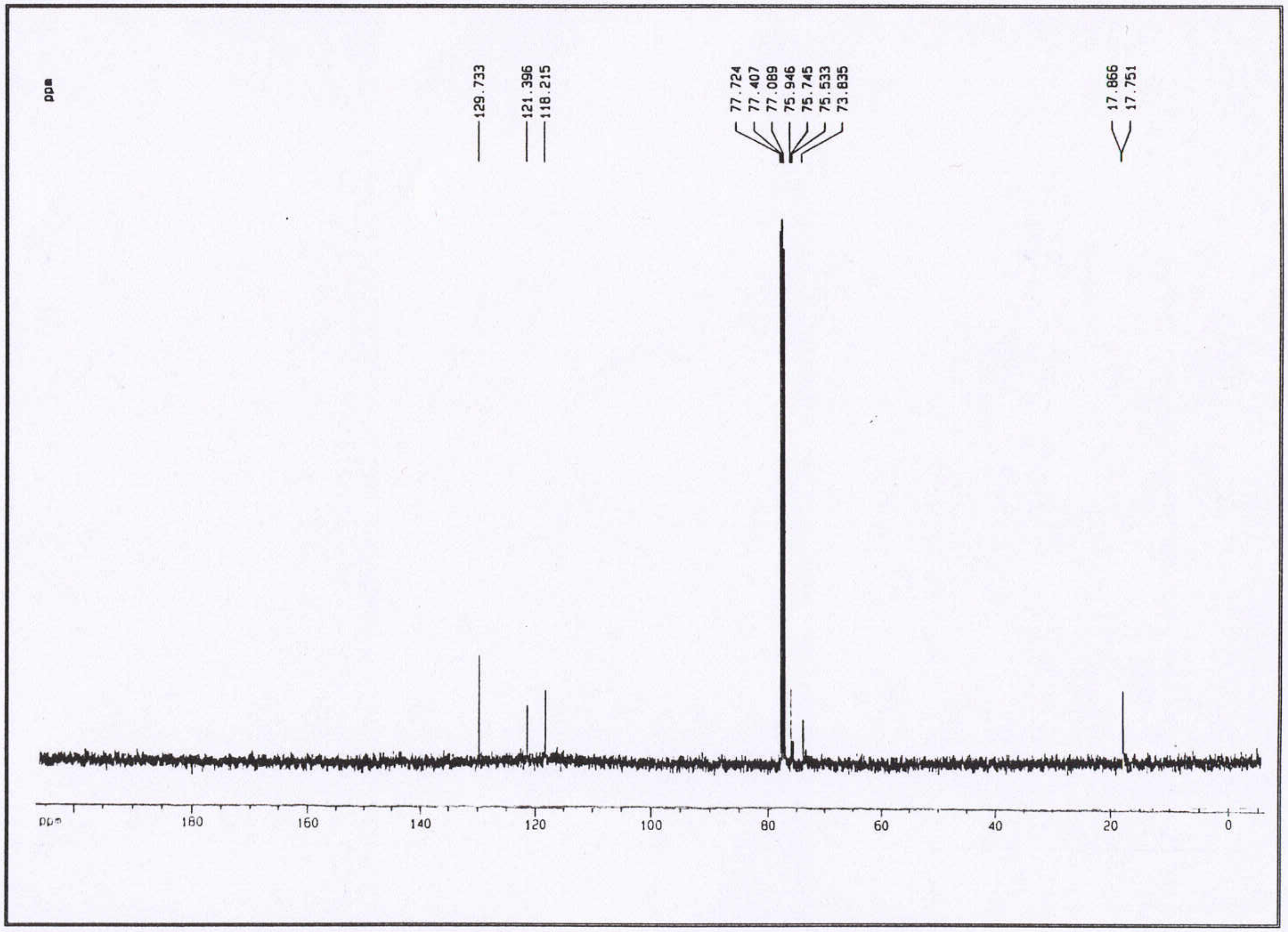


Figure B.10. ^{13}C NMR Spectrum of P_{18}

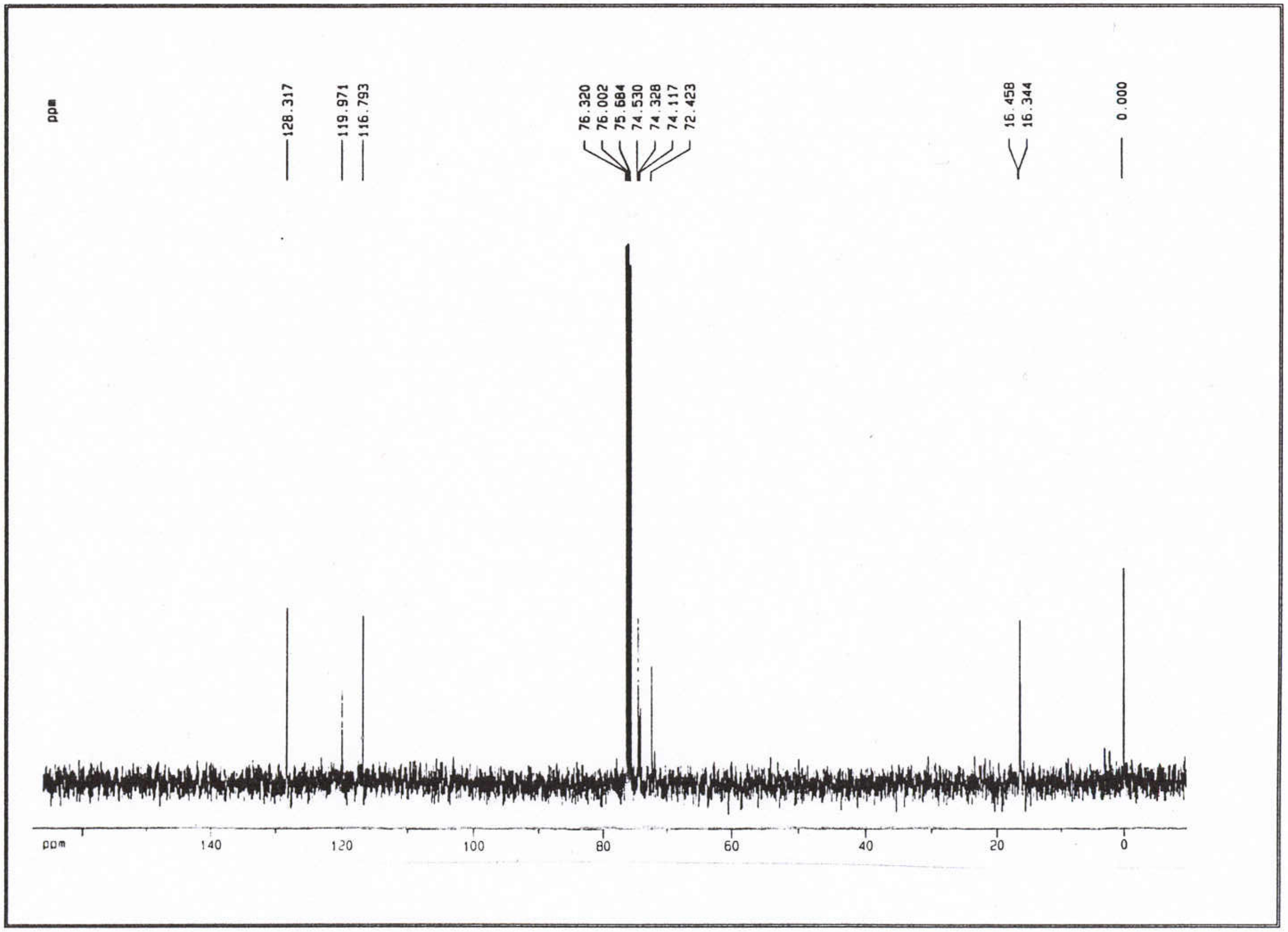


Figure B.11. ^{13}C NMR Spectrum of P_{23}

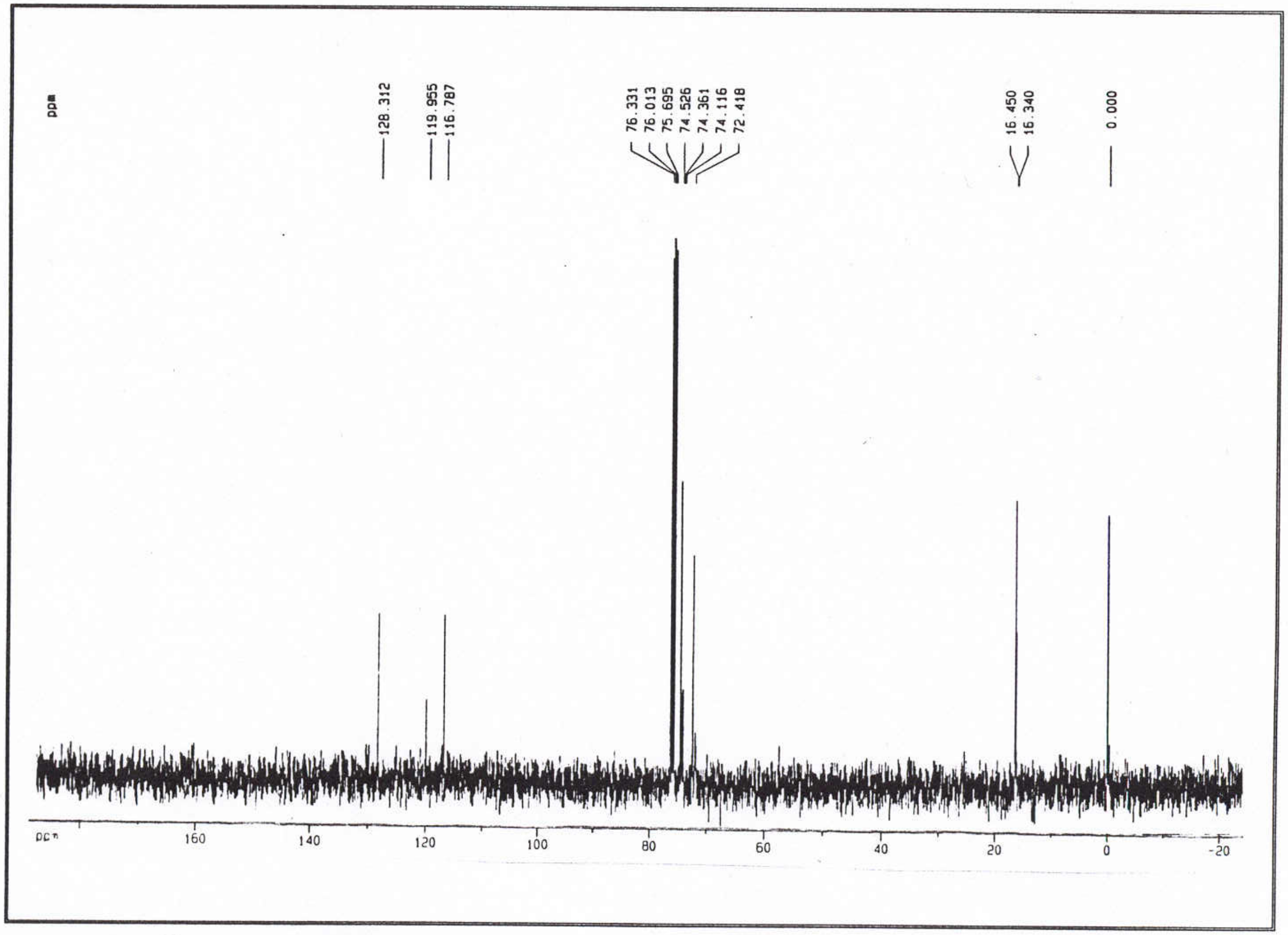


Figure B.12. ^{13}C NMR Spectrum of P_{27}

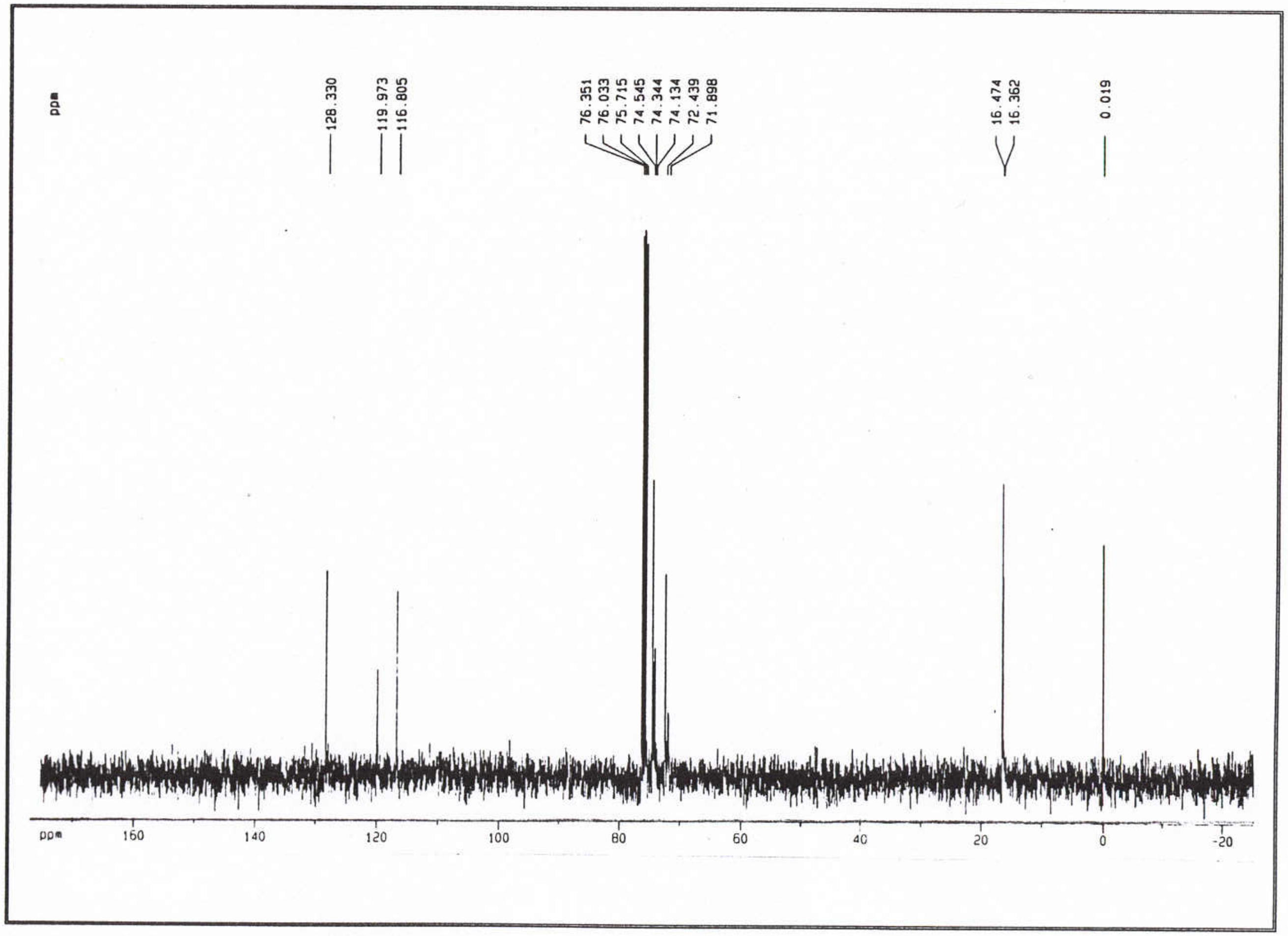


Figure B.13. ^{13}C NMR Spectrum of P_{31}

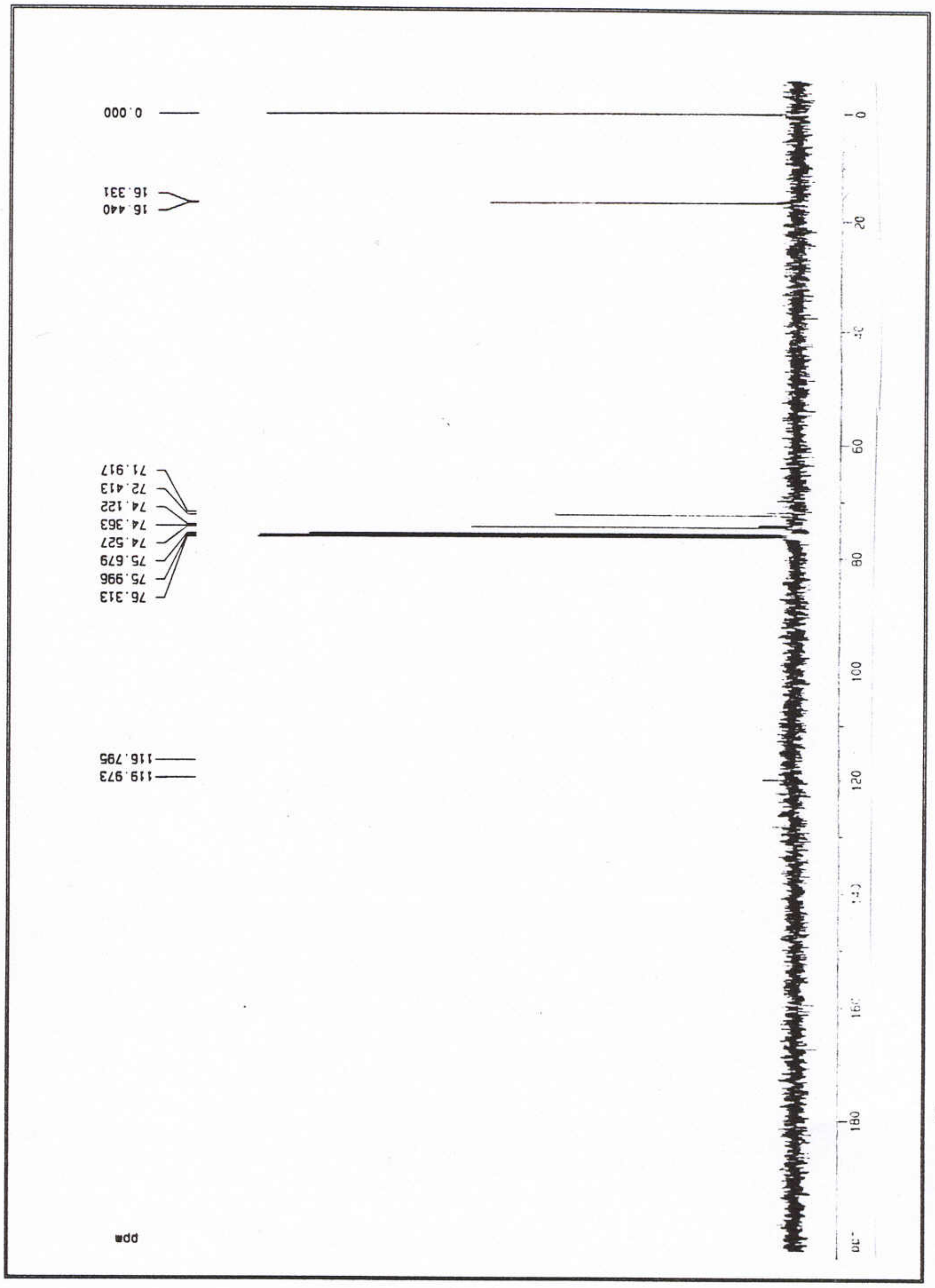


Figure B.14. ^{13}C NMR Spectrum of P_{11}

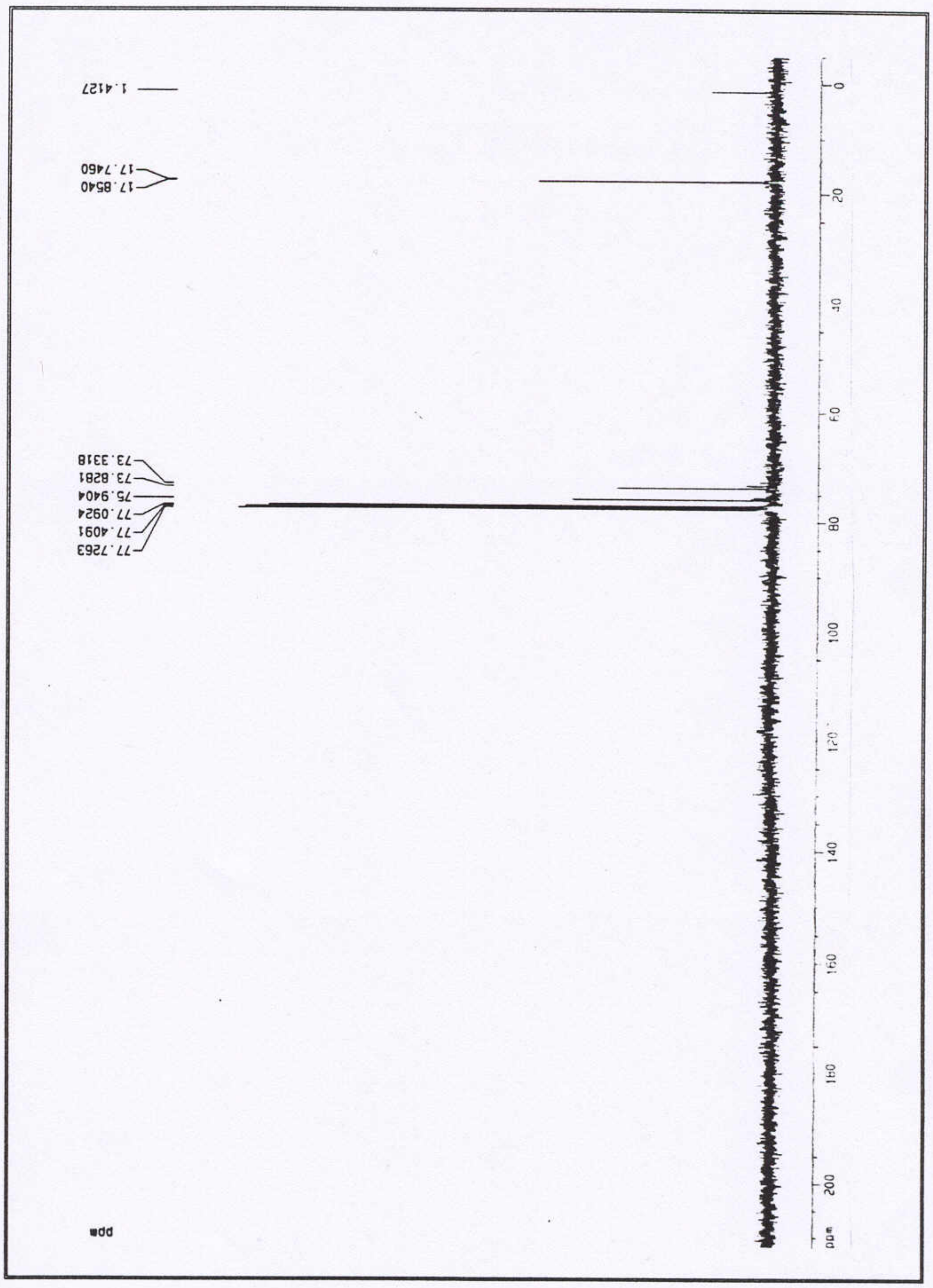


Figure B.15. ^{13}C NMR Spectrum of P_{12}

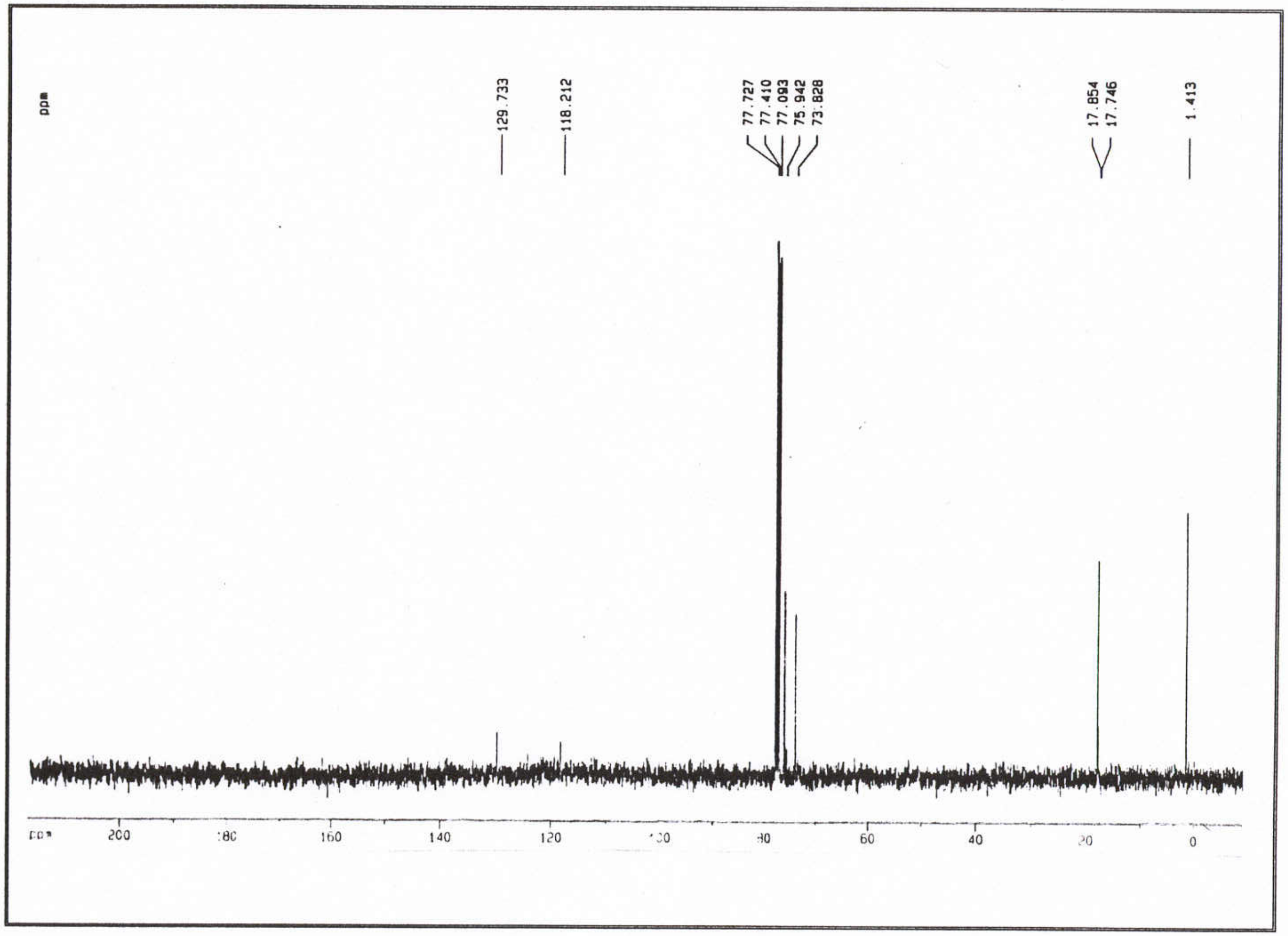


Figure B.16. ^{13}C NMR Spectrum of P_{13}

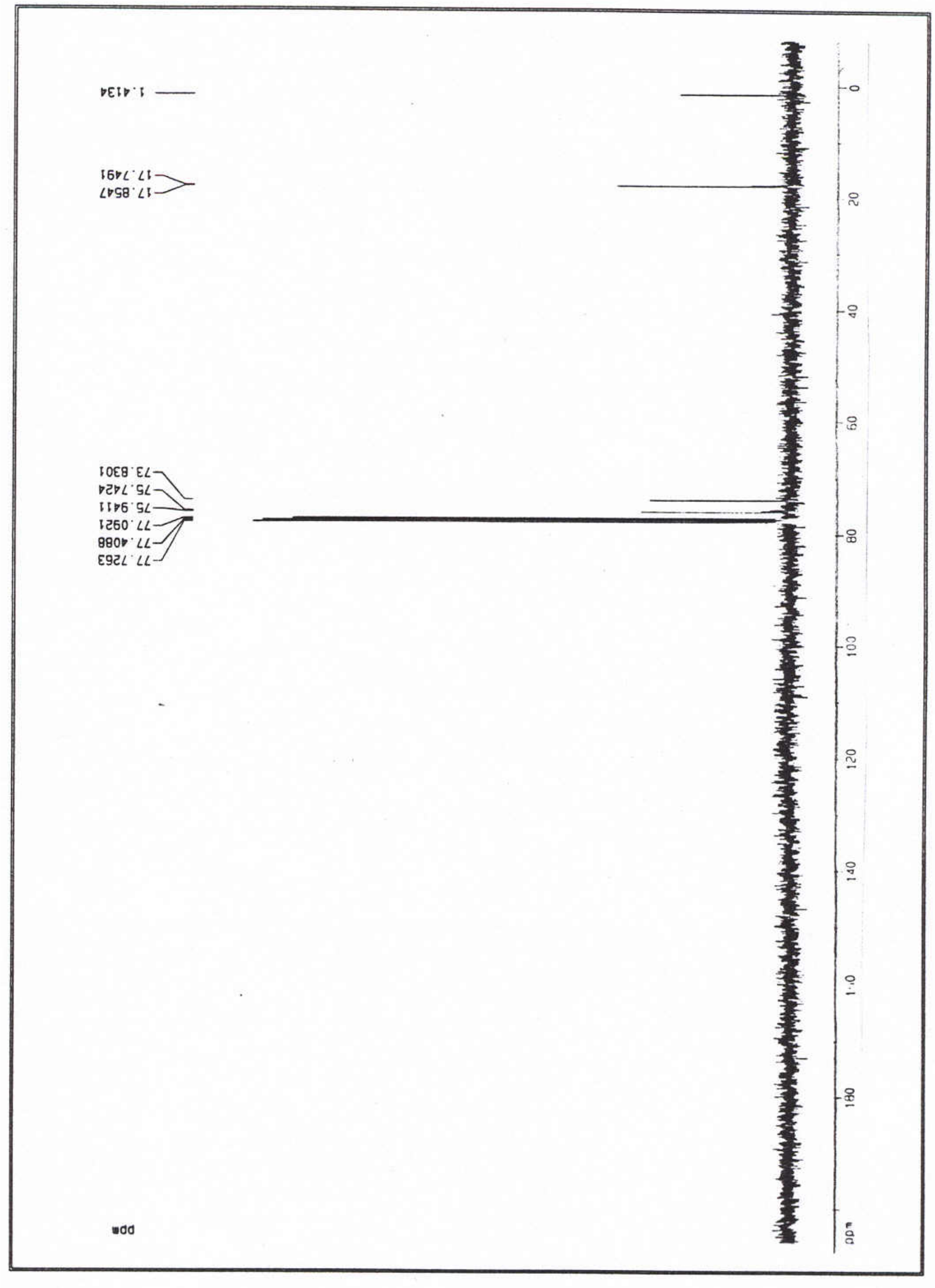


Figure B.17. ^{13}C NMR Spectrum of P_{14}

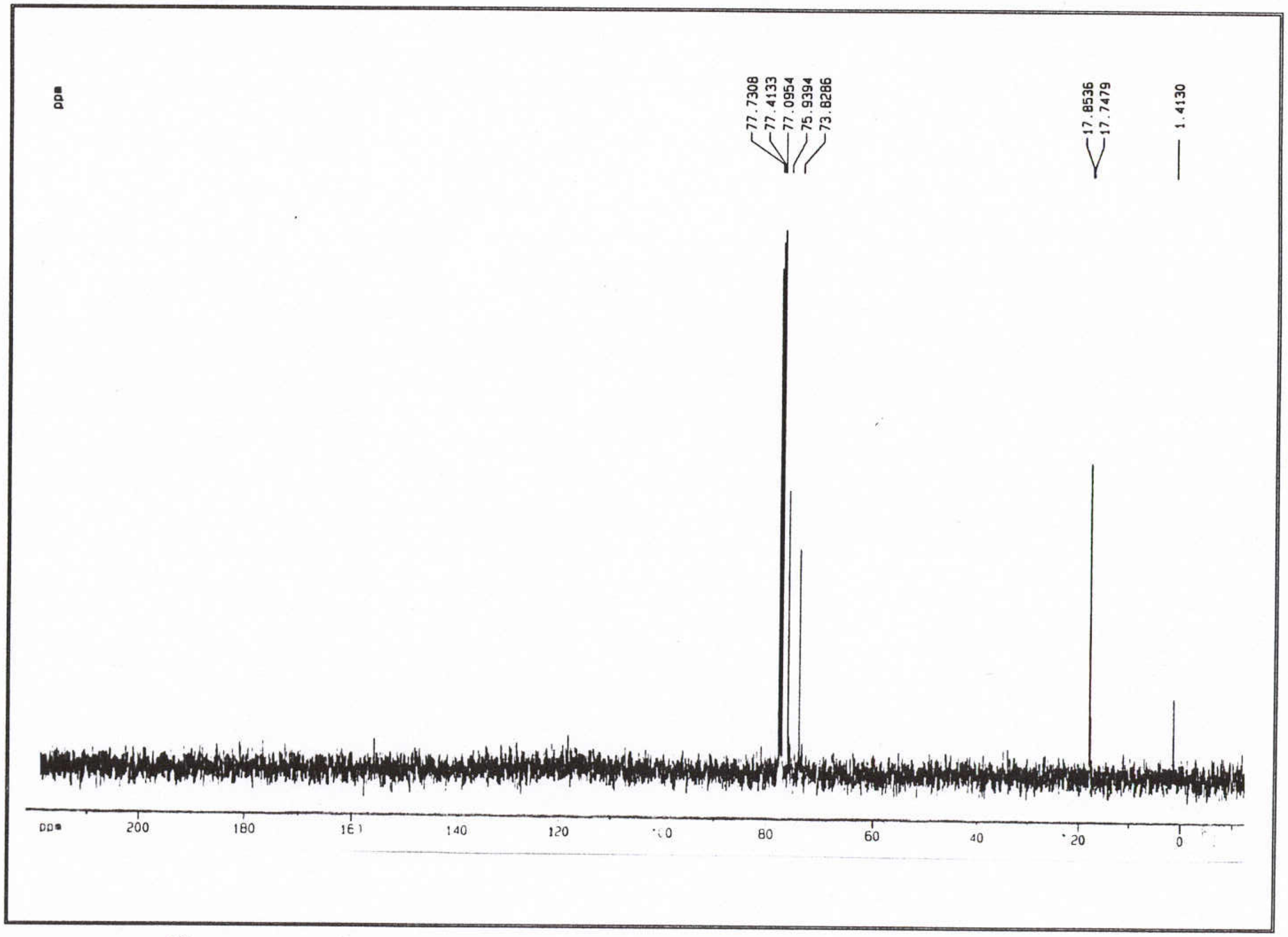


Figure B.18. ^{13}C NMR Spectrum of P_{15}

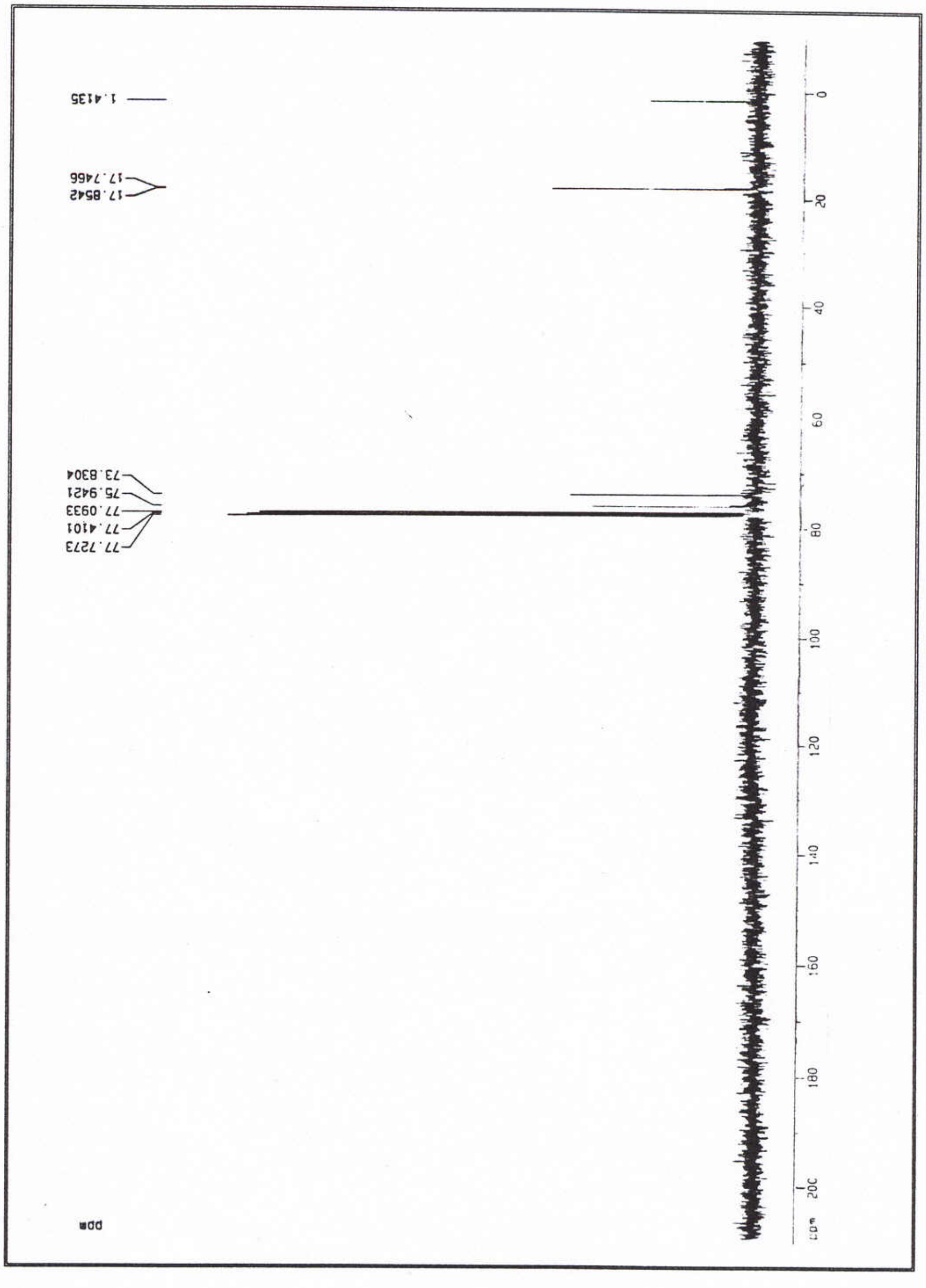


Figure B.19. ^{13}C NMR Spectrum of P_{55}