COPOLYMERISATION OF CARBON DISULFIDE, CARBON DIOXIDE AND OTHER CARBONIC ACID DERIVATIVES WITH CYCLIC ETHERS BY USING METAL XANTHATE CATALYSTS

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ABSTRACT

COPOLYMERISATION OF CARBON DISULFIDE, CARBON DIOXIDE AND OTHER CARBONIC ACID DERIVATIVES WITH CYCLIC ETHERS BY USING METAL XANTHATE CATALYSTS

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The synthesis of high molecular weight copolymer of carbon disulphide (CS_2) and propylene oxide (PO) has not reported in literature. In the present work, zinc isopropyl xanthate ($Zn(Xt)_2$) was used as catalyst for the copolymerisation of PO and CS_2 into high copolymer. However, the product can be fractionated into high and low molecular weight components. High molecular weight copolymer was rubbery products, but low molecular weight copolymers were oily products containing cyclic dithiocarbonates. Copolymers were characterized by elemental, end group analysis, DSC, TGA, GPC, Light Scattering, UV, IR, NMR spectroscopy, polarized microscopy and refractometry.

Copolymerization process was zeroth order with respect to monomers, and its non-terminated but suffered from several types of transfer reactions. As a result of transfer reactions S-(C=S)-S, O-(C=S)-O, O-(C=O)-O groups in the backbone of copolymer and SH groups at the chain terminals and cyclic dithiocarbonates are formed. Apart from SH groups, OH and double bonds were found and their amounts were determined at the chain terminals. Copolymers with high mole fractions of PO units (F_1) in the copolymer are crystallized in the shape of Malta's Cross. Melting points of products were obtained from DSC. The F_1 values are calculated from elemental analysis as well as zeroth order rate constants and from melting point of the crystals. All three results were in close agreement and changed between 0.9 –0.7. However, these ratios depend on reaction conditions (temperature, catalyst and monomer concentrations, time and dielectric constant of reaction medium).

A mechanism for coordination-copolymerization on the basis of above observation was proposed.

Keywords: Carbon disulphide (CS_2), Propylene oxide (PO), Zinc isopropyl xanthate ($Zn(Xt)_2$), Copolymer, Coordination-copolymerization

ÖZ

METAL KSENTAT KATALİZÖRLERİ KULLANILARAK KARBON DİSÜLFÜR, KARBON DİOKSİT VE DİĞER KARBONİK ASİT TÜREVLERİNİN HALKASAL ETERLER İLE KOPOLİMERLEŞMESİ

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Literatürde karbon disülfür (CS_2) ve propilen oksitin (PO), yüksek molekül ağırlıklı kopolimere sentezlenmesi ile ilgili bilgi yoktur. Bu çalışmada CS_2 ve PO, çinko izopropil ksentatla ($Zn(Xt)_2$) kopolimerleştirilerek yüksek molekül ağırlıklı kopolimerler elde edildi. Ancak, fraksiyonlandırma ile bu ürünler yüksek ve küçük molekül ağırlıklı bileşenlere ayrıldı. Yüksek molekül ağırlıklı ürünler kauçuğumsu, küçük ağırlıklılar ise halkasal ditiyokarbonat içeren yağımsı özellikte elde edildi. Kopolimerler; element analizi, uç grup analizi, DSC, TGA, GPC, Dinamik Işık Saçılımı Spektrometresi, UV, IR, NMR Spektrometresi, polarize mikroskop ve refraktometri ile incelendi.

Kopolimerleşme tepkimesin, monomerlere göre sıfırıncı dereceden olduğu, tepkimenin kinetikçe sonlanmadığı fakat çeşitli transfer tepkimeleri içerdiği bulundu. Transfer tepkimelerinin sonucu olarak polimer zinciri üzerinde S-(C=S)-S, O-(C=S)-O, O-(C=O)-O gruplarının, zincir sonlarında ise SH gruplarının, ayrıca küçük molekül ağırlıklı halkasal ditiyokarbonatların oluştuğu gözlendi. Yüksek oranda PO içeren ya da başka deyişle, kopolimerdeki PO mol kesri (F_1) yüksek olan ürünler Malta

Haçı şeklinde kristallendiler. Ürünlerin erime noktaları DSC ile elde edildi. F_1 değerleri sıfırıncı derece hız sabiti ve kristallerin erime noktalarının yanısıra element analizi ile de hesaplandı. Elde edilen değerlerin 0.9 ve 0.7 arasında ve birbirleriyle uyum içinde oldukları gözlemlendi. Ancak, bu oranın tepkime koşulları (sıcaklık, katalizör ve monomer derişimleri, tepkime zamanı ve ortamın dielektrik sabiti) ile değiştiği saptandı.

Yukarıdaki gözlemler temel alınarak, koordinasyon kopolimerizasyonu için bir mekanizma önerildi.

Anahtar Kelimeler: Karbon disülfür (CS_2), Propilen oksit (PO), Çinko izopropil ksentat ($Zn(Xt)_2$), Kopolimer, Koordinasyon kopolimerizasyonu

To My Parents
And
To My Uncle who was murdered on April 2001

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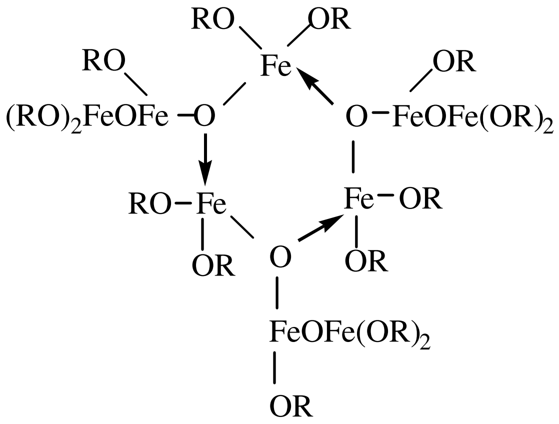
INTRODUCTION

1.1 Historical Background of Epoxide Polymerisation

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 et al. (1929 and 1933), while the earliest report of the polymerization of ethylene oxide was made by Wrutz (1863, 1879). In fact the interest in racemic epoxide polymerization began in 1950s with the industrial production of different racemic epoxides. Pruitt and Bagett (1955) who used the condensate resulting from reaction of ferric chloride with propylene oxide (PO) as the catalyst published the first report on the stereospecific polymerization of propylene oxide. The basic studies on this system were subsequently published by Price (1956). Initially only $FeCl_3$ was known as Pruitt- Baggett catalyst (PBC), then it was realized that stereoregular polymerization was only possible if $FeCl_3$ is partially hydrolyzed. Finally Çolak and Alyürük (1989) 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. (1990) showed that PBC as synthesized by Çolak and Alyürük (1989) 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. (1990) 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 and Alyürük (1994). They showed from the molecular weight measurements and electrolysis of PBC in acetonitrile in a Hitroff-cell 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 is as follows:



PO was the first cyclic ether to be polymerized in its optically active form by Price et al., 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 by Inoue et al. (1962).

It was found that the stereospecific polymerization of epoxides can be catalyzed by some organometallic compounds like $AlEt_3$, Et_2AlCl, $EtAlCl_2$, $Al(iBu)_3$, $ZnEt_2$, $MgEt_2$, $CdMe_2$ by Borrows et al. (1957). Later, it was found by Vanderberg (1959) that they were catalytically inactive unless hydrolyzed or chelated. Frukawa (1959) 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 (Gee et al., 1959) and aluminum alkyls (Colclough et al., 1964 and Jagger et al., 1960) 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 (Tsuruta (1967), Ishii et al., Gurgiolo, Frukawa et al. in 1967, Tani (1973), Sigwalt (1969)). These are iron-propylene oxide, zinc alkyl-water and aluminum alkyl-water catalyst systems.

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. (1993 and 1998). Catalytic activities of several PMAO and BMAO samples with different degrees of polymerizations (x) were investigated. Only a slight improvement of the stereoregular yield was observed by increasing the x of the used catalyst. 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".

^{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) (Öktem and Alyürük, 1998).

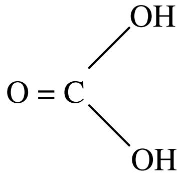
Coordination catalysts produce high molecular weight isotactic poly(propylene oxide). However;

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 (Tarkın, 2003)

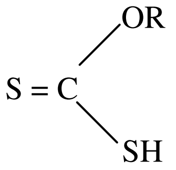
It appears that, this field of polymer chemistry requires a new coordination catalyst that is simpler in nature, more stable to atmospheric contaminations and produce higher molecular weight polymers with higher efficiency.

1.2 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 sulphur and one hydrogen atom replaced by an alkyl group (Rao,1971):



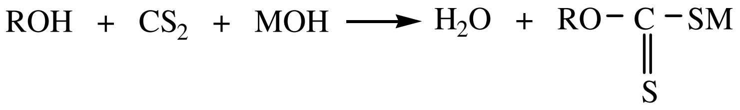
Carbonic acid



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

Xanthic acid is not stable; however, the salts of xanthic acid, xanthates, are stable. Xanthates of transition metals are sparingly soluble. Xanthates were discovered by Zeise in 1822 (Rao, 1971), but not much work was recorded on the study of their properties and reactions during the 19th century, although some of their general characteristics had been recognized.

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

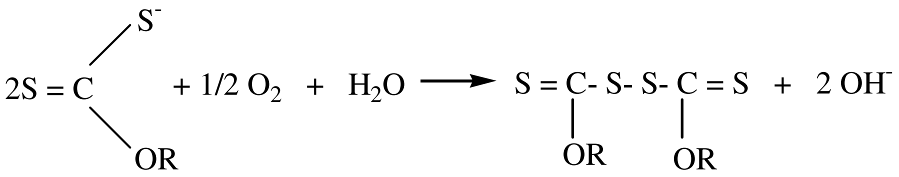


$$ROH + CS_2 + MOH \longrightarrow H_2O + RO-\underset{\underset{S}{\|}}{C}-SM$$

(1.1)

Where R stands for an alkyl and M denotes a monovalent metal ion 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:



(1.2)

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

A variety of catalyst systems comprising metal-oxygen, metal-sulphur or metal-nitrogen bonds have been reported for the polymerization of olefin oxides and olefin sulphides to high molecular weight polymers. Many such catalysts are prepared by the reaction of alkyl metals (for instance dialkyl zinc, trialkyl aluminium) with active hydrogen compounds, oxygen or sulphur. 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. Unlike alkyl metals, these new catalysts are relatively quite safe (Lal, 1967).

Polymerization of olefin oxides with xanthates was first studied by Lal (1967). 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 sulphate, cadmium chloride and ferric sulphate to form the corresponding zinc, cadmium, and ferric alkyl xanthates. The precipitates were filtered, washed with water and dried. The catalyst was purified by recrystallisation 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, and 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 xanthates in polymerizing propylene oxide in regard to both the yield and inherent viscosity of the polymer (Lal, 1967). However, Lal did not characterize polymers, on the basis of stereoregularity. Hence whether the polymers were crystalline or amorphous were not clear. Lal (1973) also investigated the mechanism of initiation in the polymerization of olefin oxides with zinc n-butyl xanthate and zinc dimetyldithiocarbamate catalysts.

In 1999, Bolat 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 $Zn(Xt)_2$ was reported wrongly as a unique catalyst to produce high molecular weight atactic PPO.

Catalytical activity of several transition metal xanthates in the coordination polymerization of propylene oxide was studied by Soysal (2001). Tin, copper and iron isopropyl xanthates were found to be catalytically active. In order to complete the work initiated by Bolat (1999), zinc xanthate catalysts were examined in detail. The effect of alkyl group on the catalytical activity studied by synthesizing isopropyl, ethyl and 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.

Since Lal (1967) did not characterize the metal xanthate synthesized PPO on the grounds of stereoregularity, Bolat (1999) and Soysal (2001) 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 Tarkın (2003) who carried out a detailed fractionation apparently contradicted those conclusions. In her work, during the microscopic studies, the spherulites were detected and melting points of the fractions were measured with a hot stage microscope and DSC. This observations show that poly (propylene oxide) synthesized by metal xanthate catalysts is crystallisable; hence has partial stereoregularity. In her study, zinc 2-octyl xanthate catalyst polymerizes PO to high molecular weight, stereoregular, crystallisable polymer (K polymer) together with low molecular weight (=500g/mol) D-polymer. D-Polymer has double bond as well as hydroxyl terminals. Presence of double bonds at the chain ends indicates an anionic coordination mechanism. K-polymers crystallize forming spherulites in the shape of Malta's Cross. K-polymers can be thermally fractionated from isooctane solution on the basis of their melting temperature rather than molecular weight.

Taş (2003) aimed to a closer look to several transition metal xanthates as potential coordination catalysts in cyclic ether polymerizations. Among Cu, Pb, Ni, Fe and Sn isopropyl xanthates only copper and tin isopropyl xanthate was found to be active catalyst in polymerization of PO. Since tin isopropyl xanthate appeared to be more active, this system was investigated in some detail. Analysis of Atomic Absorption Spectrometer (AAS) of catalyst has shown that the used catalyst had identical empirical composition to that of tin isopropyl xanthate [$Sn(C_4H_7OS_2)_2$]. Polymerization of PO with this catalyst produced two contrasting polymers together, through out the process, high-molar mass, crystalline (K-polymer) and low molar mass (D-polymer). D-polymers had both hydroxyl and double bond terminals. The polymer yield increases with catalyst concentration but molar mass of product decreases. This effect is attributable to a transfer or termination process. Molar masses of product almost stay constant through out polymerization process as expected from a chain-wise growth. Overall activation energy of K-polymer formation is negative, as a result of a termination or more likely a transfer reaction. Water as an adduct have a weak activating effect on the catalytical activity. This effect is maximum if H_2O/Sn molar ratio is 0.67. Also, tin isopropyl xanthate has very poor efficiency with respect to zinc isopropyl xanthate catalyst. Lal (1967) proposed dithiocarbamates as potential catalysts besides xanthates. Although this was a remarkable contribution no other work about these systems appeared in literature. Even the tacticity of poly(propylene oxide) obtained with these systems was not studied. Thus characterization of PPO synthesized by dithiocarbamates was also aimed in his work. Zinc diethyl dithiocarbamate was found to be active catalyst in stereoregular polymerization but it is not as efficient as zinc isopropyl xanthate catalyst.

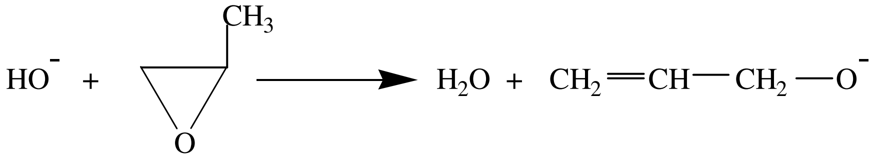
In summary, metal xanthate catalysts;
(i) produce high molecular weight, stereoregular poly(propylene oxide) with high percent conversion.
(ii) reduce polymerization time.
(iii) are relatively stable, require only semi-closed reaction systems, but not high vacuum systems as in classical coordination catalysis, which simplifies the polymerization conditions.
(iv) have high catalytical efficiency than organometallic catalysts.

1.3 Copolymerization of Epoxides with Carbon Disulfide (CS_2)

Until 1969 no attempt to copolymerise carbon dioxide and carbon disulfide with another monomer was reported. In 1969, Inoue et al. succeeded in the copolymerisation of carbon dioxide and carbon disulfide with propylene oxide using several organometallic plus water systems, such as ($AlEt_3$+H_2O and $ZnEt_2$+H_2O) in stereospecific polymerisation. They classed these polymerisation reactions as basically anionic.

The copolymerization of propylene oxide and carbon disulfide was carried out with a catalyst consisting of diethylzinc and an electron donor like a tertiary amine, tertiary phosphine or hexamethylphosphoric triamide in equimolar amounts by Adachi et al. (1977). Poly(propylene ether-co-dithiocarbonate)s obtained were of low molecular weight ($M_n = 5.6\times10^2$ g/mol) and had a monomer unit ratio (CS_2/PO) of 0.5–0.7. Among the randomly distributed comonomer units, the copolymer contained also thiocarbonate carbonyl units which were formed during the copolymerization. This reaction hinders formation of high polymers by the exchange reaction between the oxygen atom of propylene oxide and the sulphur atom of carbon disulfide. In fact, the copolymerization was found to be accompanied by the cyclization reaction, leading to the cyclic propylene dithiocarbonates, 1,3-oxathioran-5-methyl-2-thione and 1,3-oxathioran-4-methyl-2-thione (30%); however, the latter was proved not to be an intermediate in the copolymerization, it is a by-product in the copolymerisation of PO and CS_2. It is worth noting that catalysts formed in systems such as diethylzinc/water, alcohol, primary or secondary amines, which exhibit high activity for the homopolymerization of propylene oxide, were not effective for the copolymerization of propylene oxide and carbon disulfide.

On the basis of Inoue et al. (1969) claim that copolymerisation of CS_2 with PO occur with an anionic mechanism, one may expect that simple bases like KOH could be also used as an initiator for this system. In fact, PO can be homo-polymerised by KOH (Steiner et al., 1964).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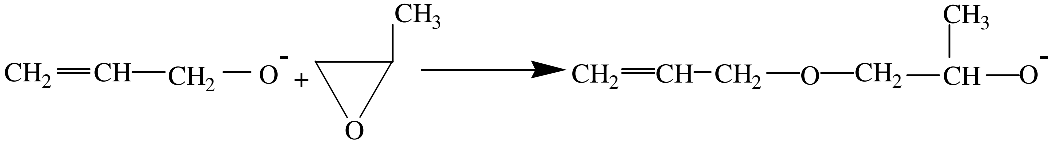
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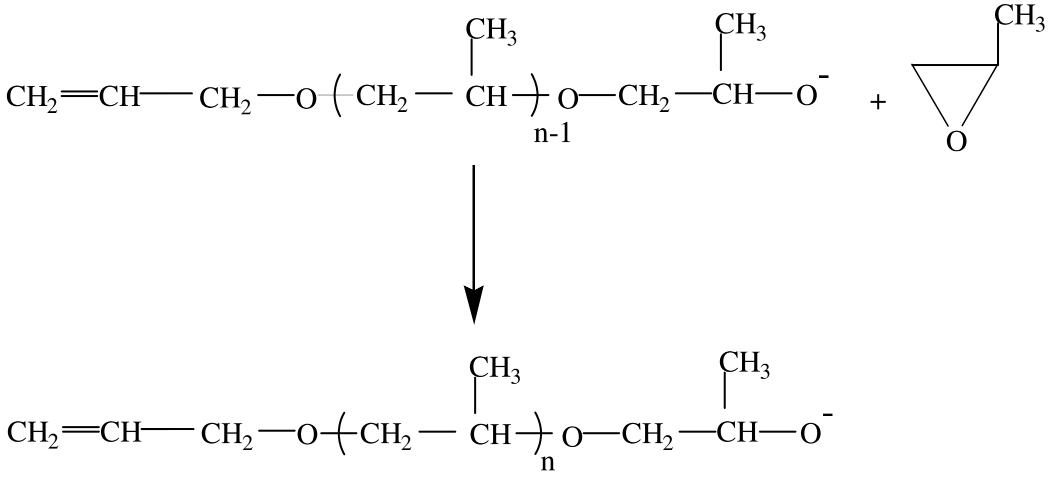
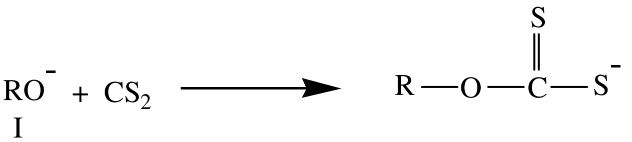

I

(1.5)

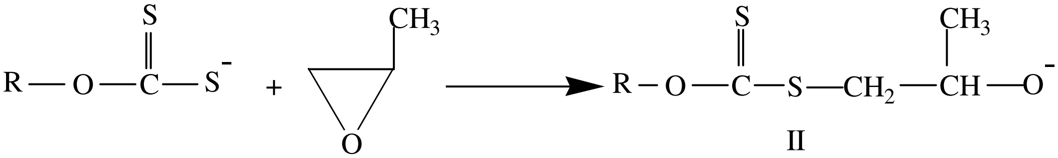
In the presence of CS_2 in the mixture, the chain carrying alkoxide groups would be converted to xanthate groups.



$$\underset{\text{I}}{RO^-} + CS_2 \longrightarrow R-O-\overset{\overset{\displaystyle S}{\|}}{C}-S^- \qquad (1.6)$$

(where R is the poly(ether) group in Eq. 1.6).

Whether copolymerization is possible or not would depend on the ability of xanthate ion to attack and open an epoxide ring.

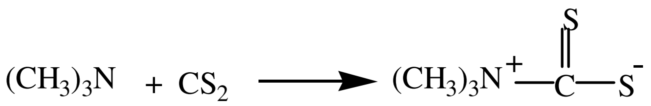


II (1.7)

Where the anion II is almost identical with the anion I. It follows that if alkali metal xanthates initiate the anionic polymerization of PO, than anionic copolymerization of CS_2 with PO can also be carried out.

Culvenor et al. (1946), Durden et al. (1960) and Razuvev et al. (1960) have already studied the reaction between alkali metal xanthates and PO. They did not expect to get a polymer since they used more than two moles of xanthate per molecule of PO, and consequently, they get a mixture of thio-carbonates. However, it is important for the present thesis that they showed that xanthates can attack and open an epoxide ring with S_N2 reaction.

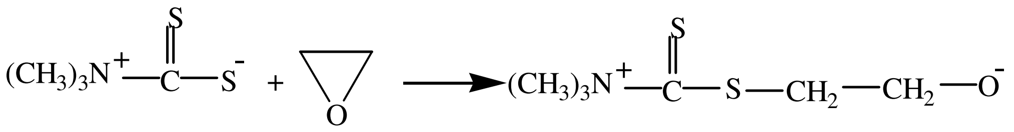
Culvenor et al. (1946) showed that ethylene oxide reacted readily with two moles of potassium ethyl xanthate (KEtXt) to yield ethylene trithiocarbonate. Durden et al. (1960) and Razuvev et al. (1960) used amines as catalysts in the reaction of CS_2 with epoxides at high pressures and temperatures, and obtained a mixture of ethylene trithiocarbonate, ethylene dithiocarbonate and ethylene carbonate. The proposed reaction mechanism involved in the following steps (Durden et al., 1960).



$$(CH_3)_3N + CS_2 \longrightarrow (CH_3)_3N^+{-}\overset{\overset{S}{\|}}{C}{-}S^-$$

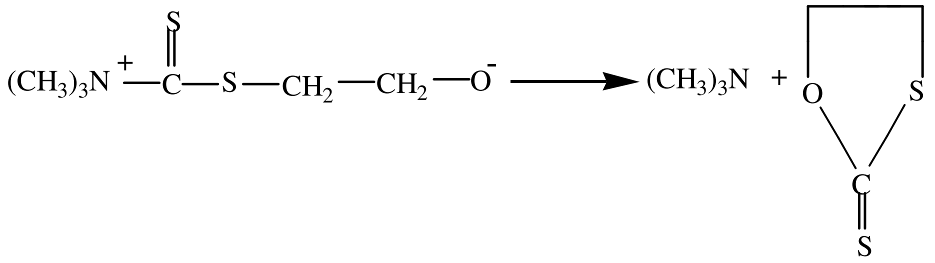
(1.8)

i. A sulphide anion through an S_N2 reaction opens the epoxide ring yielding an oxy-anion:



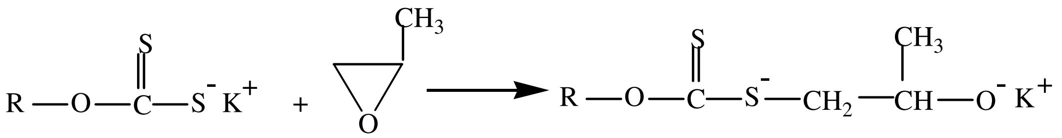
(1.9)

ii. The oxy-anion back-bites the C-N$^+$ bond to produce dithiocarbonates:



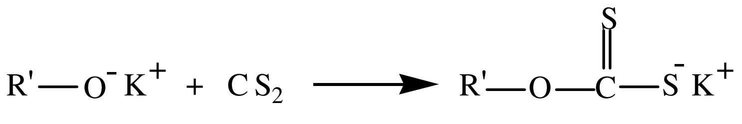
(1.10)

Under basic conditions, copolymerisation of CS_2 with PO would be possible only if xanthate anion can break the C-O bond and add to a PO molecule.



(1.11)

The resulting oxy-anion, like simpler alkoxide and hydroxide ions (Steiner et al., 1964) would polymerise PO or, in the presence of CS_2, reform the xanthate anion readily by adding a CS_2 molecule (Rao, 1971).

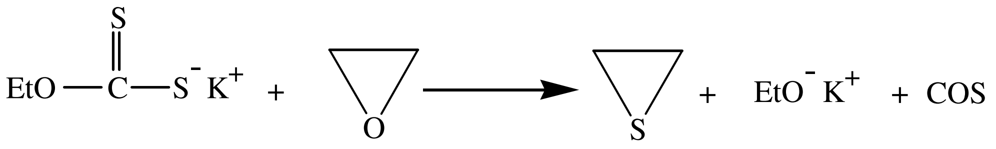


$$R'{-}O^-K^+ + CS_2 \longrightarrow R'{-}O{-}\overset{\overset{S}{\|}}{C}{-}S^-K^+$$

(1.12)

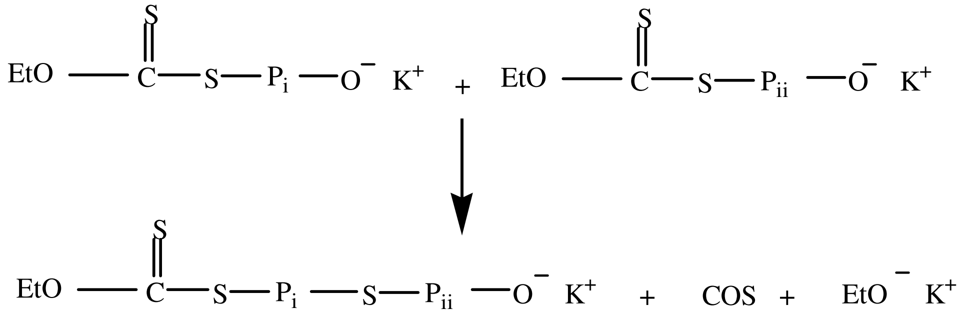
(Where R and R' = any of the possible organic moieties.)

On the other hand, Culvenor et al. (1946) proposed a concerted mechanism for the formation of ethylene sulphide from KEtXt and ethylene oxide:


(1.13)

It follows that, if the S_N2 reaction path [Eq. 1.11] instead of a concerted mechanism is followed and a large excess of epoxide to the xanthate salt is employed (Culvenor et al. (1946) reacted two or more moles of KEtXt with one mole of epoxide), it should be possible both to initiate an anionic polymerisation of epoxides with xanthate salts and also to copolymerise PO with CS_2.

From these observations, Aksoy et al. (1989) conclude that the xanthate anion breaks and opens the C-O bond of PO by S_N2 attack (Eq. 1.11) and initiates an anionic polymerisation of PO. Of other plausible competitive processes (Culvenor et al., 1946, Durden et al., 1960 and Razuvev et al., 1960) a condensation between terminal xanthate groups and alkoxide anions occurs:

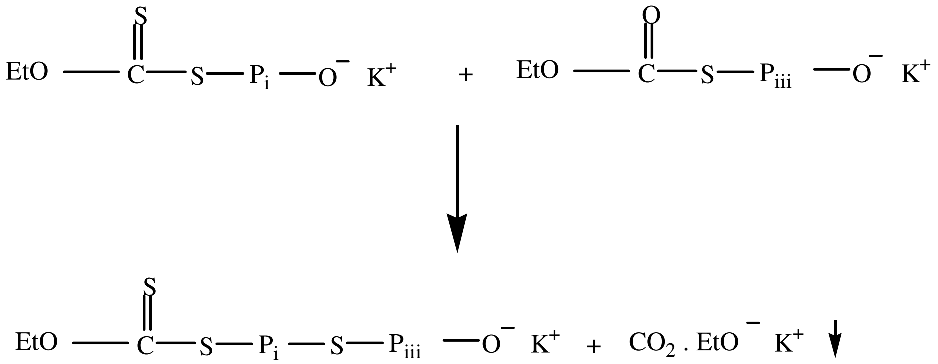


$$\mathrm{EtO{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}S{-}P_i{-}O^-\ K^+} + \mathrm{EtO{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}S{-}P_{ii}{-}O^-\ K^+} \longrightarrow \mathrm{EtO{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}S{-}P_i{-}S{-}P_{ii}{-}O^-\ K^+} + \mathrm{COS} + \mathrm{EtO^-\ K^+}$$

(1.14)

(Where Pi and Pii are PPO chains).

Intramolecular instead of intermolecular condensation of terminal groups would yield cyclic products (Culvenor et al., 1946 and Eq. 1.13]. The eliminated COS, under the action of EtO^-K^+, would initiate anionic polymerisation of PO, producing chains with EtO-CO-S end groups. The condensation of these newly formed terminal units with oxy-anions would account for the CO_2 formation and the termination process. Termination reaction was apparent since reaction stopped after a limited amount of conversion of monomer (PO). Furthermore, initially electrically conductive, homogeneous reaction mixtures become non-conductive and heterogeneous due to formation a solid phase. The solid phase decomposed with addition of HCl by CO_2 formation. Upon these observations, the termination reaction was accounted for with following reaction:



$$\mathrm{EtO{-}\overset{\overset{S}{\|}}{C}{-}S{-}P_i{-}O^{-}\ K^{+}} + \mathrm{EtO{-}\overset{\overset{O}{\|}}{C}{-}S{-}P_{iii}{-}O^{-}\ K^{+}} \longrightarrow \mathrm{EtO{-}\overset{\overset{S}{\|}}{C}{-}S{-}P_i{-}S{-}P_{iii}{-}O^{-}\ K^{+}} + \mathrm{CO_2\,.\,EtO^{-}\ K^{+}}\downarrow \qquad (1.15)$$

The reaction 1.15 leads formation of only one chain carrier from initially two and an inactive solid precipitate of $CO_2.EtO^-K^+$. Therefore, it is a termination reaction.

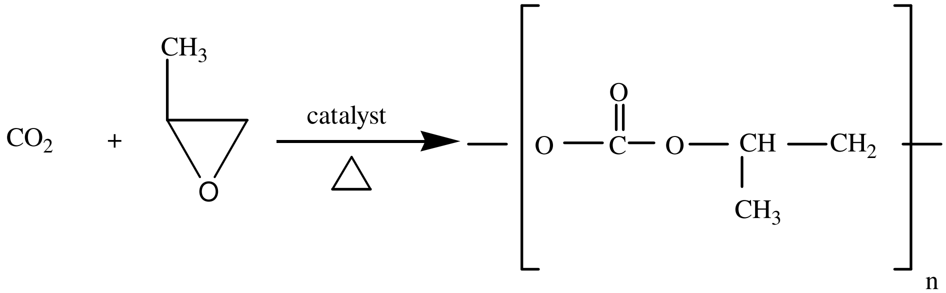
Therefore, Aksoy et al. (1989) studied the anionic polymerisation of PO by using xanthate salts and copolymerisation of CS_2 with PO. It was found that, under such conditions, PO was polymerisable into oily products; if CS_2 was added to the polymerisation mixture, an oily copolymer was obtainable. Addition of CS_2 to a system would decrease the oxy-anion concentration (Eq. 1.6). Indeed, in the experiments where CS_2 was added, no salt formation was observed and the reaction continued until the PO in the feed was consumed. No salt was precipitated if CS_2 mole ratio in the feed was sufficient. Because of the absence of precipitation, the decrease in conductivity was much slower. On the other hand, zinc isopropyl xanthate, which apparently acts as a coordination catalyst (Lal, 1967) gave high copolymers of CS_2 and PO with monomeric unit ratio (CS_2/PO) of 0.06-0.15.

Recently, in our laboratory, we obtained high molecular weight copolymer which was synthesised by CS_2 and PO by using metal xanthate catalysts. In this preliminary work, both low and high molecular weight fractions containing sulphur were obtained. For high molecular weight fraction elemental analysis results is as follows: C: 49.06%, S: 23.98%, O: 18.85% and H: 8.11% (Sezigen, 2005).

The refractive indices and densities of recently synthesised poly(thiocarbonate)s and poly(dithiocarbonate)s were measured and were used to determine the group contributions of thiocarbonate(-O-CO-S-) and dithiocarbonate (-S-CO-S-) groups to the molar refraction by Marianucci et al. (1994). The high refractive indices observed make these polymers, particularly the poly(dithiocarbonate)s, potentially interesting for optical applications (i.e. lenses and optical fibres). The recent patent literature reports many examples of sulphur-containing, high refractive index polymers which may be employed for optical materials (Masumoto et al., 1990 and Sakamoto et al., 1991). Thus, it appears that developing poly(dithiocarbonate)s by copolymerising PO and CS_2 may be rewarding.

1.4 Copolymerization of Epoxides with Carbon Dioxide (CO_2)

Carbon dioxide is a known greenhouse gas which contributes over half of the greenhouse effect. The necessity to reduce CO_2 emission has gained the consent of most of the countries in the world. One of the means to reduce CO_2 emission is to use CO_2 as a starting material in chemical reactions. In addition to environmental concerns, CO_2 may become a very important raw material in chemical industry in the future, since the sources of coal, petroleum, and natural gas are being quickly exhausted and the carbon content of CO_2 in the atmosphere and in the hydrosphere is by 1 ½ orders of magnitude more than that in coal, petroleum, and gas. Generally, CO_2 is thought of as an inert and relatively unreactive compound; there is no report so far on the homopolymerisation of CO_2. However, Inoue et al. (1969) observed that the copolymerisation of CO_2 with epoxide could proceed to form polycarbonate using organometallic compounds as catalysts (the diethylzinc/water (1:1)) under relatively mild conditions.



(1.16)

Synthesis of Poly(propylene carbonate) (PPC)

Since then, many attempts to develop new catalysts and to copolymerize other monomers with CO_2 have been made (Tan and Tsung, 1997). Results of the investigations are as follows:

1.4.1 Copolymerisation Catalysts

First class is the organometallic compounds which results in reactions of a metal alkyl and additive with at least two labile hydrogen atoms. In this group, only zinc and cadmium derivatives exhibit high activity, affording fully alternating, high molecular weight carbonates. Organoaluminum catalysts yield low molecular weight polymers which contain ether linkages in addition to carbonate ones. Organomagnesium catalysts yield trace amounts of copolymers while derivatives of calcium or lithium do not catalyse copolymerisation at all.

Second class is the coordination catalysts which are less widely studied than their organometallic ones. Among coordination catalysts, as in organometallic systems, zinc derivatives exhibit the highest activity. Again, derivatives of aluminium as well as chromium, nickel, and magnesium lead to low molecular weight polymers which contain ether linkages in addition to carbonate linkages. These catalysts are less reactive and the obtained polymers have much lower number average molecular weight (M_n) value than organometallic systems.

1.4.2 Copolymerization Conditions

a) CO_2 Pressure

Even at relatively low CO_2 pressure (~1 atm) some copolymer is produced. However, the formation of ether linkages proceeding simultaneously with the formation of carbonate ones could not be completely suppressed. The yield and M_n of the poly(propylene carbonate) was found to increase with increasing CO_2 pressure up to approximately 30-50 atm. However, in the case of CO_2 copolymerisation with epoxycyclohexane in the presence of di-ethylzinc-water catalysts, even under low CO_2 pressure (~1.3 atm), the alternating copolymer is produced.

b) Reaction Temperature

Increasing the reaction temperature causes an increase of the copolymer yield and a drop of M_n of the polymer produced. It seems to be caused at least partially by polymer degradation reactions taking place in the reaction systems.

c) Reaction Time

After an induction period the polymer yield as well as M_n grow relatively fast with increasing polymerisation time until maximum is reached. Further prolongation of reaction does not appreciably affect the polymer yield; however, it may bring about a substantial decrease of M_n of the copolymer produced**.** The latter fact was proved, in the case of organozinc catalysts, to be due to subsequent degradation and depolymerisation of the poly(propylene carbonate) by organozinc compounds present in the polymerisation system. The presence of an induction period in the CO_2–PO copolymerisation may indicate that the process involves a coordination of monomers at active centers of the catalyst or catalyst activation, consisting in the formation of active zinc-carbonate linkages from zinc-oxygen ones, prior to the copolymerisation (activity of organic catalysts in the CO_2/ethylene oxide copolymerisation increases remarkably when they are prepared under CO_2 atmosphere or treated with CO_2 prior to copolymerisation).

d) Solvent

Solvent appear to be polar, aprotic and have relatively low donor strength. It was shown that the presence of strong electron donors in the polymerisation system, either as additives or as solvents, prevents or ultimately discontinues the copolymerisation due to the competition of the electron donor with PO for coordination at the active center of the catalyst (in the CO_2-epoxycyclohexane copolymerisation by alkyaluminum amides, the more basic the solvents used, the lower the yield of copolymer, but the CO_2 molar fraction of the copolymers was similar).

1.4.3 Properties of Copolymers

Poly(alkylene carbonate)s show low combustion heat. The high molecular weight, insoluble in methanol, copolymers of CO_2 with ethylene, propylene, cyclopentene and cyclohexene oxides, butyl and phenyl glycidyl ethers, and epichlorohydrin are rubber like white solids. All the copolymers are soluble in methylene dichloride, chloroform and with the exception of CO_2-ethylene oxide copolymer, also in acetone, benzene, and tetrahydrofuran. The relationship between the intrinsic viscosity of the poly(propylene carbonate)(PPC), in ml/g in benzene at 35 ^{0}C, and number average molecular weight of the polymer has been established as:

$$[\eta]\times 10^{-2} = 1.11\times 10^{-4} \times M_n^{\,0.8} \tag{1.17}$$

CO_2 copolymers with ethylene and propylene oxides, cyclohexene oxide, cyclopentene and styrene oxides, butyl and phenyl glycidyl ethers, and epichlorohydrine shows that thermal decomposition of these copolymers begins at temperatures above 180-200 ^{o}C. Nevertheless, at 140-150 ^{o}C the CO_2-ethylene oxide and CO_2-PO copolymers can be melted and/or molded without appreciable decomposition. The thermal stability of this copolymer might be improved by end-capping. The conversion of the terminal hydroxyl groups of poly(alkylene carbonate)s to oxygen-sulphur, oxygen-phosphorous or oxygen-carbon bonds can raise the decomposition temperature of the polycarbonates from ~210 to ~250 ^{o}C (Kuran et al., 1981).

Ree et al. (1999) studied zinc glutarate from zinc oxide and glutaric acid which was found to be most active catalyst. The catalyst was determined to have a relatively high crystallinity and low surface area. Synthesised PPC shows a high molecular weight in a relatively high yield, 64-70 g polymer per gram of the catalyst, using the excessively loaded PO monomer as the reaction solvent in the polymerisation. This was achieved by using 2000 ml of reactor. The high polymer yield obtained by this paper is marked as the highest yield among all the polycarbonate yields reported so far (twice as much as). The results confirms that the excessively loaded PO, which is a good solvent to PPC, plays an important role to improve the efficiency of mixing the reaction medium during the copolymerisation and consequently to enhance the polymerisation yield. In comparison, for this copolymerisation the excessively loaded PO is a better reaction medium than any other solvent that has appeared in the literature. The copolymers showed a Tg of 38 ^{o}C, a Td (decomposition temperature) of 252 ^{o}C, Young modulus 1.9 Gpa, tensile strength 29 MPa etc. based on the properties. The PPC copolymer considered to have potential applications in industry as binder resins, substitutes of thermoplastic polyolefins and degradable polymers.

1.5 Aim of This Work

No reports on high molecular weight copolymer of CS_2 and synthesis of such materials are existed in the literature. On the other hand, high copolymers of PO and CS_2 are expected to have dithiocarbonate groups and such products would have valuable optical and physical properties (Marianucci et al., 1994).

Based on previous work on this department, the present work was initiated with the aim of copolymerising CS_2 and PO to high copolymer by zinc isopropyl xanthate catalyst. The cross linking of copolymers to three dimensional network structures, and studying the mechanical and optical properties were also aimed.

CHAPTER 2

EXPERIMENTAL

2.1 Purification of Materials

All the reagents (PO, CS_2) those are used in copolymerization were rigorously purified. The solvents (benzene, isooctane) were purified by standard methods prior to fractionation on a 1-meter fractional distillation column with an efficiency of approximately 20 theoretical plates. Following the purification of materials, they were kept over CaH_2 under high vacuum and handled under these conditions.

2.1.1 Solvents

Benzene (C_6H_6); was supplied by Merck A.G. and purified with fractional distillation before use (Bp: 78 ^oC at 685 mmHg) and then it was dried over CaH_2 and filtered.
Isooctane (2,2,4-trimethylpentane); was supplied by Lab. Scan. It was fractionated on the 1-meter column and the fraction boiling at 96 ^oC at 685 mmHg was collected and then it was dried over CaH_2 and filtered.
Diethyl ether; was supplied by Lab Scan. It was refluxed over metallic sodium for several days prior collecting the fraction boiling at 32 ^oC at 685 mmHg. It was stored over CaH_2 in vacuo.

2.1.2 Reagents

Propyleneoxide (PO-monomer); was the product of Merck A.G. It was refluxed over CaH_2 for several days before fractionation. Then, the distillate boiling at 32 ^oC at 685 mmHg was collected by using 1-meter fractionation column and stored over CaH_2 in vacuum.

Carbon Disulfide (**CS_2-monomer**)**;** was supplied by Merck A.G. It was shaken for three hours with three portions of potassium permanganate solutions (5g/L), twice for six hours with mercury (to remove sulphide impurities) until no further darkening of the interface occurred, and finally with a solution of mercuric sulfate (2.5 g/L). It was dried with calcium chloride, further dried by refluxing with phosphorous pentoxide in diffuse light, and fractionally distilled, collected on calcium hydride at 43.1 ^oC, at 685 mmHg pressure. With this purified CS_2 and nonpurified CS_2, polymerizations were done and same results were obtained. After this, CS_2 was used without further purification.

Acetone; was supplied by Merck A.G and purified with fractional distillation before use (Bp: 53 ^oC at 685 mmHg) and then it was dried over CaH_2 and filtered.

Isopropyl Alcohol (2-propanol), Potassium Hydroxide and $ZnSO_4$. $7H_2O$ were the products of Merck A.G. and they were used without further purification.

Phthalic Anhydride (Fisher Scientific Company), **Pyridine** (Lab. Scan) and **NaOH** (Merck A.G.) were used without purification and used in determining hydroxyl content of polymer.

Potassium Hydrogen Phthalate was supplied by Merck A.G. It was dried in a glass container at 120 ^oC for two hours and then it was cooled in a desiccator. It was used for the standardization of NaOH.

Chloroform (Dop)**, Glacial Acetic Acid** (Merck A.G.)**, Br_2** (Acros Organics), **KI** (Merck A.G.)**, $Na_2S_2O_3.5H_2O$** (Atabay Ltd. Şti.) were used without purification and used in determining double bond content of polymer.

Potassium Iodate (KIO_3); was the product of Merck A.G. It was dried in a glass container at 110 ^oC at least one hour and then it was cooled in a desiccator. It was used for the standardization of $Na_2S_2O_3.5H_2O$.

Sodium chloride (NaCl); was the product of Atabay Ltd. Şti. Primary standard quality of NaCl was put and heated at least an hour at 110 ^oC or higher in a beaker then cooled in a desiccator and weighed accurately. Then, it was transferred quantitatively to a 1-

Liter volumetric flask, rinsed with distilled water at the level of the graduation mark on the neck of the flask.

Silver Nitrate ($AgNO_3$); was supplied by Merck A.G. After preparation, it was standardized by NaCl solution. Then, it was kept in the dark when it was not used.

Cyclohexane, H_2SO_4, Formic acid and H_2O_2; were the products of Merck A.G. and they were used without further purification in hydroxylation of double bonds.

Desmodur N-100; was the product of Bayer G and used without purification.

Acetonitrile (CH_3N); was supplied by Merck A.G. and purified with fractional distillation before use (Bp: 80 ^{o}C at 685 mmHg) and then it was dried over CaH_2 and put under vacuum.

2.2 Apparatus

2.2.1 Dry box

Zinc Isopropyl Xanthate ($Zn(Xt)_2$) catalyst was prepared under dry N_2 atmosphere. The dry box permits, handling air sensitive reagents with gloves under inert gas (N_2) atmosphere. Dry box atmosphere was further dried by using P_2O_5. The internal pressure of the box was regulated and using an oil-trap at the outlet of N_2 stream prevented leakage of the atmospheric air.

2.2.2 The Vacuum-line

An all glass vacuum-line was used for experiments .The assembly allows:

- Storage of reagents with measuring and transferring the possibilities in vacuum.
- Mixing the reagents in vacuum and measurement of the amount of evolved gas.
- Storage of reaction products in vacuum with the possibility of handling them without exposure to atmosphere.

The Vacuum-line is evacuated by:

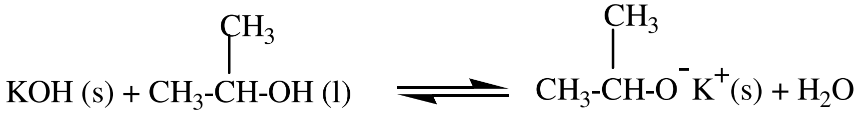
Fore pump, a Sargent-Welch Scientific Co. rotary pump that can provide an evacuation below $1*10^{-4}$ mmHg.

Liquid nitrogen traps, Pyrex flasks chilled with liquid nitrogen in order to evacuate the system.

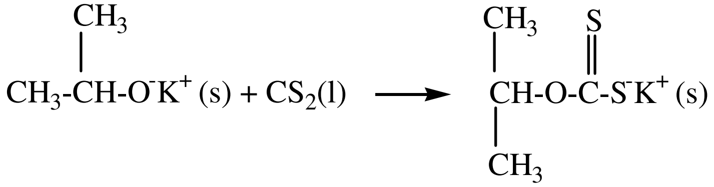
2.3 Procedure

2.3.1 Preparation of Potassium Isopropyl Xanthate (KXt)

50 ml isopropyl alcohol and 40 g KOH were refluxed for one hour. At the end of reflux, the warm solution was decanted. 40 ml CS_2 was added dropwise 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. The mixture was filtered and washed with two portions of diethyl ether (25 ml each). The precipitate was dissolved in acetone. Diethyl ether which is a poor solvent for the product was added until production of precipitate. The mixture was decanted and the residue was collected. This process was done twice. The obtained potassium isopropyl xanthate was put into dry box. The reactions are as follows;



$$KOH\,(s) + CH_3\text{-}\overset{\overset{CH_3}{|}}{C}H\text{-}OH\,(l) \rightleftharpoons CH_3\text{-}\overset{\overset{CH_3}{|}}{C}H\text{-}O^-K^+(s) + H_2O \qquad (2.1)$$

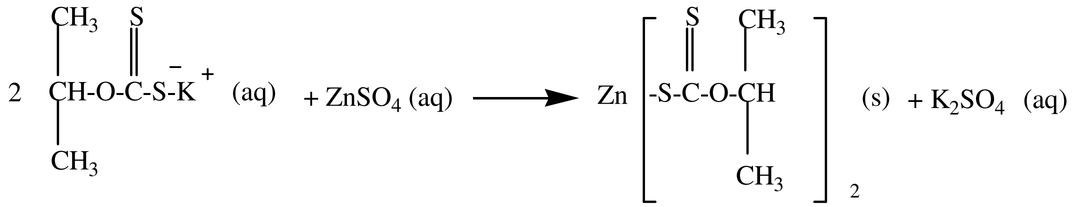


$$CH_3\text{-}\overset{\overset{CH_3}{|}}{C}H\text{-}O^-K^+\,(s) + CS_2(l) \longrightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}H\text{-}O\text{-}\overset{\overset{S}{\|}}{C}\text{-}S^-K^+\,(s)$$

Potassium Isopropyl Xanthate (2.2)

2.3.2 Preparation of Zinc Isopropyl Xanthate ($Zn(Xt)_2$)

Metal xanthates are quite stable, but they would decompose in prolonged exposure to moist air. Therefore, in this synthesis maximum care was taken to protect the product from air. Solutions of KXt (3.8 %) and $ZnSO_4$ (11.6 %) in degassed water were both prepared under dry nitrogen atmosphere. These solutions were also mixed in the dry box by adding $ZnSO_4$ solution on to KXt solution by continuous mixing. The mixture was allowed for sometime to settle down completely. The solid phase decanted and transferred on a vacuum line without exposing to atmosphere. The product was pumped for several hours for complete dryness.



$$2\,(CH_3)_2CH\text{-}O\text{-}C(=S)\text{-}S^{-}K^{+}\,(aq) + ZnSO_4\,(aq) \longrightarrow Zn\left[\text{-}S\text{-}C(=S)\text{-}O\text{-}CH(CH_3)_2\right]_2\,(s) + K_2SO_4\,(aq) \quad (2.3)$$

Zinc Isopropyl Xanthate

2.3.3 Recrystallisation of $Zn(Xt)_2$ and Preparation of Catalyst Solution

Recrystallisation was done twice with 1.9 g of $Zn(Xt)_2$. In the first recrystallisation 150 ml benzene was added to $Zn(Xt)_2$ in dry box but it did not dissolved completely. Therefore, it was put into a water bath at 70-80 ^{o}C. After having a saturated solution, the solution was filtered in dry box. The funnel used while filtering was about 90 ^{o}C in order to prevent the precipitation of $Zn(Xt)_2$. The solution was cooled to room temperature, precipitation occurred and the solution was decanted. The crystals of $Zn(Xt)_2$ were recrystallised in 50 ml of benzene with the same procedure. Finally, crystals were dried under vacuum and 1.79 g product was obtained. A solution of $Zn(Xt)_2$ in benzene having a concentration 6.01×10^{-6} mol Zn/ml was prepared and stored in a stoppered bottle under nitrogen atmosphere in dry box.

2.3.4 Polymerisation of PO with $Zn(Xt)_2$

Polymerization experiments were carried out under high vacuum conditions. A measured amount of catalyst solution was added 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. The solvent of the catalyst solution was pumped off to dryness. Measured amount of PO was distilled on to the catalyst under vacuum by chilling the polymerization tube with liquid N_2. The polymerization tube was sealed off by flame and placed in a constant temperature bath at 80 ^{o}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.

2.3.5 Copolymerization of CS_2 with PO by Using $Zn(Xt)_2$

Copolymerisation of CS_2 with PO in the presence of $Zn(Xt)_2$ was studied in some details. Copolymerization experiments were carried out under high vacuum conditions.

a) The Change of Copolymer Composition with Feed Composition

In this study, the catalyst concentration was kept constant in the range 5.73×10^{-3} M– 6.44×10^{-3} M Zn. The feed composition was altered by increasing the mole fraction of CS_2 (f_2), step by step from $f_2 = 0.113$ up to $f_2 = 0.730$ keeping the total volume of mixture about approximately as 10 ml at 80 ^{o}C for 20 h polymerization time. However, f_2 values which were 0.403, 0.487 and 0.730 were studied after 5 months. And also f_2= 0.730 was repeated at the same conditions. Also, acetonitrile which have a high dielectric constant (about 10 ml) was added before sealing in order to see dielectric constant effect.

b) The Change of Yield Composition of Copolymer with Polymerisation Time

For this purpose, for a fixed f_2 (0.162 and 0.266) and catalyst concentration, the polymerization time was increased (20, 48, 120 and 240 hour), step by step, and products were characterized.

c) Effect of Catalyst Concentration on Polymerisation

Same procedure was applied to study effect of catalyst concentration on polymerization. For this purpose, catalyst concentration was changed between 5.73×10^{-3} M to 2.0×10^{-2} M Zn. In these experiments f_2 values were kept constant as 0.162 and 0.266 and two days polymerization time at 80 ^oC was allowed.

d) Effect of Temperature on Polymerisation

The temperature effect on polymerization was studied for the concentration of catalyst as 0.011 M Zn between 60~100 ^oC. In these experiments again the same f_2 values that were 0.162 and 0.266 were used and reaction time was 2 days.

e) Synthesis of Larger Quantity of Copolymers

In order to obtain larger quantity of copolymer, catalyst concentration as 0.0169 M and 0.0178 M Zn were used. f_2 values as 0.266 and 0.487 and reaction time 10 days at 80 ^oC were used for the polymerization. These experiments were also repeated by using "aged" catalyst. In order to obtain aged catalyst, the freeze dried catalyst was heated at 80 ^oC with an oil bath, and pumped of continuously for 24 h. Following the heating treatment, monomer mixtures were introduced and general procedure of polymerization was applied.

2.3.6 Fractionation of Copolymer

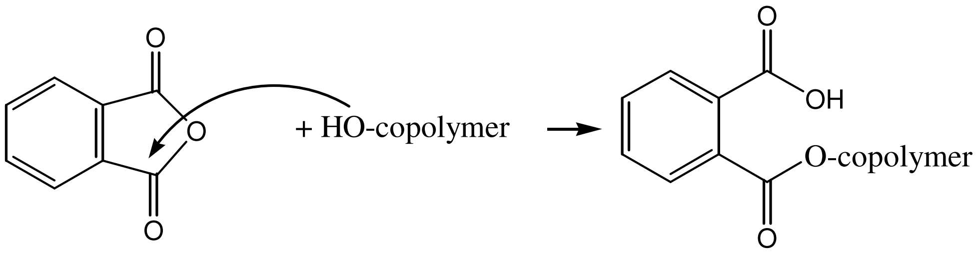
Copolymers of CS_2 and PO were separated to 0 ^{o}C-insoluble fraction in isooctane (high molecular weight) and 0 ^{o}C-isooctane soluble (low molecular weight) fractions. Copolymers dissolved in 70 ^{o}C isooctane (1.7 g copolymer/100 ml isooctane). The solution was chilled to 0 ^{o}C for 24 h. The supernatant solution decanted from the precipitated high molecular weight fraction. Low molecular weight fraction was obtained by evaporation of the supernatant solutions. Both fractions were dissolved in benzene, filtered, freeze-dried and weighed.

The low molecular weight fraction was oily substance whereas the high molecular weight fraction was rubbery product. The color of the high molecular weight product becomes more yellowish as the f_2 values were increased.

2.4 Characterisation of Copolymer

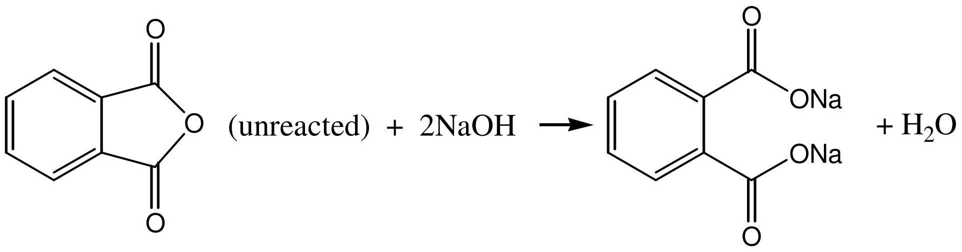
2.4.1 Determination of Number Average Molecular Weight (M_n) by End Group Method

End group determination was performed in order to find out hydroxyl and double bond functionality of copolymer. Hydroxyl group functionality was determined by using phthalic anhydride esterification method. Copolymer (~1g) and blank solution were refluxed with 0.03 M phthalic anhydride in pyridine at 100 ^{o}C. After cooling the solutions with ice, 10 ml of distilled water was added to hydrolyze residual anhydride 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 reactions are as follows (Equation 2.4 and 2.5):



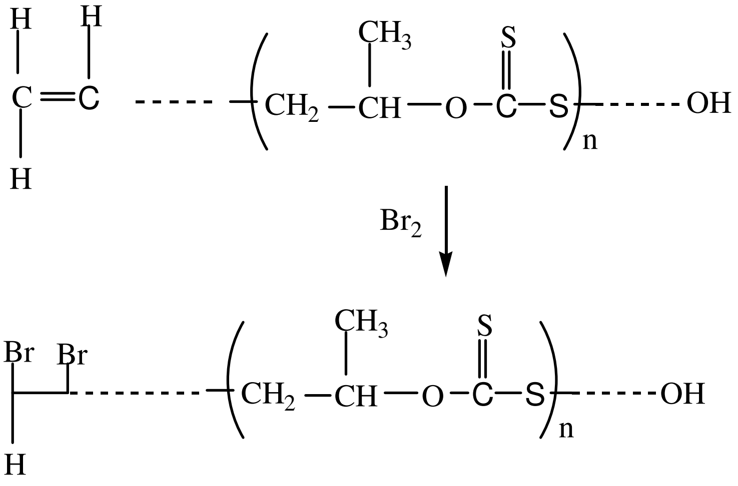
(2.4)

Titration



(2.5)

Double bond content was determined by bromination of double bonds. Copolymer was dissolved in a mixture of 10 ml $CHCl_3$ + 10 ml glacial acetic acid. The mixture was cooled in an ice bath and 10 ml 0.08 M Br_2 in glacial acetic acid was added slowly with a pipette. After standing exactly two minutes, 25 ml 10% aqueous KI was added and the solution was titrated with 0.05 M $Na_2S_2O_3$ using starch indicator. The titration difference between sample and blank gave the amount of double bonds in copolymer. The reactions are (Equation 2.6, 2.7, 2.8):



(2.6)

Titration

$$Br_2\ (\text{unreacted}) + 2I^- \longrightarrow 2Br^- + I_2 \tag{2.7}$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^- \tag{2.8}$$

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;

$$M_n = 1\ \text{g polymer} / (C_{OH} + C_{DB})/2 \tag{2.9}$$

C_{OH}: Moles of hydroxyl groups in 1-gram polymer
$C_{DB:}$ Moles of double bonds in 1-gram polymer

2.4.2 Combustion of Chlorinated Polymers in an Oxygen Filled Flask

After hydroxyl group determination, it was found that the amount of hydroxyl groups is too small therefore it was thought that HCl during the extraction may be the cause. Because Cl and OH anions substitution might occur during extraction. Copolymers were combusted in order to convert covalently bound Cl atoms into chloride anion.

For the combustion, an Erlenmeyer flask of 250-ml capacity with B-24 ground glass joint was used (Figure 1). The sample (3 – 25 mg) was weighed on filter paper and folded to form a through. After weighing, the sample was enclosed in the paper, which was then clamped in the glass joints. The paper was positioned so that the fuse points away from the stopper. And then, 10 ml 0.01 N NaOH solution was put in to the flask.

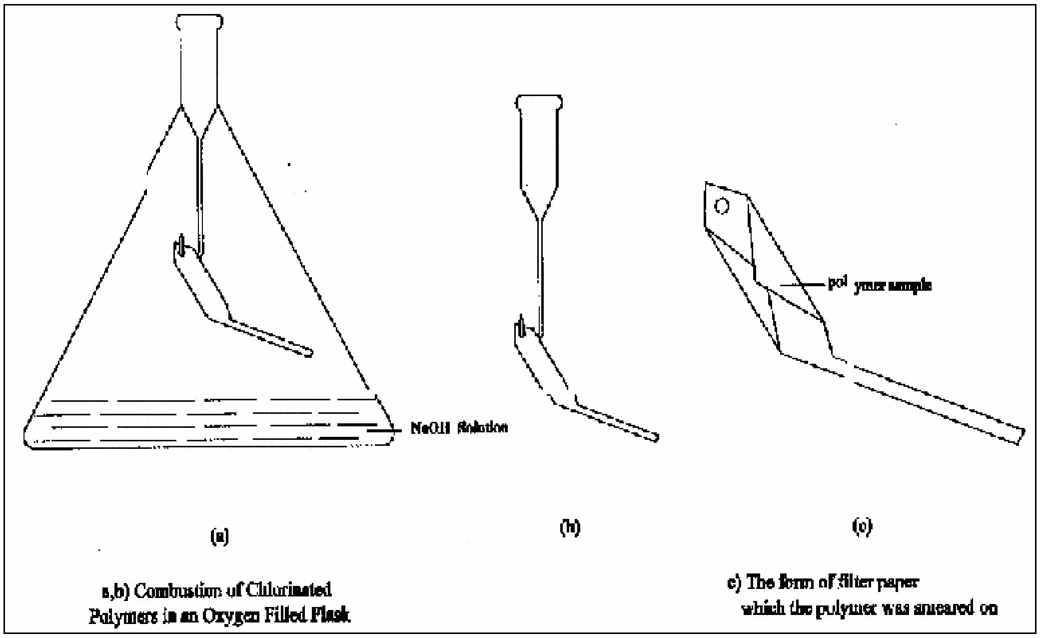


Figure 1: Combustion of chlorinated polymers with an oxygen filled flask

After this, the flask was filled with oxygen gas and the paper fuse lit in the flame and the stopper quickly inserted in the flask. The flask was inverted so that the solution provides a liquid seal around the stopper. After combustion, the flask was placed upright and left for 15 minutes until the combustion gases had been absorbed in the solution.

The important point in this microanalysis technique is the amount of sample. The sample size should be between 3-25 mg. Sample sizes greater and smaller than this amount were combusted, however no accurate results were found. If greater amount were used, then incomplete combustion due to C formation would occur.

In order to test the reliability of this method m-chloro-nitro-benzene ($C_6H_4NO_2Cl$ MW: 157.6 g/mole) was combusted. The Cl content in this compound was found as 23.7 % (the theoretical value is 22.5) in my previous research (Öztürk, 2000).

2.4.3 Determination of Chloride in Mohr Method

By using Mohr Method, the amount of chloride ion in combusted polymer samples was determined. For this, 10-ml NaOH solution was taken after the combustion and diluted to 50 ml with water. After that, it was refluxed in a water bath at 65 °C for one hour and then reagents methyl orange, HNO_3 (to neutralize the solution), $NaHCO_3$ (to finer adjustment of pH), K_2CrO_4 (the indicator anion in precipitation titration) were added and titrated against with 0.05 N $AgNO_3$ solution. If the end point was passed, then back titration with NaCl could be done.

The titration was carried out in a dark room because if it were done in direct sunlight, then formed AgCl would be decomposed by absorption of light.

$$2\,AgCl \rightarrow 2\,Ag + Cl_2 \qquad (2.10)$$

2.4.4 Calculation of the Extend of Chlorination by Using Mohr Method

The extend of chlorination was calculated by using the following equation;

$$\%\,Cl = (\text{Vol. } AgNO_3 \times \text{N } AgNO_3 \times \text{MW of Cl} \times 100) / (1000 \times \text{wt. of sample}) \qquad (2.11)$$

2.5 Determination of Crystallinity

In order to understand if copolymer has a crystal structure or not, benzene solutions of high molecular weight fractions (about 0.2-1 %, g/ml) were prepared and drop wisely on a microscope slide. Each drop addition of solution was continued until a film of polymer with proper thickness obtained on a microscope slide, benzene was evaporated under Infra-Radiator lamp. The deposited films of copolymer on microscope slides were melted in an oven by increasing the temperature to 100 °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 by using a hot stage polarizing microscope. For this work, different f_2 values in different polymerization conditions were studied.

In order to investigate details, high molecular weight polymer of experiment 10 in Table 4 that has f_2 value as 0.162 was also studied. The copolymer sample was taken and dissolved with isooctane at 70 ^{o}C in a fractionation flask and chilled to 35 ^{o}C and then the supernatant solution was separated from the precipitated polymer rich phase by filtering with glass wool which was named as Fraction 1. Fraction 2 which was the fraction between 35-25 ^{o}C was taken after one night waiting in a water bath after filtering with a glass wool. Small amount of these samples were dissolved in chloroform (about 0.2-1 %, g/ml) and dropped wisely on a microscope slide. Chloroform was evaporated under Infra-Radiator lamp. The deposited films of polymer on microscope slide were melted in an oven by increasing temperature to 100 ^{o}C. The temperature of the oven was decreased gradually to room temperature in at least 12 hours. These fractions were then taken and put under a hot stage polarizing microscope.

2.6 Stability of Catalyst

Experiment 9 in Table 1 in Section 3 that has f_2 value as 0.162 (5.73×10^{-3} M Zn) was studied again after 4 months at the same conditions (experiment 27) in order to find if any change in the catalyst efficiency occurred or not at 80 ^{o}C for two days. Experiment 9 was also repeated by using “aged” catalyst (experiment 28). In order to obtain aged catalyst, the freeze dried catalyst was heated at 80 ^{o}C in an oil bath, and pumped off continuously for 24 h. Following the heating treatment, monomer mixtures were introduced, the only difference is that after putting monomers, the color of the catalyst solution was misty and then general procedure of polymerization was applied.

2.7 Hydroxylation of Double Bonds

2.7.1 Concentrated Sulfuric Acid Method

Polymer containing 6.257×10^{-4} mol double bond/1g polymer was dissolved in 30 ml cyclohexane solution in a water bath at 70 °C and nitrogen gas passed through it, closed and put in the refrigerator. 30 ml, 66% (by weight) of H_2SO_4 was also prepared and cooled. And then acid was added slowly, with constant and vigorous agitation during the course of 20-25 minutes. The temperature should be 20-25 °C. Again it was stirred for one hour and then 60 ml of degassed water was added on it and agitated. Phases were separated and upper phase washed with water and freeze-dried (Vogel, 1966)

2.7.2 H_2O_2/H_2O Method

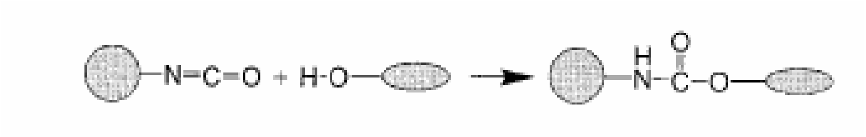
2 g of copolymer containing 6.257×10^{-4} mol double bond/1g polymer was dissolved in 30 ml 87 % formic acid in a water bath at 70 °C and cooled. Into this mixture, 12 ml of 30% H_2O_2 was added slowly with continuous stirring. The temperature rose to 40 °C in 15 minutes and remained at that point by outside cooling and then stirred for three hours at this degree. Then the reaction mixture placed in the refrigerator overnight. The excess peroxide was decomposed by using aqueous $Na_2S_2O_3.5H_2O$. The polymer was taken up in ether and neutralized with 20 % NaOH. An excess of 20 ml of 20 % NaOH added and the solution was refluxed for two hours to saponify any formate esters. The organic portion was again taken up 50 ml of ether and shaken with HCl to remove any base carried over. Then the ether removed in rotavapor and polymer was taken into the benzene solvent. However, an emulsion is formed upon addition of benzene which was broken down by addition of NaCl. The benzene phase finally, washed with water and freeze dried (Raphael et al., 1960).

2.8. Cross-linking of Hydroxylated Copolymers

Hydroxylated copolymer was (experiment 25 and f_2=0.487) tried to cure with trifunctional isocyanate Desmodur N-100. The binder formulations are usually named as gumstocks. Crosslinking ratio of the polymer (XR) 1.2 was prepared and its formula is as follows:

XR= (NCO functionality of Desmodur N-100) / (OH functionality of copolymer) (2.12)

The reaction of Desmodur with OH groups of the copolymer can be depicted in a simple manner:



(2.13)

2.8.1 Preparation of Gumstocks

Hydroxylated copolymer and Desmodur N-100 was calculated to mix with a crosslinking ratio of 1.2. For this, copolymer sample was transferred into a beaker and Desmodur N-100 was added. Resulting mixture was stirred about 15 minutes and put under vacuum desiccator to remove gas bubbles from the gumstocks nearly half an hour. Finally, mixtures were transferred into the mould and held 60 °C for 3 days and 80 °C for another 3 days.

Calculation of the XR values is seen in below formula:

$$XR = (5.21\times10^{-3} \times m_{DN100}) / (5.86\times10^{-5} \times m_c) \qquad (2.14)$$

XR: Cross-linking Ratio
5.21×10^{-3}: Functionality of Desmodur N-100 (mol/g)
m_{DN100}: The used weight of Desmodur N-100
5.86×10^{-5}: Hydroxyl functionality of copolymer (mol/g)
m_c: The used weight of copolymer sample

2.9 Characterisation of Copolymer

2.9.1 Elemental Analysis

LECO, CHNS-932 instrument in central laboratory was used. In order to find the sulphur, carbon, hydrogen and oxygen content of the copolymer, elemental analysis were done. The elemental analyzer offers a rapid simultaneous multi-elemental determination of carbon, hydrogen, nitrogen, and sulfur in homogenous micro samples (2 milligrams). Independent oxygen result is attainable with the VTF-900 High-Temperature Pyrolysis Furnace.

2.9.2 Gel Permeation Chromatography (GPC) Measurements

PL-GPC 220 in central laboratory was used. Measurements were done at 30 °C. So as to learn molecular weight distribution of copolymers, they were dissolved in tetrahydrofuran (THF) and calibration measurements were done with polyethylene oxide (PEO) and polypropylene glycol (PPG) standards. Refractive index detector (viscotek model 300 TDA) was used only. 1-5 mg/ml concentration in THF and 1 ml/min flow rate in each run were used. PL gel 5µ MiniMIX-C column were used.

2.9.3 Dynamic Light Scattering

Malvern CGS-3 instrument in central laboratory is used. Samples were studied with four different concentrations. Data are evaluated by Berry and Guinier plots.

2.9.4 IR Spectroscopy

A Nicholet 510 model FT-IR spectro-photometer was used to get IR spectra of the polymers. Polymers were dissolved in $CHCl_3$, and then dropped on KBr pellets.

2.9.5 ^{1}H and ^{13}C NMR Measurements

Bruker-Spectroscopic Avance DPX 400 Ultra Shield instrument was performed. For ^{1}H and ^{13}C NMR measurements, 400 and 100 MHz frequencies were used respectively. Measurements were done in deuterio-chloroform ($CDCl_3$). DEPT-135 (Distortionless Enhancement by Polarization Transfer) and HSQC (Heteronuclear Single Quantum Coherence) were also recorded by the same apparatus.

2.9.6 DSC Measurements

A Perkin-Elmer model 1-B differential scanning calorimeter was used to determine glass transition temperatures. For DSC measurements, samples (10 mg) were heated from -150 ^{o}C to 80 ^{o}C at a heating rate of 5 ^{o}C/min and then cooled to -150 ^{o}C at a cooling rate 5 ^{o}C/min under nitrogen atmosphere.

2.9.7 TGA Measurements

Perkin Elmer Pyris 1 TGA instrument in central laboratory was used. Samples were heated from room temperature to 300 ^{o}C at a heating rate of 5 ^{0}C/min with a flow rate of 20 ml/min under nitrogen atmosphere.

2.9.8 UV Measurements

Hewlett Packard 8452A Diode Array Spectrophotometer was used. Diethyl ether was used as a solvent.

2.9.9 Refractive Index Measurements

Refractive indices were measured at room temperature with an Abbé refractometer (equipped with a light source) on thin films which were obtained by casting the polymers, in chloroform solutions (3 %), directly onto the prism of the refractometer (Marianucci et al., 1994).

CHAPTER 3

RESULTS AND DISCUSSION

3.1 $Zn(Xt)_2$ Catalyst

3.1.1 Visible/UV Spectrum and Efficiency of $Zn(Xt)_2$ Catalyst

Bolat (1999) reported that the efficiency of $Zn(Xt)_2$ catalyst would change with the degree of purification and the storage conditions. If the catalyst solution is not kept in closed conditions, in prolonged storage, initially clear solution become turbid and the efficiency decreases. The color of catalyst solution also depends on the degree of purification. If the catalyst is properly purified by re-crystallisation, solution is colorless otherwise it appears pale yellow. The catalyst solution used in this work was tested in homopolymerisation of PO. UV spectrum of KXt and $Zn(Xt)_2$ were taken. For both cases, there is no absorption between 550 and 600 nm in yellow color range. KXt gives two absorption peak at 208 and 302 nm. But $Zn(Xt)_2$ gives two absorption peak at 224 and 294 nm**.** The efficiency of catalyst was tested in homo-polymerization of PO using Zn concentration as 6.01×10^{-3} M at 80 ^{o}C in 20 h polymerization time and 43.3 % conversion was obtained. Bolat's catalyst in comparable conditions yielded only 15 %.

3.1.2 Stability of $Zn(Xt)_2$ as a Catalyst in CS_2+PO Copolymerisation

In order to detect if catalytical activity of $Zn(Xt)_2$ change with aging some of the reactions were repeated after about 4-13 months period. These experiments are shown in Table 1. It appeared that efficiency of catalyst increased in copolymerization with aging as time passes. However, the composition of copolymer almost stays constant with aging, but the yield of copolymer increased. Similar aging effect was also observed by Bolat (1999) in $Zn(Xt)_2$ catalyzed PO polymerization.

In order to accelerate aging by heating, the catalyst was kept at 80 ^{0}C under vacuum for 24 h (Ex. 28 in Table 1). Indeed as expected efficiency increased without any change of the solubility of catalyst in the polymerization mixtures. Similarly, aged catalysts were also soluble, and gave clear solutions. The initial mixtures were colorless but they become yellow as copolymerization progress.

Table 1: Catalyst stability

Ex	Time (month)	% HMW	f_2	Py (g)	%C	%H	%S	F_2
5	0	62	0.332	0.563	52.2	8.33	15.1	0.133
29	13	87	0.332	1.198	56.8	9.18	10.1	0.096
8	0	61	0.730	0.542	55.8	9.50	5.58	0.046
30	8	81	0.730	0.662	57.4	9.51	7.80	0.072
9	0	89	0.162	1.176	53.9	8.83	11.4	0.099
27	4	92	0.162	2.061	51.5	8.75	13.8	0.117
28	4	94	0.162	2.288	52.4	8.85	13.2	0.114

Ex: Experiment number
Time (month): Aging of the catalyst in months
% HMW: Per cent of high molecular weight fraction
f_2: Mole fraction of CS_2 in the feed
Py: Polymer yield in gram
F_2: Mole fraction of CS_2 in the polymer
Note: Other values are in the Appendix A

Soysal (2001), have shown that when $Zn(Xt)_2$ heated around 100 ^{o}C under vacuum, catalyst (3.01×10^{-2} g) yielded a volatile product, which can be condensed as a white feathery solid (1.42×10^{-3} g) on the cold glass tubes of the vacuum line. She suggested that since 32 g volatile product is formed from two mole of $Zn(Xt)_{2,}$ the volatile product in vacuum at 100 ^{o}C is S and it is formed from a condensation reaction between two moles of $Zn(Xt)_{2,}$ plausibly forming a Zn-S-Zn bond.

The activity of Zn-O-Zn bonds and Zn-S-Zn bonds are well known in coordination polymerization of cyclic ethers. The increase in the catalytic efficiency with aging/accelerated aging can be tentatively attributed to formation of Zn-S-Zn bonds.

3.2 Copolymerization of PO with CS_2 by Using $Zn(Xt)_2$ Catalyst

3.2.1 Effect of CS_2 Mole Fraction on the Yield and Properties of Polymers at 20 h. Polymerization Time

In Table 2, the results of polymerization experiments in 20 h. reaction time with different CS_2 mole fraction (f_2) in feed are given. In Figure 2, the mole fraction of PO residue in polymer (F_1) is plotted versus mole fraction of PO (f_1) in the feed. F_1 is calculated as;

$$F_1 = \left\{ \frac{(\text{g S}/32.06)\times 1/2}{(\text{g O}/16)} + 1 \right\}^{-1} \tag{3.1}$$

Table 2: Copolymerisation of PO with CS_2 and elemental analysis of product

Ex	f_2	Py (g)	%C	%H	%S	F_2	f_1	F_1	r_1	ε
1	0.113	1.190	57.1	9.22	10.1	0.096	0.887	0.904	1.07	7.57
2	0.162	0.566	54.7	8.98	12.3	0.113	0.838	0.887	1.32	7.30
3	0.225	0.519	44.0	6.98	15.3	0.102	0.775	0.898	2.26	6.94
4	0.266	0.554	51.9	8.69	13.1	0.110	0.734	0.890	2.57	6.71
29	0.332	1.198	56.8	9.18	10.1	0.096	0.668	0.904	4.18	6.34
6	0.403	1.037	56.7	8.98	11.6	0.113	0.597	0.887	4.62	5.94
7	0.487	1.051	56.6	9.10	12.2	0.121	0.513	0.879	5.95	5.47
8	0.730	0.542	55.8	9.50	5.58	0.046	0.270	0.954	53.4	4.11
30	0.730	0.662	57.4	9.51	7.80	0.072	0.270	0.928	32.1	4.11
31	0.730	0.078	39.9	6.32	29.0	0.226	0.270	0.774	6.56	21.4

Ex: Experiment number
f_2: Mole fraction of CS_2 in the feed
Py: Polymer yield in gram
F_2: Mole fraction of CS_2 in the polymer
r_1: k_{11}/k_{12} (reactivity ratio of PO)
ε: Dielectric constant (approximately)
h, l: high and low molecular weight fraction
Note: Other values are in the Appendix A

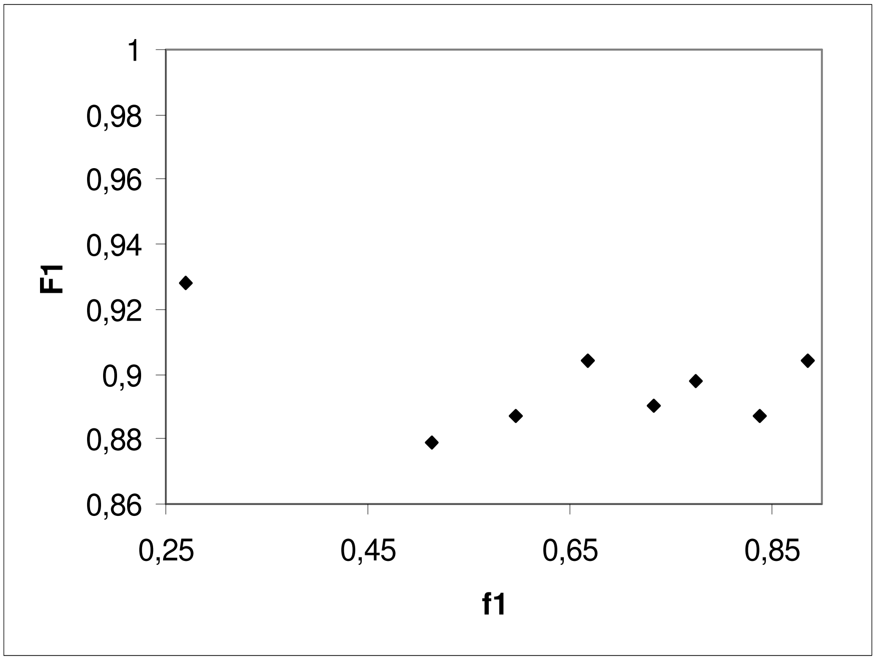


Figure 2: Copolymerisation curve for 20 h polymerization time

The reactivity ratio of PO (r_1) was also calculated and given in Table 2. The reactivity ratios are defined in literature as $r_1=k_{11}/k_{12}$, $r_2=k_{22}/k_{21}$ where k_{11} is the rate constant of addition of a PO molecule to a growing chain with a PO terminal unit whereas k_{12} is addition of CS_2 to a growing chain with PO terminals.

The classical copolymerization equation gives $F_1= (1-F_2)$ as a function of $f_1= (1-f_2)$ and f_2 as

$$F_1= (r_1f_1^2 + f_1f_2) / (r_1f_1^2 + 2\ f_1f_2 + r_2\ f_2^2) \qquad (3.2)$$

However, since a CS_2 terminated active chain will not react with a CS_2 molecule (i.e. $k_{22}=0$), without any fear r_2 in above equation can be taken as zero. Thus, above equation boils down to

$$r_1 = f_2\ (2F_1-1) / f_1(1-F_1) \qquad (3.3)$$

Both of the equations can be used to obtain r_1 value. But for this determination the percent conversion should not exceed say 5% in order to keep f_1 constant. However, since r_1 value is not much larger than 1, these values are calculated for different experiments in Table 2.

Following trends are observed in Table 2 and Figure 2.

a) F_1 is almost insensitive to f_1 value except for very low values of f_1 (i.e. $f_1=0.270$ in experiment 8).

b) However, the r_1 value increases with decreasing f_1. In other words, as the solution becomes poor in PO, the possibility of a chain terminated with PO unit, reacting with a PO molecule over CS_2 molecule markedly increases.

c) As a consequence of this trend, in a feed, which is very poor in PO but rich in CS_2, almost pure poly(propylene oxide) is obtained. This result at first look seemed to be absurd; hence experiment 8 was repeated again (experiment 30 in Table 2). As observed in table, same trend was observed. Furthermore, this result was confirmed by NMR spectroscopy (Section 3.10).

This result may be explained by assuming that the rate of reaction is controlled by dielectric constant (ε) of the medium. In PO rich mixtures (higher dielectric constant), coordinated PO molecules on the active sites may be dissociated to leave vacant sites for CS_2 to coordinate. But in low dielectric medium (rich in CS_2), stronger association of PO to coordination site, in spite of low PO concentration, is favored, thus CS_2 mole fraction in polymer decreases (ε of PO= 8.2 (Chen et al., 1993), ε of CS_2=2.60).

In order to test this explanation, polymerization with a high dielectric constant medium was also carried out (exp.31 in Table 2). In this experiment, monomer mixture used in exp.30 was diluted with equal volume of acetonitrile (ε=38.8 at 20 ^{o}C, Schefland and Jacobs, 1953). In agreement with the expectation, F_2 increased from 0.072 to 0.226. Apart from increasing F_2, the yield and molecular mass of product (it was in oily appearance) drastically decreased. The decrease in the yield is not only due to high dielectric constant, but plausibly it is because of competition for coordination sites between monomers and acetonitrile. However, in following sections it shall be argued that in this system the growing chain terminal is not free as in classical copolymerization hence; the equation 3.3 may not be used for calculation of r_1.

Polymers were separated into two fractions by precipitating in a solution of isooctane at 0 ^{o}C, as high and low molecular weight fractions. These fractions show some different characters. The low molecular weight fraction was yellow oils with higher sulphur content. On the other hand, high fractions were rubbery solids with lower sulphur content. In Figure 3, F_1 versus f_1 is plotted. The r_1 values of high fractions showed marked increase of F_1 as f_2 increased. Analytical data and percent high fractions are given in Table 3.

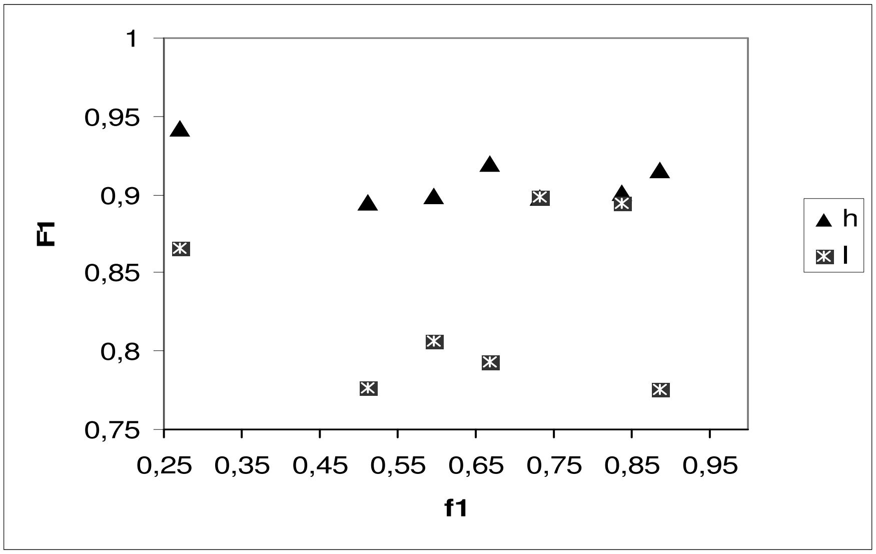


Figure 3: Copolymerisation curve for high and low molecular weight fractions of copolymers

The difference in the sulphur content of high and low fractions is also observed in r_1 values (Table 3). This difference indicates a termination or transfer reaction forming small, by-product molecules with di or three thio carbonate groups. Indeed, dithio carbonate group with a cyclic structure has been detected in low fraction of copolymers in NMR spectrum. These by-products would associate to lower tail of copolymer in the fractionation experiments.

Table 3: High (h) and low (l) molecular weight fractions of copolymers

Ex	f_2	% HMW	% C		% H		% S		F_2		M_n		r_I	
			h	l	h	l	h	l	h	l	h	l	h	l
1	0.113	90.7	57.7	51.3	9.34	8.04	8.86	21.8	0.084	0.224	-	-	1.26	0.31
2	0.162	78.9	56.4	53.4	9.34	8.80	10.4	12.2	0.098	0.106	2364	722	1.58	1.44
4	0.266	71.6	55.4	55.3	9.14	8.93	11.0	11.1	0.101	0.101	2024	753	2.86	2.86
29	0.332	86.8	57.6	51.6	9.39	7.82	8.54	20.7	0.080	0.207	-	-	5.22	1.41
6	0.403	87.1	57.8	49.4	9.16	7.78	10.2	21.0	0.100	0.194	-	-	5.40	2.13
7	0.487	85.8	57.5	51.4	9.31	7.82	10.6	21.8	0.105	0.223	3966	875	7.14	2.36
8	0.730	61.3	57.9	52.5	10.1	8.55	4.80	6.81	0.042	0.050	-	-	59.0	48.7
30	0.730	80.8	58.1	54.4	9.73	8.58	6.29	14.2	0.057	0.134	-	-	42.0	14.8

Ex: Experiment number
f_2: Mole fraction of CS_2 in the feed
% HMW: Per cent of high molecular weight fraction
F_2: Mole fraction of CS_2 in the polymer
r_I: k_{11}/k_{12} (reactivity ratio of PO)
h, l: high and low molecular weight fraction
Note: Other values are in the Appendix A

3.2.2 Conversion of Monomer Mixture with Reaction Time

Conversion of monomer was studied by keeping reaction conditions constant but increasing reaction time from 20 to 240 hours. In this study, in first set of experiments, the mole fraction of CS_2 in feed (f_2) was 0.162 (Table 4) and in the second set it was 0.266 (Table 5). Conversion (g polymer) versus time graphs, resulted straight lines (Figure 4 and 5) indicating a zero order reaction rate law.

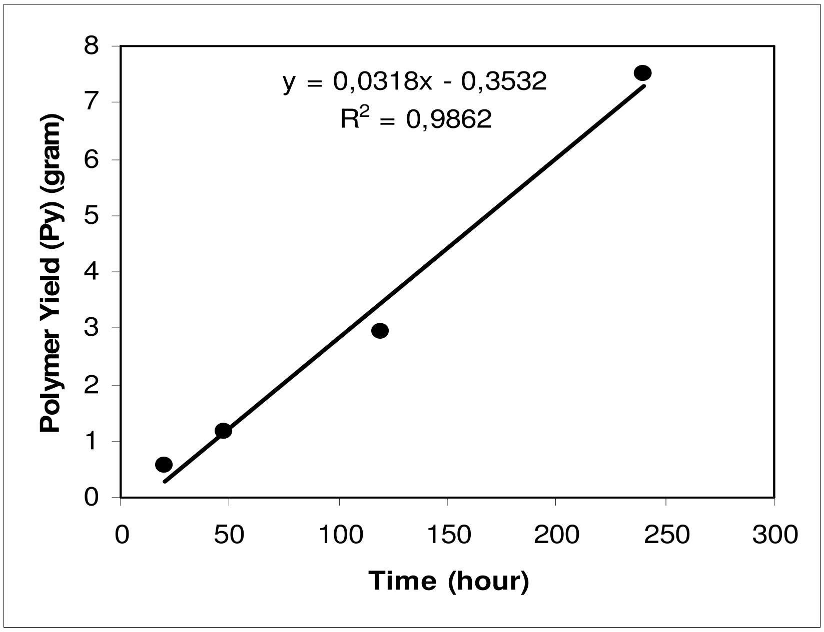


Figure 4: Polymer Yield (Py) vs. Time graph for f_2=0.162

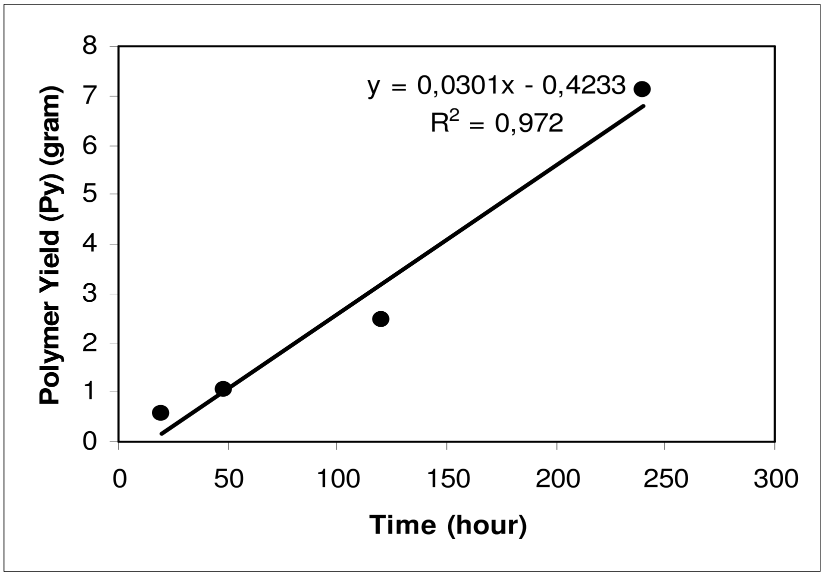


Figure 5: Polymer Yield (Py) vs. Time graph for f_2=0.266

Table 4: Conversion of monomer mixture (9.36 g) with reaction time (f_2=0.162)

Ex	t(h)	% HMW	Py (g)	% C		% H		% S		F_2		M_n	
				h	l	h	l	h	l	h	l	h	l
2	20	78.9	0.566	56.4	53.4	9.34	8.80	10.4	12.2	0.098	0.106	2364	722
9	48	89.1	1.176	54.4	49.7	8.96	7.76	10.7	17.4	0.093	0.147	2685	705
10	120	92.9	2.941	54.1	47.1	9.23	7.17	14.0	23.8	0.133	0.213	3605	446
11	240	93.7	7.518	52.5	44.3	8.07	6.31	18.3	34.5	0.178	0.366	3807	282

Table 5: Conversion of monomer mixture (9.79 g) with reaction time (f_2=0.266)

Ex	t(h)	% HMW	Py (g)	% C		% H		% S		F_2		M_n	
				h	l	h	l	h	l	h	l	h	l
4	20	71.6	0.554	55.4	55.3	9.14	8.93	11.0	11.1	0.101	0.101	2024	753
12	48	86.6	1.038	52.9	51.1	8.89	7.77	14.2	17.9	0.129	0.161	1378	551
13	120	90.9	2.475	54.1	51.3	9.11	8.07	13.0	17.8	0.120	0.162	2863	647
14	240	96.0	7.124	52.3	38.6	7.91	5.81	21.0	25.6	0.218	0.176	2506	344

Ex: Experiment number
t (h): Time in hour
% HMW: Per cent of high molecular weight fraction
Py: Polymer yield in gram
F_2: Mole fraction of CS_2 in the polymer
M_n: Number average molecular weight of polymer
h, l: High and low molecular weight fraction
Note: Other values are in the Appendix A

The rate constant of zero order reactions were obtained by plotting instantaneous concentrations of PO and CS_2 for high and low fractions (Figure 6-13). In a rate process which is zeroth order for each monomer the classical copolymerization equation can not be used (Eq. 3.2 and 3.3) instead r_1^* and F_2^* is given in equations 3.4 and 3.5 omitting the dielectric effect on the rate.

$$r_1^* = k_{PO} / k_{CS2} \tag{3.4}$$

$$F_2^* = k_{CS2} / (k_{PO} + k_{CS2}) \tag{3.5}$$

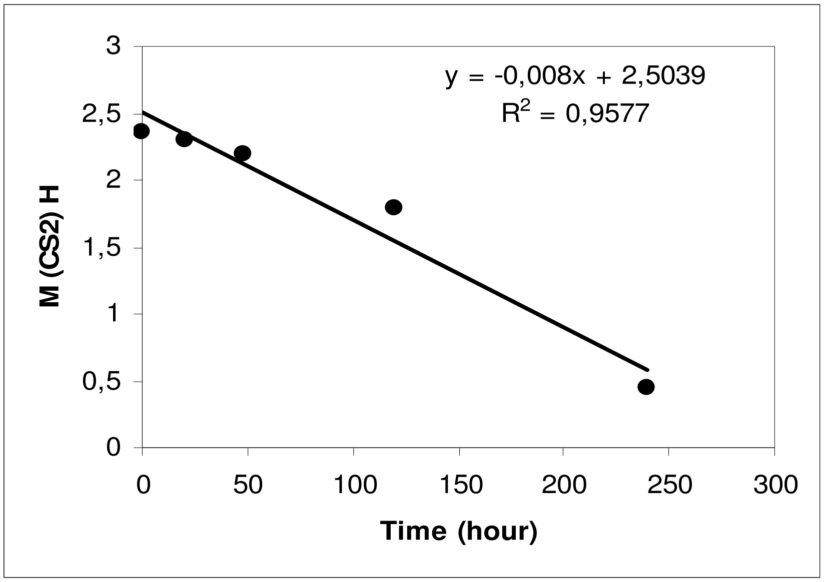


Figure 6: Molarity of CS_2 vs. Time graph (high fraction, f_2=0.162)

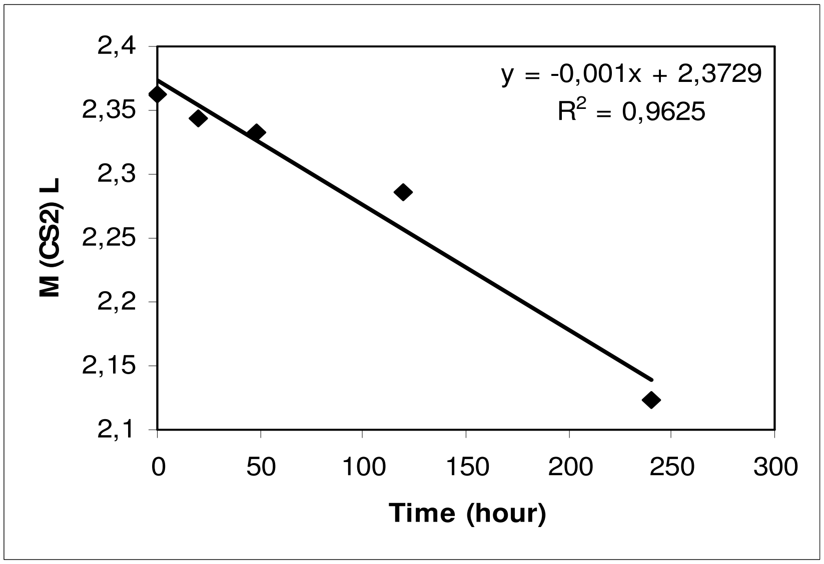


Figure 7: Molarity of CS_2 vs. Time graph (low fraction, f_2=0.162)

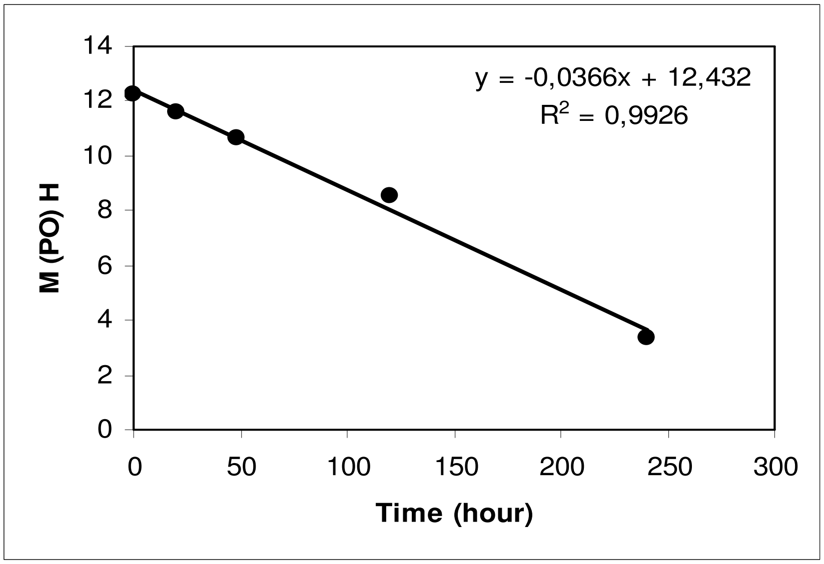


Figure 8: Molarity of PO vs. Time graph (high fraction, f_2=0.162)

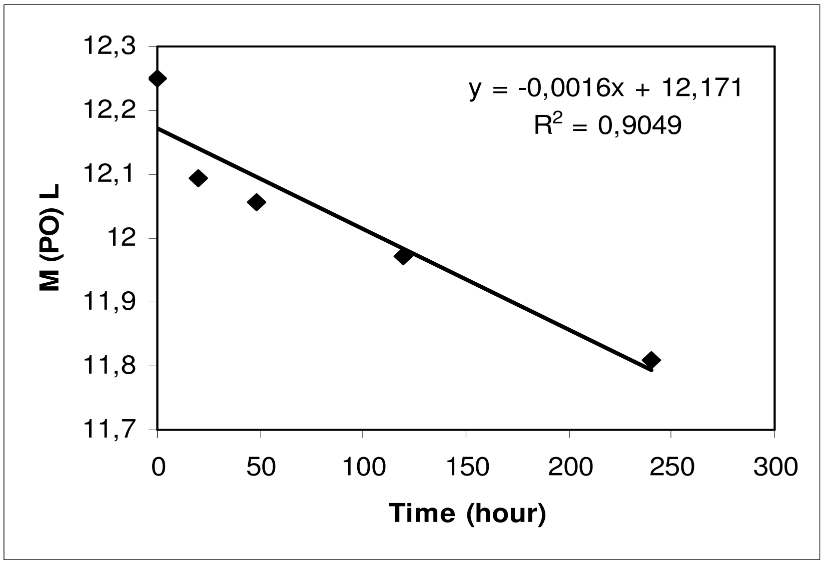


Figure 9: Molarity of PO vs. Time graph (low fraction, f_2=0.162)

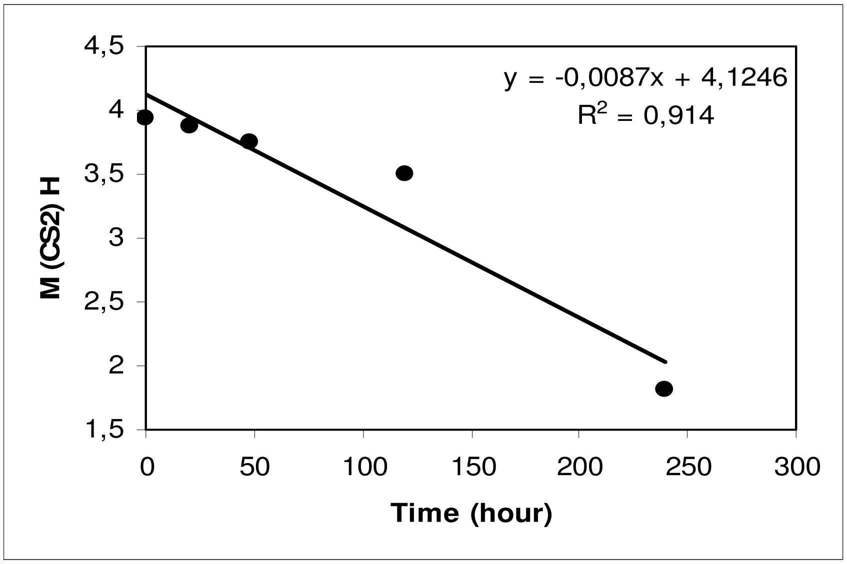


Figure 10: Molarity of CS_2 vs. Time graph (high fraction, f_2=0.266)

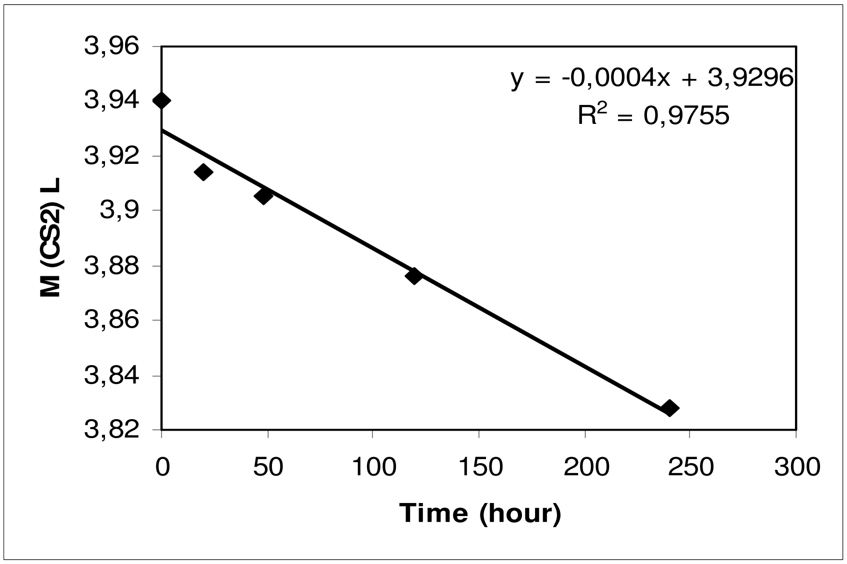


Figure 11: Molarity of CS_2 vs. Time graph (low fraction, f_2=0.266)

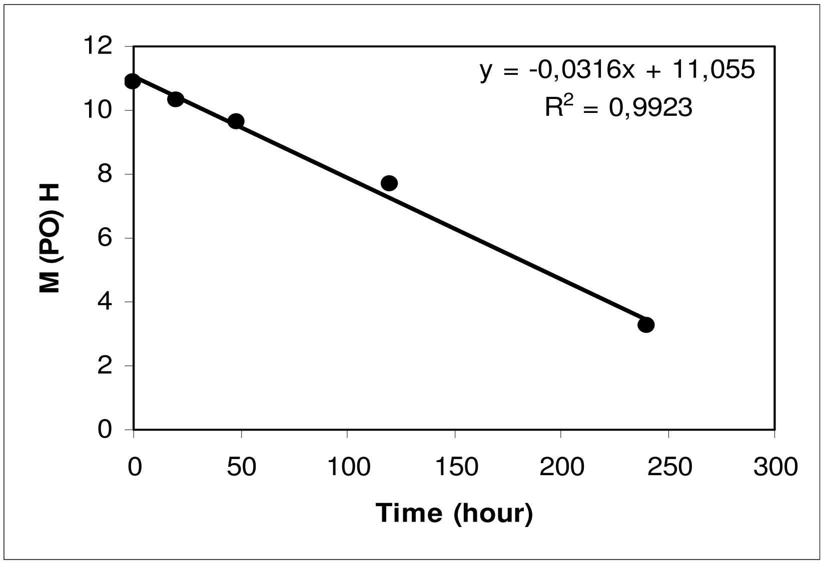


Figure 12: Molarity of PO vs. Time graph (high fraction, f_2=0.266)

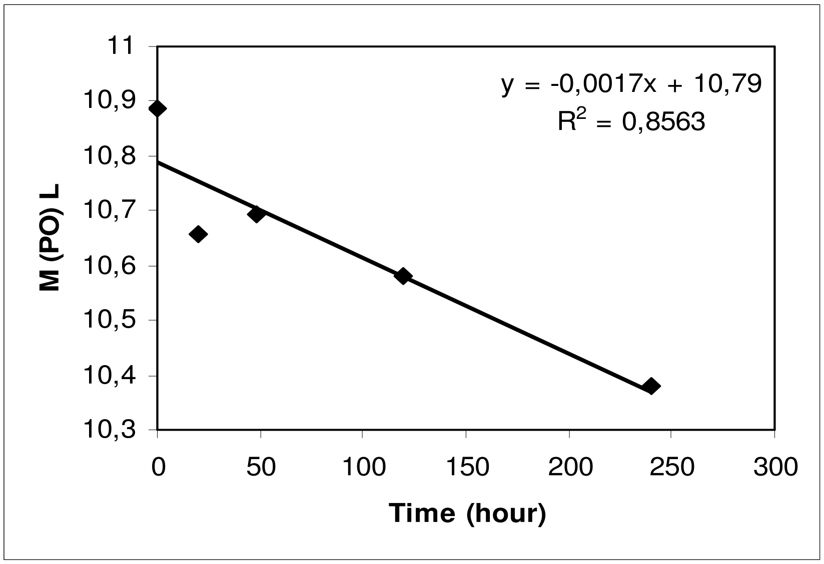


Figure 13: Molarity of PO vs. Time graph (low fraction, f_2=0.266)

Indeed as expected from Eq. 3.5, the F_2 values for 20 h polymerizations was almost constant (Table 2) and experimental values of F_2 were quite close the value obtained from Eq. 3.5 (~0.2). On the contrary for prolonged polymerization F_2 values showed a steady increase with polymerization time (Table 4 and 5). This increase is possibly due to accelerated aging of catalytic species in polymerization reactor (at 80°C, up to 240 hours). Zeroth order rate constants of PO and CS_2 were calculated from graphs and given in Table 6.

Table 6: Zeroth order rate constants of PO and CS_2 with different f_2 values

f_2	$k_{CS2\ (mol/Ls)}$		$k_{PO(mol/Ls)}$		F_2*		r_1*	
	h	l	h	l	h	l	H	l
0.162	2.22×10^{-6}	2.70×10^{-7}	1.02×10^{-5}	4.38×10^{-7}	0.18	0.38	4.58	1.62
0.266	2.43×10^{-6}	1.20×10^{-7}	8.78×10^{-6}	4.92×10^{-7}	0.22	0.20	3.62	4.10

It must be pointed out that r_1* and F_2* values calculated from equation 3.4 and 3.5 must be in some error due to dielectric constant effect. Since r_1* is greater than unity, PO is consumed in the feed faster than CS_2 decreasing the dielectric constant. Therefore, the rate characteristic of process would change with the conversion.

3.2.3 The Effect of Catalyst Concentration on Copolymerization Yield

Increasing catalyst concentration increased the yield of copolymer, linearly. However, the effect of catalyst was not only to increase the rate but affected the characteristics of process in a complicated manner (Table 7 and 8). The moles of PO polymerized per liter of reaction mixture (M_{PO}) at 48 h reaction time at $f_2 = 0.162$ can be given in following equations as:

M_{PO} = 554.6[Zn] -1.665 (r^2 =0.9986) (for high fraction) (3.6)

M_{PO} = 14.339[Zn] +0.1303 (r^2 = 0.9251) (for low fraction) (3.7)

For f_2= 0.266 in similar conditions:

M_{PO} = 588.09[Zn] -2.4589 (r^2 =0.9841) (for high fraction) (3.8)

M_{PO} = 8.9423[Zn] +0.128 (r^2 =0.9248) (for low fraction) (3.9)

For same copolymers the moles of CS_2 polymerized per liter of reaction mixture can be given as:

M_{CS2} = 125.71[Zn] -0.5764 (r^2 = 0.9988) (for high fraction f_2 = 0.162) (3.10)

M_{CS2} = 7.611[Zn] + 0.0098 (r^2 = 0.7806) (for low fraction f_2 = 0.162) (3.11)

For f_2= 0.266 in similar conditions:

M_{CS2} = 127.93[Zn] –0.6198 (r^2 = 0.9859) (for high fraction f_2 = 0.266) (3.11)

M_{CS2} = 5.68[Zn] + 0.0163 (r^2 = 0.8539) (for low fraction f_2 = 0.266) (3.12)

These relations are open to some errors coming from experiments such as: measuring out monomers and catalyst, isolation of copolymers, fractionation and isolation of fractions finally errors in elemental analysis. However, at least they show qualitatively that process leading to low and high molecular weight copolymer formations are quite different. This fact better observed by comparing M_{CS2} values for low copolymer fractions both for f_2 = 0.162 and 0.266 values.

Table 7: Conversion of monomer mixture with different concentration of catalyst (f_2=0.162)

Ex	[Zn] (M)	% HMW	Py (g)	% C		% H		% S		F_2		M_n	
				h	l	h	l	h	l	h	l	h	l
9	5.73x10^{-3}	89.1	1.176	54.4	49.7	8.96	7.76	10.7	17.4	0.093	0.147	2685	705
15	1.13x10^{-2}	92.3	3.755	54.0	44.6	8.82	6.35	15.7	30.1	0.154	0.284	5338	391
16	2.0x10^{-2}	95.3	7.430	50.9	44.9	7.98	6.93	18.6	28.7	0.171	0.269	4184	350

Table 8: Conversion of monomer mixture with different concentration of catalyst (f_2=0.266)

Ex	[Zn] (M)	% HMW	Py (g)	% C		% H		% S		F_2		M_n	
				h	l	h	l	h	l	h	l	h	l
12	5.73x10^{-3}	86.6	1.038	52.9	51.1	8.89	7.77	14.2	17.9	0.129	0.161	1378	551
17	1.13x10^{-2}	92.9	3.113	54.2	47.0	8.73	6.79	16.3	30.4	0.164	0.324	3787	463
18	2.0x10^{-2}	96.0	7.081	49.2	45.3	7.52	6.91	19.7	29.1	0.172	0.280	3394	372

Ex: Experiment number
[Zn] (M): Concentration of catalyst in molarity
% HMW: Per cent of high molecular weight fraction
Py: Polymer yield in gram
F_2: Mole fraction of CS_2 in the polymer
M_n: Number average molecular weight of polymer
h, l: High and low molecular weight fraction
Note: Other values are in the Appendix A

3.2.4 Effect of Temperature on Polymerization

Polymerisation results, at different temperatures keeping the catalyst, monomer concentrations and reaction time constant are given in Table 9 and 10. Activation energy of process was calculated tentatively from the conversion of PO and CS_2 in g/L reaction mixture in 48 hour reaction time at different temperatures. Activation energies for f_2=0.162 and 0.266 and for high and low copolymers were calculated separately (Figure 14-21 and Table 11).

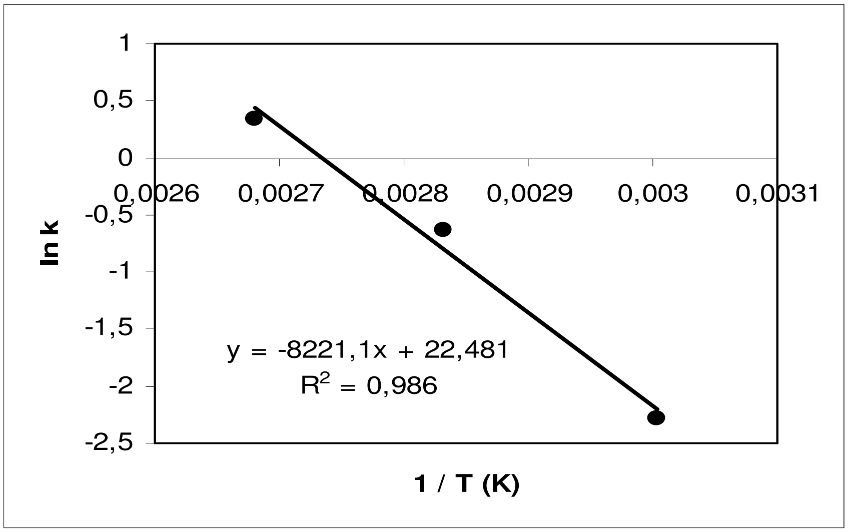


Figure 14: lnk vs. 1/T graph for high fraction of CS_2 for f_2=0.162

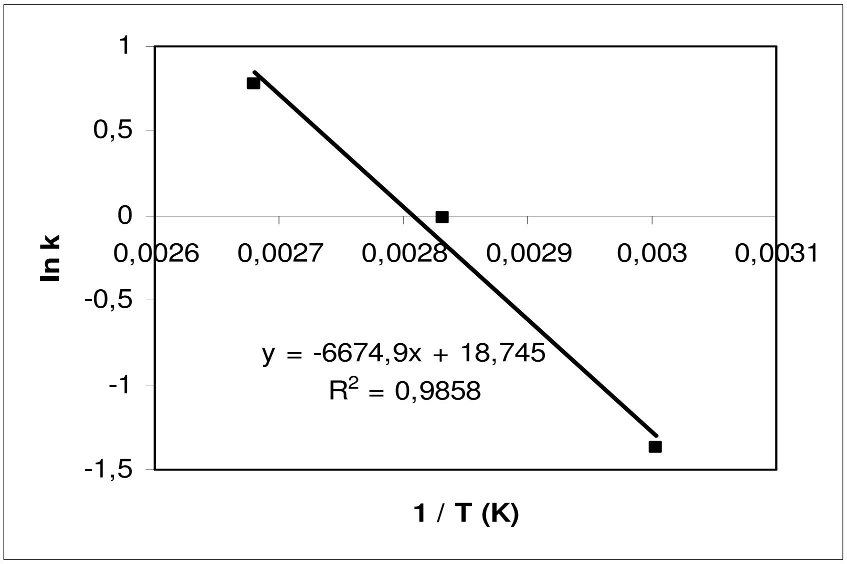


Figure 15: lnk vs. 1/T graph for low fraction of CS_2 for f_2=0.162

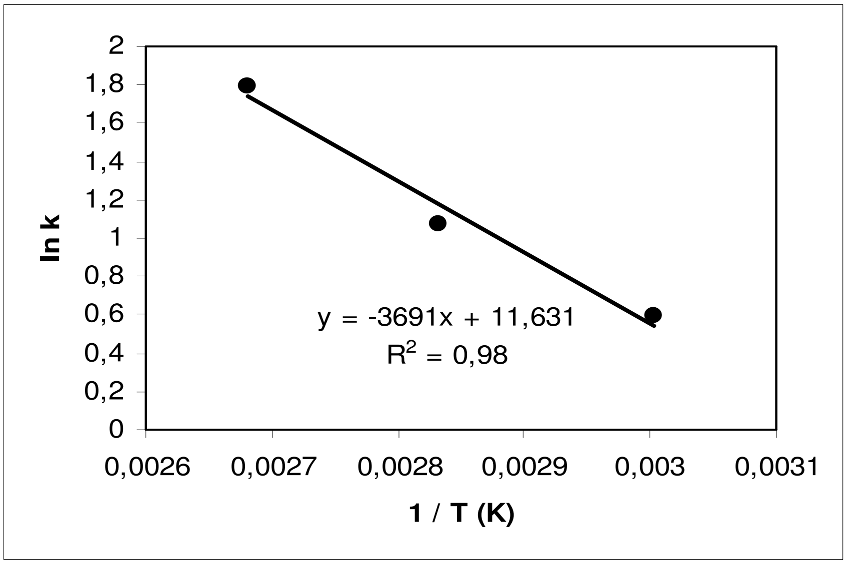


Figure 16: lnk vs. 1/T graph for high fraction of PO for f_2=0.162

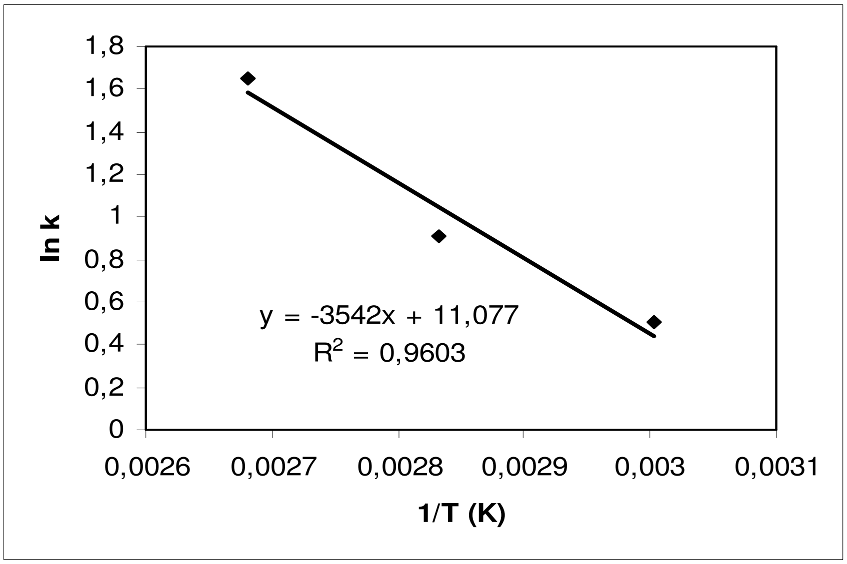


Figure 17: lnk vs. 1/T graph for low fraction of PO for f_2=0.162

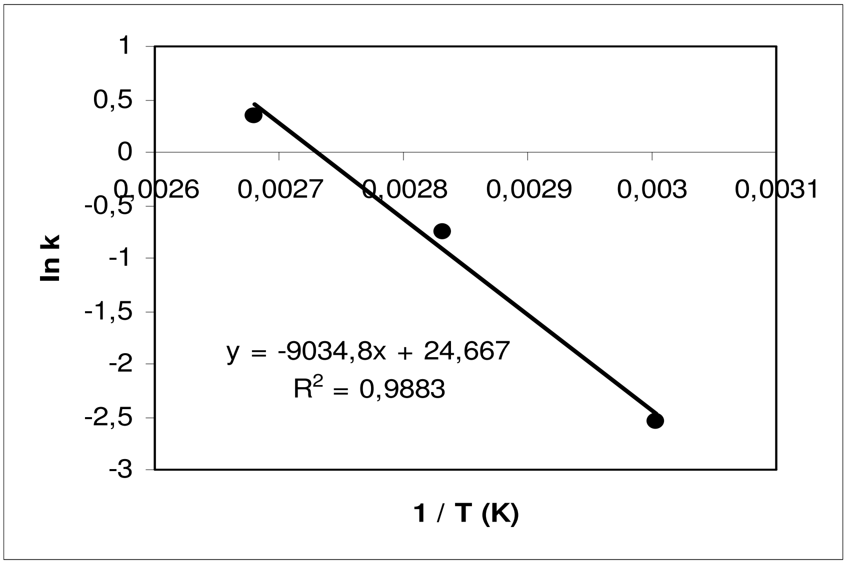


Figure 18: lnk vs. 1/T graph for high fraction of CS_2 for f_2=0.266

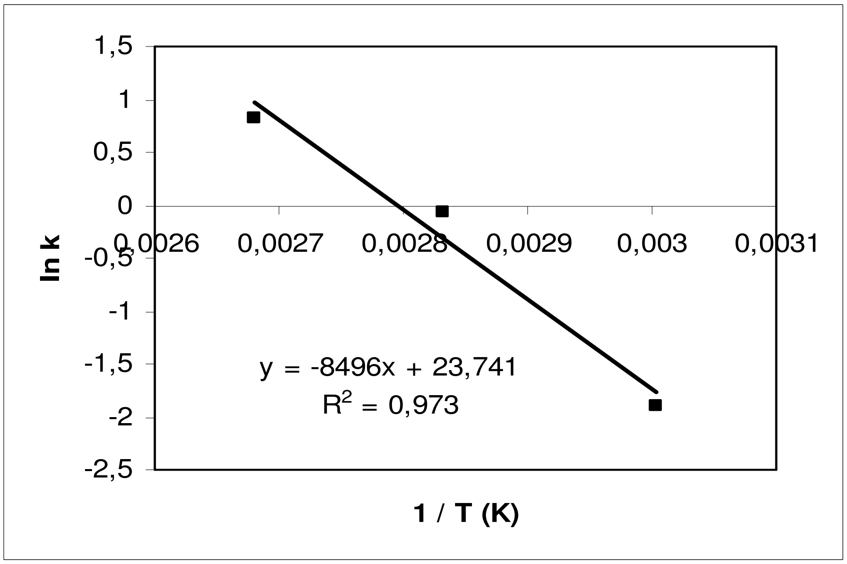


Figure 19: lnk vs. 1/T graph for low fraction of CS_2 for f_2=0.266

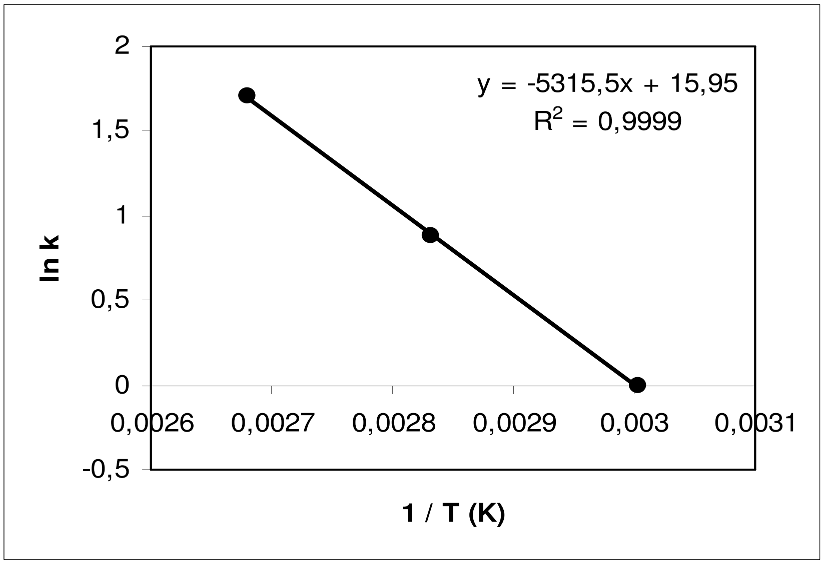


Figure 20: lnk vs. 1/T graph for high fraction of PO for f_2=0.266

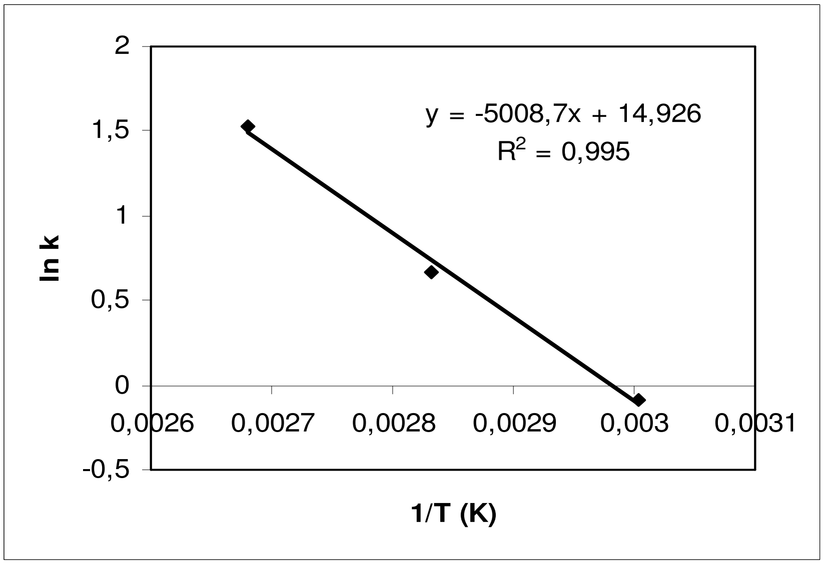


Figure 21: lnk vs. 1/T graph for low fraction of PO for f_2=0.266

Table 9: Conversion of monomer mixture (9.36 g) with different temperatures (f_2=0.162)

Ex	T (°C)	% HMW	Py (g)	% C		% H		% S		F_2		M_n	
				h	l	h	l	h	l	h	l	h	l
19	60	95.6	1.998	59.0	51.3	9.79	7.88	5.73	15.5	0.053	0.133	4805	1189
15	80	92.3	3.755	54.0	44.6	8.82	6.35	15.7	30.1	0.154	0.284	5338	391
20	100	95.7	7.713	53.4	45.8	8.60	6.81	18.5	29.6	0.191	0.293	6198	452

Table 10: Conversion of monomer mixture (9.79 g) with different temperatures (f_2=0.266)

Ex	T (°C)	% HMW	Py (g)	% C		% H		% S		F_2		M_n	
				h	l	h	l	h	l	h	l	h	l
21	60	91.2	1.172	57.3	47.5	9.72	7.48	7.88	17.7	0.073	0.140	3770	920
17	80	92.9	3.113	54.2	47.0	8.73	6.79	16.3	30.4	0.164	0.324	3787	463
22	100	95.1	7.261	51.4	45.6	7.81	6.50	20.7	31.8	0.205	0.330	3590	522

Ex: Experiment number
T (°C): temperature in °C
% HMW: Per cent of high molecular weight fraction
Py: Polymer yield in gram
F_2: Mole fraction of CS_2 in the polymer
M_n: Number average molecular weight of polymer
h, l: High and low molecular weight fraction
Note: Other values are in the Appendix A

Activation energies from slopes of the equations were calculated and given in Table 11.

Table 11: Activation energy values for high and low fraction of CS_2 and PO

f_2	E_a $CS_{2\ (kj/mol)}$		E_a $PO_{(kj/mol)}$	
	h	l	h	l
0.162	68.4	55.5	30.7	29.4
0.266	75.1	70.6	44.2	41.6

Apparently, different F_2 values for high and low copolymers, and presence of di-trithio carbonates in the low copolymer and different effects of catalyst concentration on the yield for high and low fractions, may suggest that these polymers are formed in different reactions with different mechanisms. On the other hand, estimated E_a values for PO and CS_2 for high and low copolymers were quite close to each other. Therefore, fundamentally different mechanisms seem unlikely.

3.3 End Group Analysis Result

One of the aims was to crosslink the copolymers by reacting terminal OH groups with using triisocyanates. For this purpose, the OH functionality (moles of OH groups per gram of polymer) was determined. Hydroxyl end groups is expected since, polymers are terminated with HCl (aq) in extraction process.

$$\text{Zn-O-CH}_2\text{-CH(CH}_3\text{)-P} + \text{H}_2\text{O} \xrightarrow{H^+} \text{Zn-OH} + \text{HO-CH}_2\text{-CH(CH}_3\text{)P} \qquad (3.14)$$

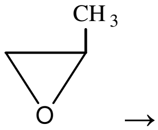
and

$$\text{Zn-S-(C=S)-O-CH}_2\text{-CH(CH}_3\text{)-P} + \text{H}_2\text{O} \xrightarrow{H^+} \text{Zn-OH+ HS-(C=S)-O-CH}_2\text{-CH(CH}_3\text{)-P} \qquad (3.15)$$

But since xhanthate acid is unstable in acidic conditions.

$$\text{HS-(C=S)-O-CH}_2\text{-CH(CH}_3\text{)-P} \xrightarrow{H^+} \text{CS}_2 + \text{HO-CH}_2\text{-CH(CH}_3\text{)-P} \qquad (3.16)$$

Double bonds may be present at the chain ends due to transfer reactions.

$\text{Zn-O-CH}_2\text{-CH(CH}_3\text{)-P+}$  $\rightarrow \text{Zn-O-CH}_2\text{-CH=CH}_2\text{+P-CH(CH}_3\text{)-CH}_2\text{-OH}$ (3.17)

Another possibility is the Cl terminated chains, those formed in the isolation of polymers,

$$\text{P-O-CH}_2\text{-CH=CH}_2 + \text{HCl (aq)} \rightarrow \text{P-O-CH}_2\text{-CH(Cl)CH}_3 \qquad (3.18)$$

or substitution of -OH groups with Cl^-

$$\text{P-O-CH}_2\text{-CH(CH}_3\text{)-OH} + \text{HCl} \rightarrow \text{PO-CH}_2\text{-CH(CH}_3\text{)-Cl} + \text{H}_2\text{O} \qquad (3.19)$$

Therefore, in end group analysis both Cl, -OH and double bond terminals were studied.

Cl determination was made by combusting a sample in an erlenmayer flask that contained O_2 (g) and product of chloride ions were titrated by Mohr method. In the analysis, both the Cl contents of blank and copolymer sample were same (1 %), and it did not change when the polymerisation terminated with HNO_3 (aq) instead of HCl (aq).

Double bond f(DB) and hydroxyl functionality f(OH) of several samples are given in Table 12. The M_n values are calculated as:

$$M_n = 2 / [\ f(OH)+f(DB)\ ] \qquad (3.20)$$

In Table 12, M_n values estimated by GPC are also given. However, GPC values are likely to be in some error since, the software of GPC did not function properly. In GPC experiments polyethylene oxide (PEO) and polypropylene glycol (PPG) samples which have (quite) close structure to the copolymers were used in calibration and refractive index detector was used only.

In order to determine hydroxyl and double bond content of polymers, high molecular weight fractions of experiment 11, 16, 23, 24, 25 and 26 were used. Experiment 23, 24 (f_2 =0.266) and 25, 26 (f_2=0.487) are the larger quantity of copolymerisation experiments. In order to obtain these copolymer, catalyst concentration as 0.0169 M and 0.0178 M Zn were used and f_2 values as 0.266 and 0.487 and reaction time 10 days at 80 ^{o}C were used for the polymerization. Experiments of 24 and 26 were done at the same conditions with an aged catalyst. The results are in Table 12.

Table 12: GPC and end group analysis result for M_n values

Ex	f(OH) (mol/1g polymer)	f(Double Bond) (mol/1g polymer)	M_n (a)	M_n (b)
11	1.73×10^{-5}	6.38×10^{-4}	3051	3807
16	1.08×10^{-5}	2.76×10^{-4}	6967	4184
23	1.21×10^{-5}	6.26×10^{-4}	3136	------
24	1.60×10^{-5}	7.60×10^{-4}	2579	------
25	1.14×10^{-5}	6.58×10^{-4}	2989	------
26	4.06×10^{-5}	5.72×10^{-4}	3267	------

Ex: Experiment number
(a) M_n determined by end group analysis
(b) M_n determined by GPC
Note: Other values are in the Appendix A

According to these results, polymer end groups mostly (95%) consist of double bonds and a small amount of hydroxyl end groups exists.

3.4 Attempts to Hydroxylate Double Bond Terminals of CS_2/PO Copolymers

In order to crosslink copolymers, several attempts have been done to increase the hydroxyl functionality by hydration of double bonds.

For this purpose, both H_2O_2/H_2O and H_2SO_4 methods have been used. H_2O_2 method degraded polymers possibly oxidizing the backbone S atoms. In experiment 23, copolymerisation carried out for 10 days at 80 °C, $f_2=0.266$ and $Zn(Xt)_2$ was 0.0169 M. The high fraction of this copolymer was yellow as usual. However, following the H_2O_2 treatment the color become white and S % decreased from ~25 % to 2.23 %. Therefore, H_2O_2/H_2O method turned to be inapplicable for hydroxylation of double bonds.

On the other hand, H_2SO_4 treatment did not result in degradation. But the hydroxyl functionality did not appreciably increase, in expense of double bond functionality. These results are given in Table 13. In this table the original hydroxyl and double bond functionalities of copolymer Ex. 25, and calculated M_n value is given in the first row. The same quantities were determined after first H_2SO_4 treatment and results are given in Ex. 31. The copolymer after first treatment (Ex. 31) was treated again with H_2SO_4 and results are given in Ex. 32 in Table 13. Thus, the H_2SO_4 treatments for hydroxylation of double bonds were not successful either.

Table 13: The results of H_2SO_4 method

Ex	f(OH) (mol/1g polymer)	f(D.B) (mol/1g polymer)	M_n (a)
25	1.14×10^{-5}	6.58×10^{-4}	2989
31	5.31×10^{-5}	6.21×10^{-4}	2966
32	5.86×10^{-5}	6.17×10^{-4}	2961

Ex: Experiment number
(a) M_n determined by end group analysis
Note: Other values are in the Appendix A

3.5 GPC and Light Scattering Result

Since software of GPC seemed more troublesome with universal calibration, following data was obtained by using only conventional calibration. Light scattering (LS) measurements were also done in order to compare the results. Moreover, heterogeneity indexes (HI=M_w/M_n) were found for these two methods. In Table 14, results of polymers of high molecular weight fractions were given. These results are not in agreement with each other. GPC instrument used in this experiment showed some serious defects during the present work due to its software[1]. On the other hand, the operator who runs the LS measurements has taken an approximate value for dn/dc (0.15) instead of measuring it properly. In spite of the disagreement of the results are, following conclusions can be deduced.

a) Copolymers show very broad molecular weight distributions.
b) High polymers have very high M_w components.

Table 14: Comparison of results for GPC and LS

Ex	M_n (I) (GPC)	M_w (I) (GPC)	HI(I) (GPC)	M_n(II) (GPC)	M_w(II) (GPC)	HI(II) (GPC)	M_w (LS)	HI(I) (LS)	HI(II) (LS)
10	3605	7.08×10^4	19.6	1916	1.24×10^4	6.47	7.66×10^4	21.2	40.0
15	5338	9.35×10^4	17.5	3574	1.40×10^4	3.92	1.74×10^4	3.26	4.87
19	4805	9.90×10^6	2060	1394	1.0×10^4	7.17	4.27×10^5	88.9	306

Ex: Experiment number
M_n (GPC): Number average molecular weight obtained by GPC
M_w (GPC): Weight average molecular weight obtained by GPC
HI (GPC): Heterogeneity index for GPC results
M_w (LS): Weight average molecular weight obtained by LS
HI (LS): Heterogeneity index for LS result
I= two of 5μ MiniMIX-C column are used in GPC
II = 5 and 10 μ MiniMIX-C column are used in GPC

---

[1] for example for experiment 11, GPC with conventional calibration gave: $M_w = 2.42x10^8$. However, by manual calculation from the chromotogram $M_w = 5.9\ x10^5$.

3.6 Crystallisation of Copolymers

High molecular weight products of experiment 1, 3 and 8 were crystallized in the form of spherulites and observed on a polarizing microscope. On the other hand, in spite of several attempts, high molecular weight products of experiment 11, 14, 16 and 18 could not be crystallized. In order to get crystallize-able fractions; high molecular weight products of experiment 10 and 13 (120 h polymerization with f_2=0.162 and 0.266 respectively) were further fractionated from isooctane in temperature ranges between 70-35 °C and 35-25 °C were not crystallized either. It must be pointed out that formation and observing crystals in polypropylene oxide sample might be very difficult if the sample has high concentrations of amorphous material. Indeed, Bolat (1999) and Soysal (2001) could never crystallized PPO obtained from $Zn(Xt)_2$ catalyst. But Tarkın (2003) crystallized these polymers after a detailed fractionation. Thus, in this work only copolymers with high F_1 values are crystallized. From this result, we can say that the polymer which have propylene oxide amount is higher can be crystallized. The shape of the crystals (Maltese Cross) is given in Figure 22.

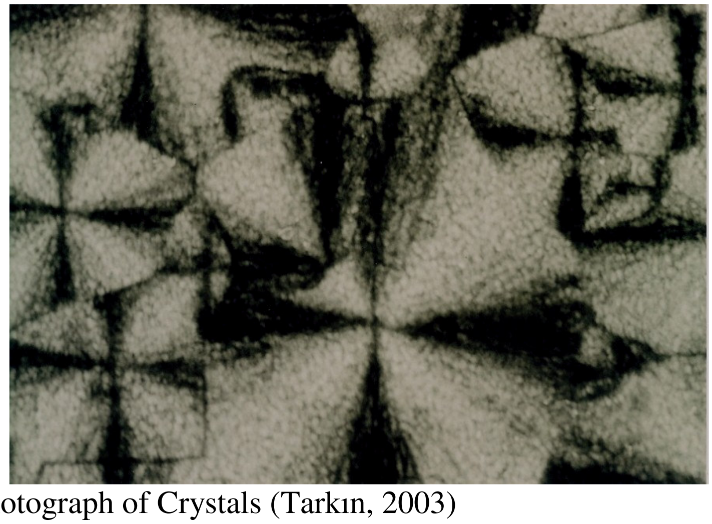


Figure 22: Photograph of Crystals (Tarkın, 2003)

3.7 Results of DSC Measurements

Glass transition temperatures for low and high copolymers ranges from -74 to -38 ^{o}C as measured by DSC (Tg value for PPO= -75 ^{0}C and for f_2=0.113 it is -74 ^{0}C). The Tg values of copolymers increase as sulphur content of copolymer increases. DSC spectrum of copolymers from Ex. 1 (f_2=0.113), Ex. 2 (f_2=0.162) and Ex. 9 (f_2=0.162) showed endothermic melting peaks of crystals as 55.5 ^{o}C, 46.6 ^{o}C and 48.9 ^{o}C respectively (Figure 23-28).

Block or random copolymers (with r_1 sufficiently larger than r_2), would crystallise even if only one of the monomer crystallisable. In such copolymers segments having crystalline and non- crystallisable monomers will be present. If the total weight fraction of 1st type segments (formed from crystallisable units) those are above a critical segmental length were; large enough: such copolymers would crystallize (Lenz 1967.). However 2nd type segments will not associate in the crystal phase, but they act as an impurity and lower the melting point. Flory has related the average mole fraction of 1st type monomers (F_1**) with the melting temperature T_m as (Flory, 1953):

$$1/T_m - 1/T_m^o = (- R / \Delta H_u) \ln (F_1^{**}) \tag{3.21}$$

Where T_m^o = melting temperature of homopolymer of 1st type monomer, and ΔH_u is enthalpy of fusion per mole of first type repeat units.

Similarly, joint units combining two different segments act as impurity; hence Flory calculated average number of first type monomers between two joint units as:

$$1/T_m - 1/T_m^o = (R / \Delta H_u) (2 / X_n) \tag{3.22}$$

Where X_n is the average degree of polymerisation of the crystallisable segments.

In the poly(PO-co-CS_2), the crystallisable PO segments are connected to each other with dithiocarbonate units (-O-(C=S)-S-) which function as an impurity. Hence, taking Tm^o and ΔHu as 355 K and 8360 J / repeat unit; as literature values (Uğur and Alyürük, 1989) F_l** and X_n values are calculated. Results are given in Table 15, and F_l** values from Flory equation are compared with those obtained from elemental analysis and from zero order rate constants.

It should be noted that poly(PO-co-CS_2) is more complicated than a mixture of crystalline and non-crystalline segments. That is because PO is a racemic monomer hence could give two different isotactic segments, each formed from different enantiomers. Therefore depending on the nature of process two different structures are possible. The first structure formed from combination of identical segments through dithiocarbonate units; on the other hand, the second structure is formed by joining different segments randomly. Determination the structure of chains would elucidate the nature of stereo regulation in the polymerization mechanism. If stereo regulation is due to the inherent asymmetry catalyst first type structure is expected. In this model: addition of a CS_2 would interrupt the growing a segment, but since catalyst selects always same enantiomer, the new segment would have identical structure with the preceding one. In the second model the asymmetry of the growing terminal (that is reactive chain end) would be effective in selecting next monomer to be added. Therefore, after a CS_2 addition any one of the two enantiomers might start to grow of a new segment leading a random distribution of different segments throughout the chain.

No attempt has been done to determine the microstructure of chains in the present work. But organization of randomly occurring different structure segments (with X_n =6-9) in a crystal lattice may seem rather difficult. Therefore, a catalyst asymmetry control of stereoregularity appears to be more probable. Öktem Z. (1985) has reported several experimental data in favor of catalyst asymmetry control of stereoregularity.

Table 15: F_1 and X_n results calculated from Flory's formula

Ex	T_m (°C)	$X_{n\ (a)}$	$F_1{}^{**}{}_{(b)}$	$F_1{}^{*}{}_{(c)}$	$F_{1\ (d)}$	$r_1{}^{**}{}_{(e)}$	$r_{1^*\ (f)}$	$r_{1\ (g)}$
1	55.5	8.81	0.797	---	0.916	3.93	----	1.26
2	46.6	6.41	0.732	0.82	0.902	2.73	4.58	1.58
9	48.9	6.90	0.748	0.82	0.907	2.97	4.58	1.69

T_m: T_m value obtained from DSC measurement
(a) X_n value calculated from equation 3.22
(b) $F_1{}^{**}$ value calculated from equation 3.21
(c) $F_1{}^{*}$ value obtained from zero order rate constants
(d) F_1 value obtained from elemental analysis
(e) $r_1{}^{**} = F_1{}^{**} / (1-F_1{}^{**})$
(f) $r_1{}^{*}$ value obtained from zero order rate constants
(g) r_1 value obtained from elemental analysis
Note: Other values are in the Appendix A

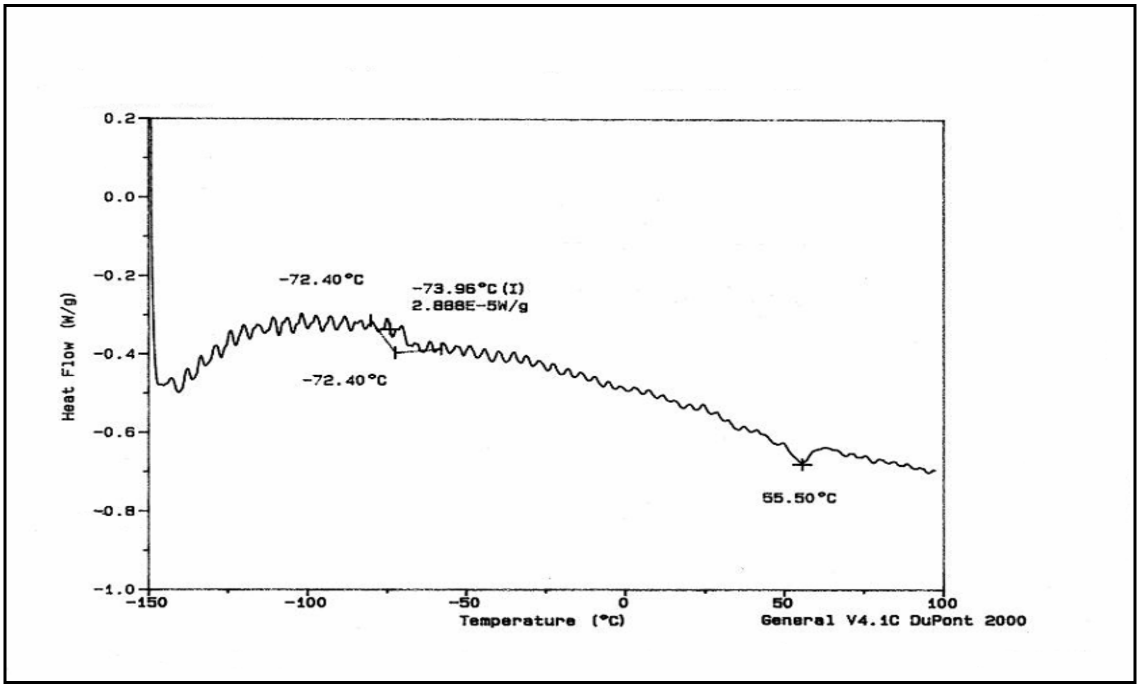


Figure 23: DSC thermogram of high fraction of experiment 1 (S %= 8.86, f_2=0.113)

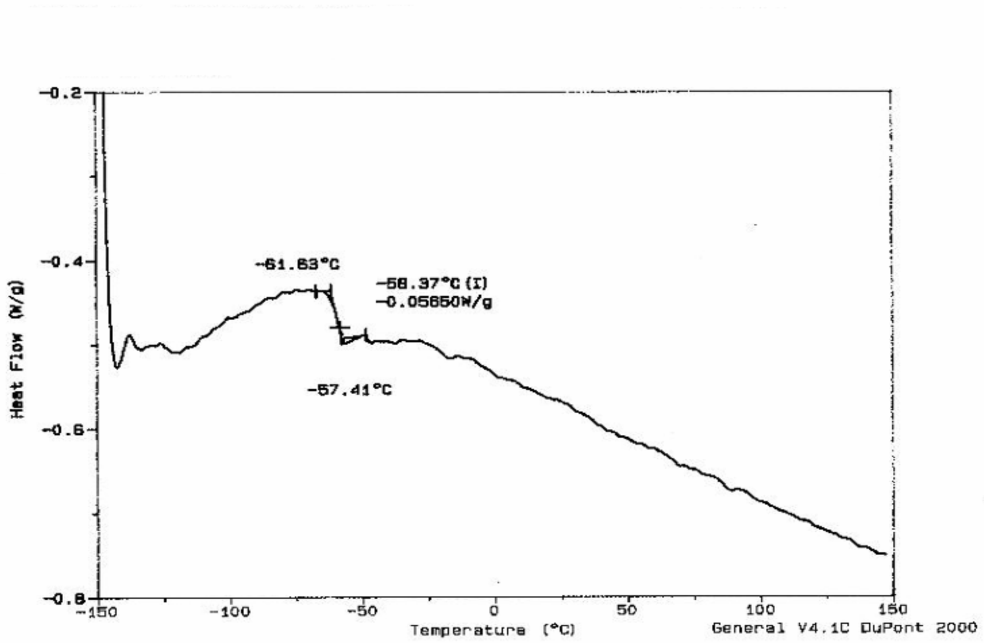


Figure 24: DSC thermogram of low fraction of experiment 2 (S %= 12.2, f_2=0.162)

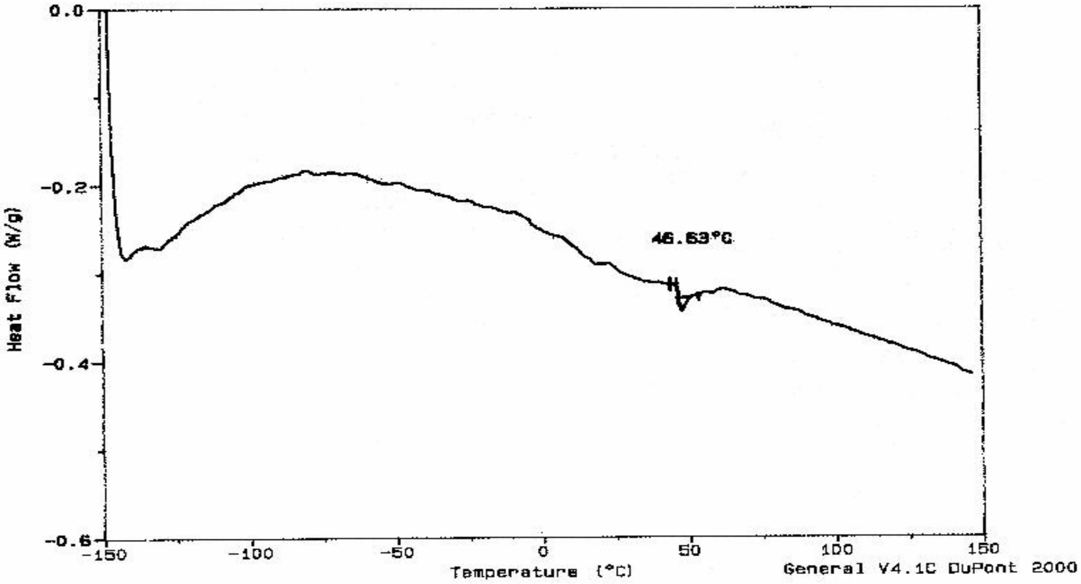


Figure 25: DSC thermogram of high fraction of experiment 2 (S %= 10.4, f_2=0.162)

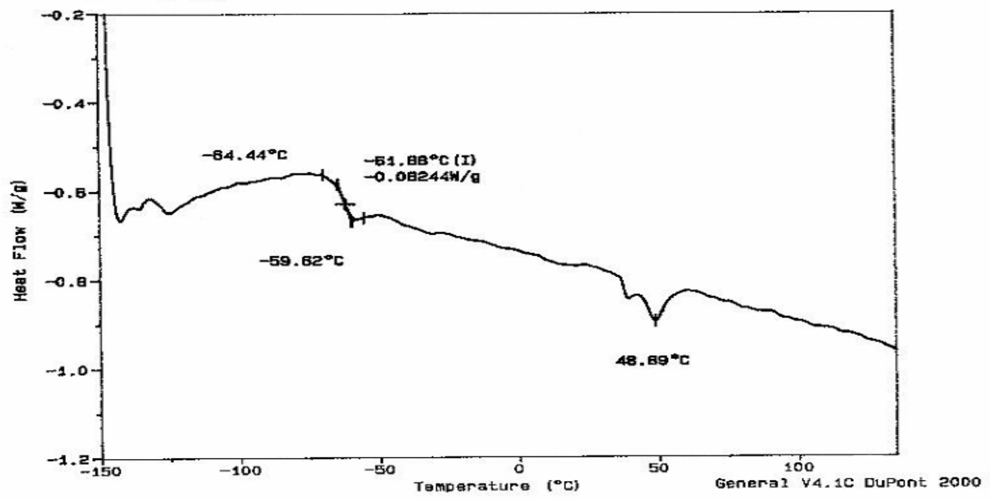


Figure 26: DSC thermogram of high fraction of experiment 9 (S %= 10.7, f_2=0.162)

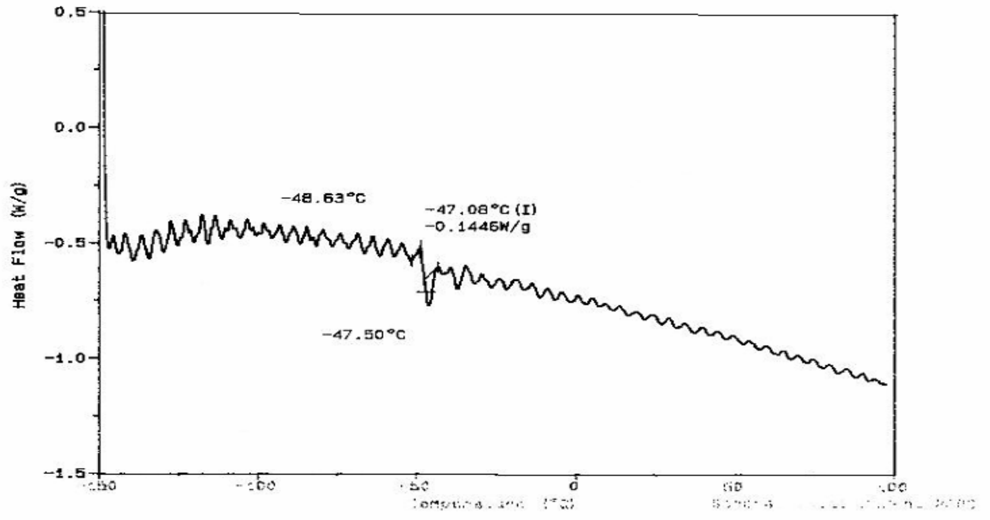


Figure 27: DSC thermogram of low fraction of experiment 14 (S %=25.6, f_2=0.266)

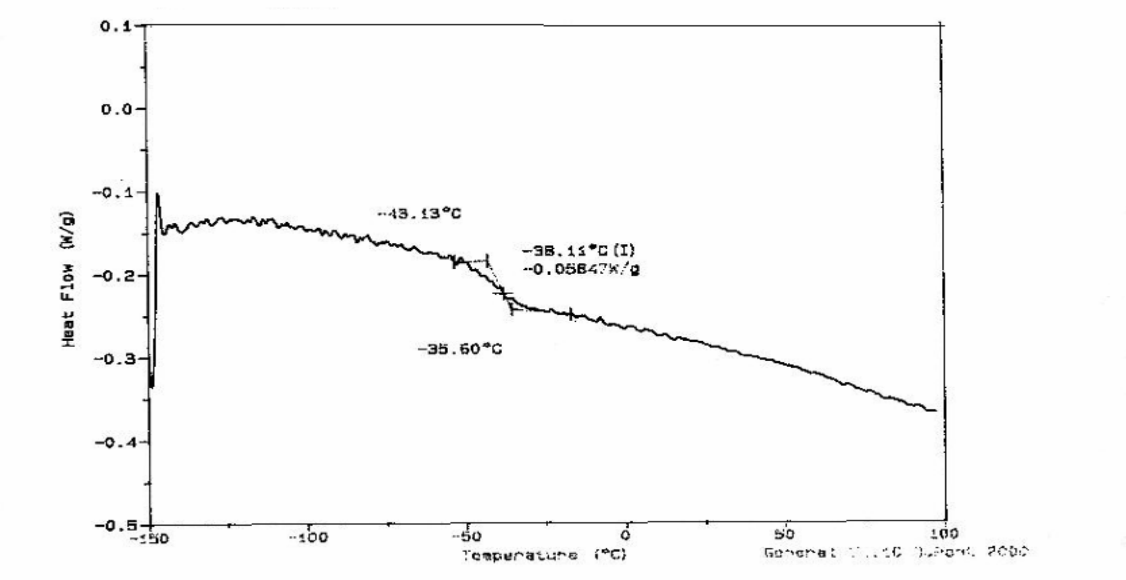


Figure 28: DSC thermogram of high fraction of experiment 14 (S%= 21.0, f_2=0.266)

3.8 Results of TGA Measurement

TGA thermograms showed one step decomposition for high and two step decomposition for low copolymers as seen in Figure 29 and 30. For high copolymers, decomposition starts at 125 ^{0}C and ends after 300 ^{o}C with 40 % weight loss. But in low copolymers decomposition start at 70 ^{o}C and its accelerated about 110 ^{o}C and slows down about 150 ^{o}C and the weight loss is 25 %. After 150 ^{o}C decomposition progress and at 300 ^{o}C the weight loss was 70 %. The faster decomposition at lower temperature of low copolymers may be due to vaporization of cyclic-dithio compounds. For example 1, 3-oxathioran-5-methyl-2-thione (molecular formula is given in section 3.10) boils at 46 ^{o}C under 3 mmHg (Adachi et al., 1977).

TGA results of the polymers were shown in Figure 29 and 30:

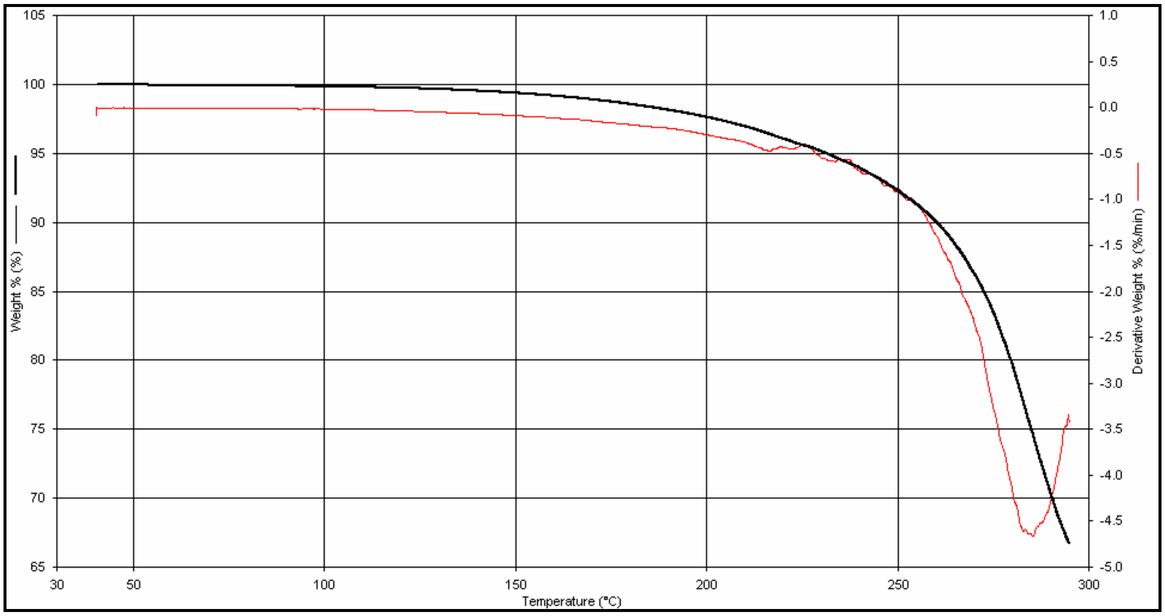


Figure 29: TGA thermogram of high molecular weight product of experiment 28

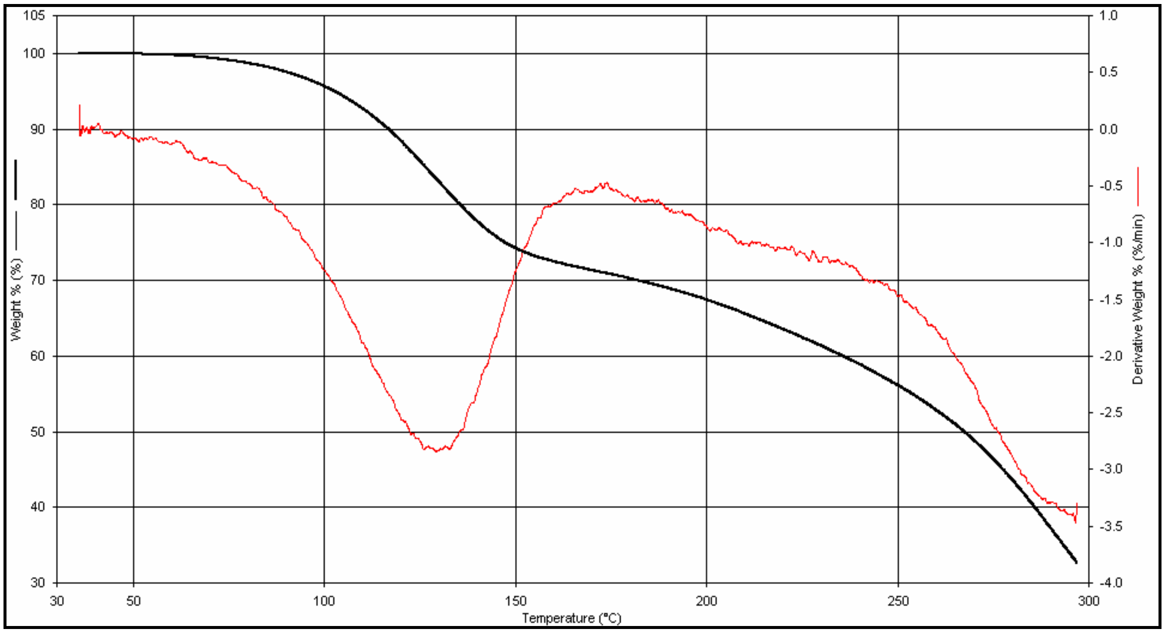


Figure 30: TGA thermogram of low molecular weight product of experiment 28

3.9 Results of IR Spectroscopy

Several copolymer fractions were examined with infrared spectroscopy (Figure 31-39). All of the spectra were obtained with the potassium bromide pellet technique.

Following conclusions can be withdrawn by an inspection of the spectroscopic data:

i) It would be expected that variation of reaction conditions would reflect onto the IR spectra of the products. At first sight spectrums are similar to each other, but there exist some differences (Figure 31-39).

ii) Although the absorption band of C-H stretching between 2850-2970 cm^{-1} and C-H bending between 1340-1470 cm^{-1} have practically constant absorption intensity in all the spectra (Figure 31-39), the intensity of bands appearing at 1740, 1710, 1645 cm^{-1} etc. vary with changing reaction conditions. These wavenumbers related with –O-(C=O)-O, –O-(C=O)-S and –S-(C=O)-S groups respectively (Adachi et al., 1977). The bands at 1740, 1265 and 795 cm^{-1} are also characteristics of carbonate group (Inoue et al., 1969).

iii) In literature, –O-(C=S)-S group is observed at about 1185-1205 cm^{-1} (Steblyanko et al., 2001) and –O-(C=S)-O is nearly 1200 and –S-(C=S)-S is between 1000-1100 cm^{-1} (Soga et al., 1975). Moreover, C-O-C group between 1000 and 1200 cm^{-1} overlapped with these peaks. In this work, spectra with a number of peaks were observed between 950 and 1200 cm^{-1} especially with higher intensity in low molecular weight fractions (Figure 31-35). Thus IR results show the presence of –O-(C=S)-O, –O-(C=S)-S and –S-(C=S)-S groups.

iV) OH stretching intensity occurring at 3435 cm^{-1} in the IR spectra is very small when compared with other values. This result is also consistent with the result of end group analysis (Figure 31-39).

V) The carbon-carbon double bond stretching shows itself as absorption of medium intensity between 1540 and 1695 cm^{-1} that overlaps with the other peaks in the spectrums. Absorptions arising from carbon-hydrogen bending vibrations of alkenes occur in the 600-1000 cm^{-1} region. Mono-substituted alkenes give two strong peaks in the 905-920 cm^{-1} and 985-1000 cm^{-1} region (Pouchert, ALDRICH). The peak between 905 and 920 cm^{-1} is sharp; however 985-1000 cm^{-1} region peak again overlapped with the other peaks (Figure 31-39). However, the peak at 985-1000 cm^{-1} has a consistent placement with an obvious overtone between 1785 and 1820 cm^{-1}. In the spectrums also a small peak nearly 1800 cm^{-1} exist. These results show existence of double bonds at the chain ends. However, observation of these bands were rather difficult due to very low concentrations (about 6x10^{-4} mol/g copolymer)

Vi) S- H stretch is one of the weaker absorptions in the infrared spectrum. Fortunately, its position at 2565 cm^{-1} allows it to be recognised in most instances. Notice, however, that in the long chain, the overtone bands between 2630 and 2780 cm^{-1} are as strong as or stronger than the S-H bond. It is therefore, very difficult to identify these compounds. (Pouchert, ALDRICH). However, S-H stretching band occurring at 820-940 cm^{-1} exist in the spectra for low fractions because as sulphur content increases the intensity of the peak at 868 cm^{-1} also increases (Figures 31-35). However, for sample richest in CS_2 (f_2=0.730-Figure 33) absorptions attributed to SH bonding were extremely weak. For the high molecular weight fraction almost same was observed but the intensity of these peaks were weaker (Figure 36 and 39). When high and low molecular weight fraction of same polymer was compared, S-H stretching value is greater in low ones.

Vii) Moreover, C-S stretch band is weak and ill-defined between 625 and 715 cm^{-1} and beyond. Of course this region is also occupied by bands from most other functional groups (Pouchert C.J., ALDRICH). In the spectrums of the copolymer also the absorption intensity of C-S (at 667 cm^{-1}) stretching increases slightly as S content in the copolymer increase (Figure 31-39). C-S stretch band value is better understood from ^{13}C NMR Spectroscopy result (Section 3.10).

In summary, IR spectroscopy yielded following information:

a) Expected CH stretching and bending, C-O-C, –O-(C=S)-S bands were observed.

b) C=C and –OH absorptions with very weak intensities were observed. These groups were assigned as terminal groups.

c) Unexpected O-(C=S)-O, O-(C=O)-O, S-(C=S)-S and S-H groups were also detected. The presence of these bonds will be discussed in section 3.13.

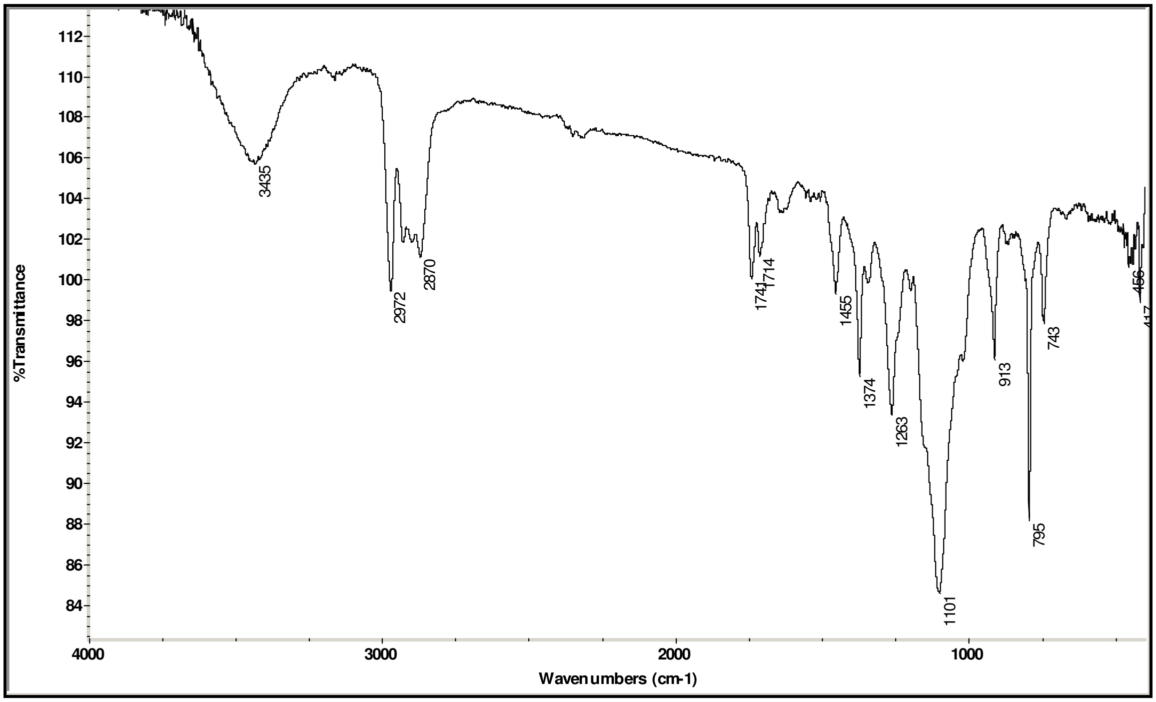


Figure 31: IR Spectrum of low fraction of experiment 2 (% S=12.2, f_2=0.162)

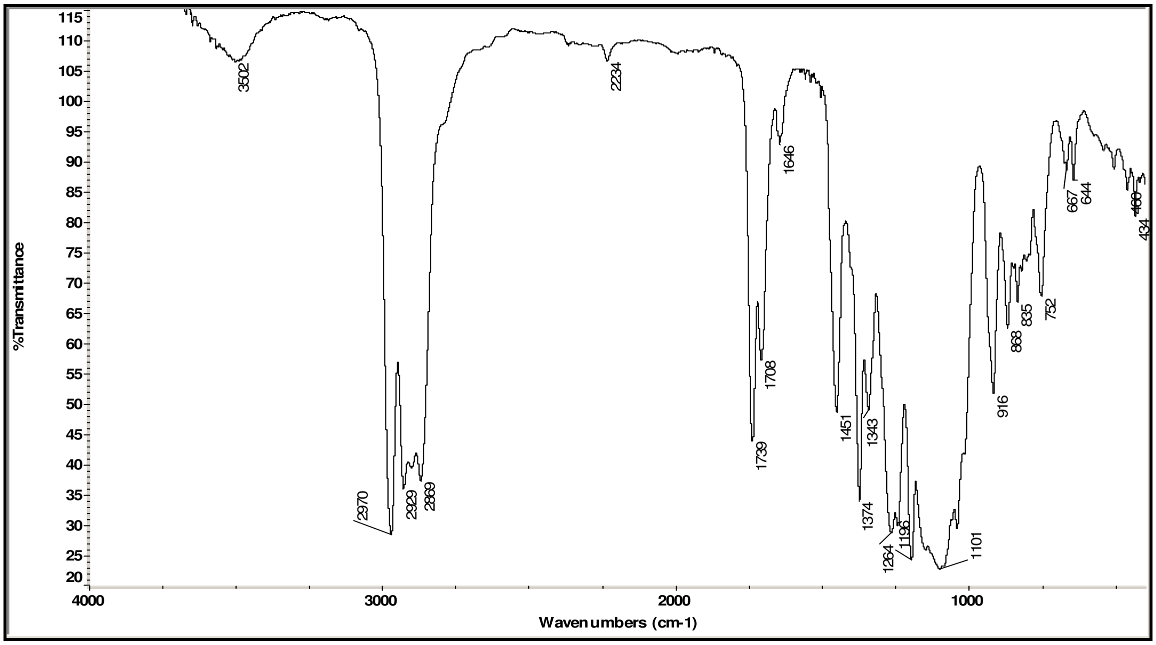


Figure 32: IR Spectrum of low fraction of experiment 7 (% S=21.8, f_2=0.487)

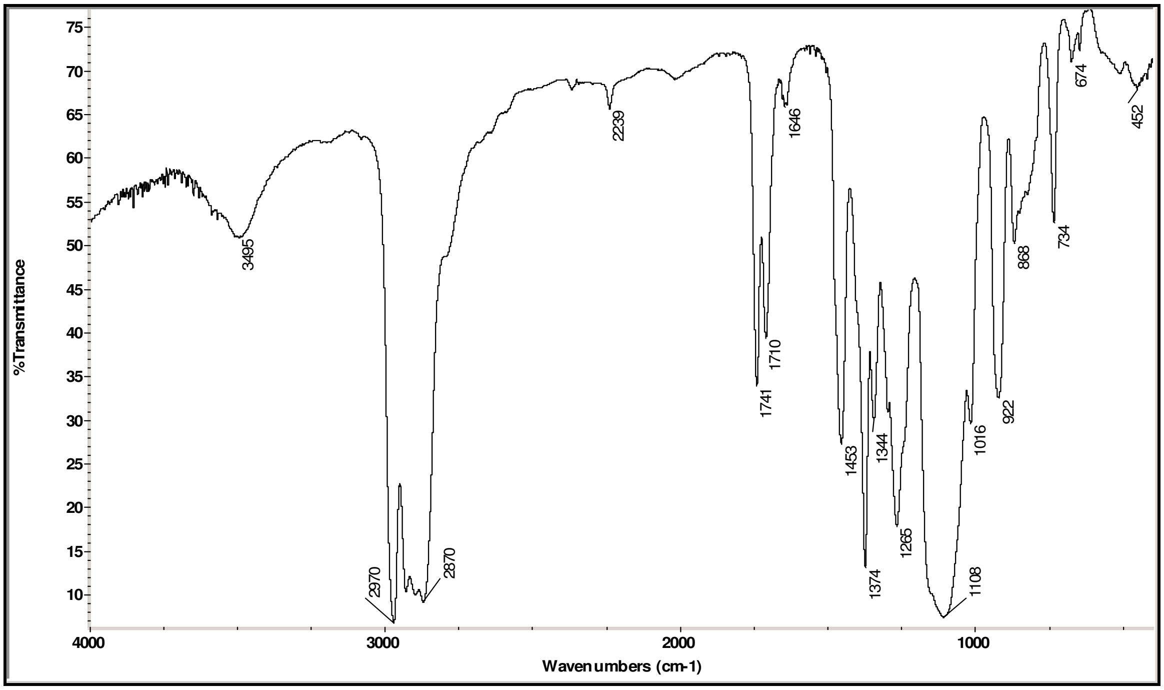


Figure 33: IR Spectrum of low fraction of experiment 8 (% S=6.81, f_2=0.730)

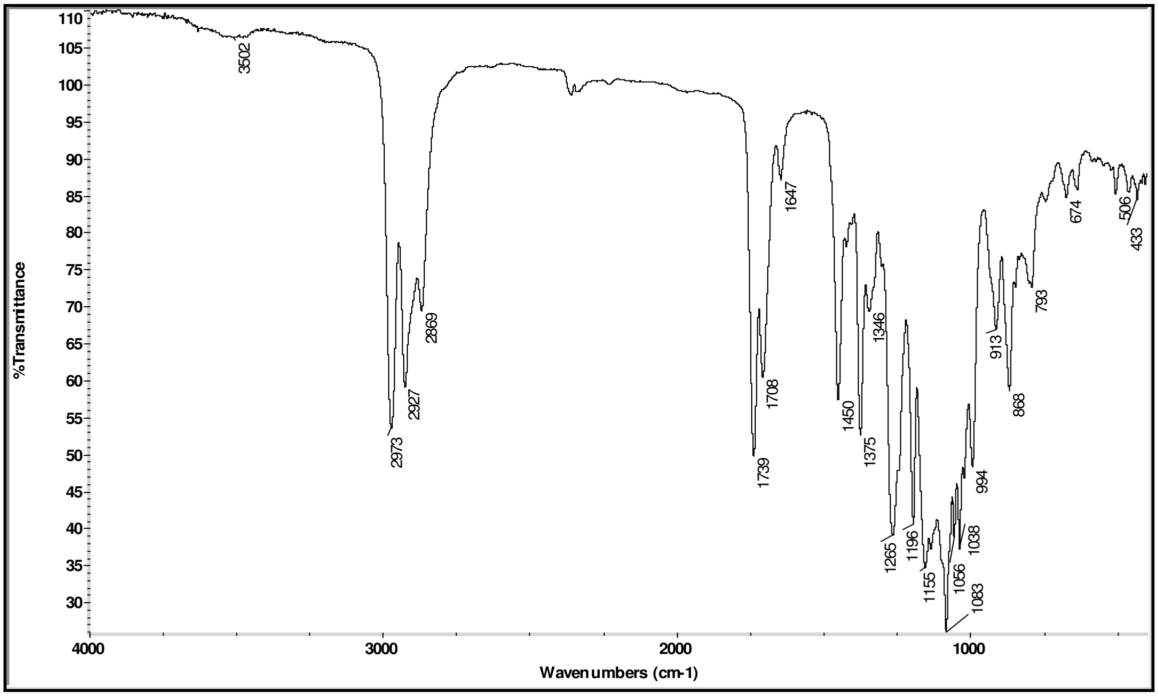


Figure 34: IR Spectrum of low fraction of experiment 10 (% S=23.8, f_2=0.162)

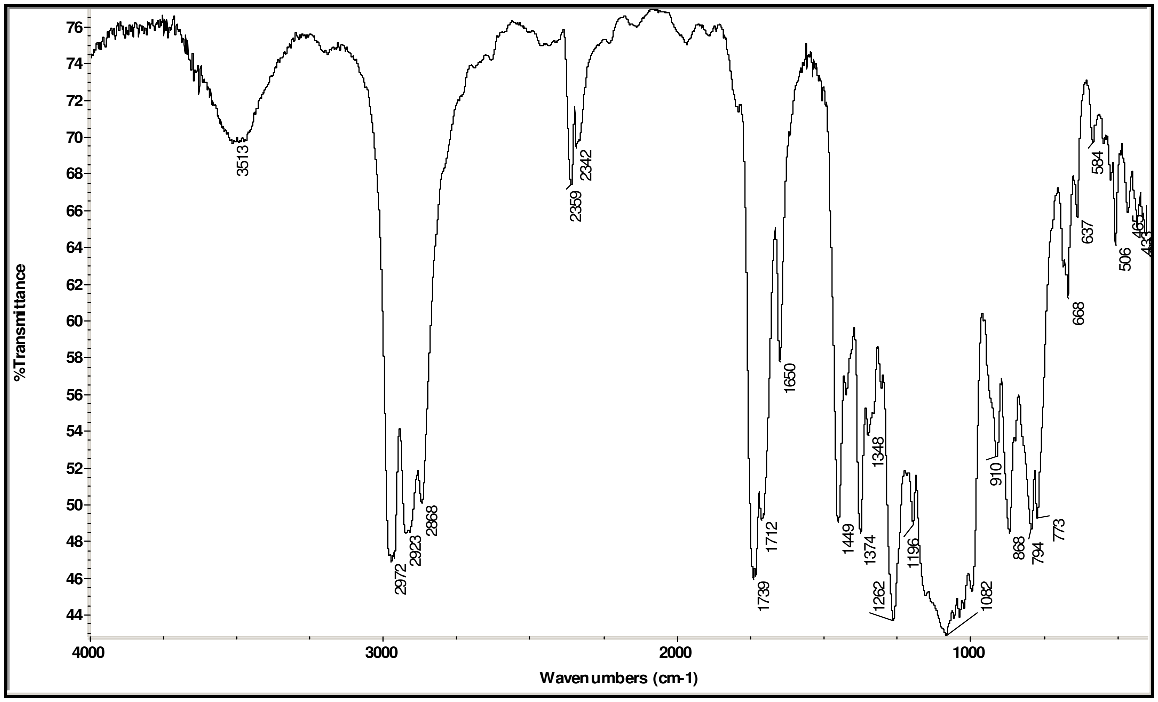


Figure 35: IR Spectrum of low fraction of experiment 11 (% S=34.5, f_2=0.162)

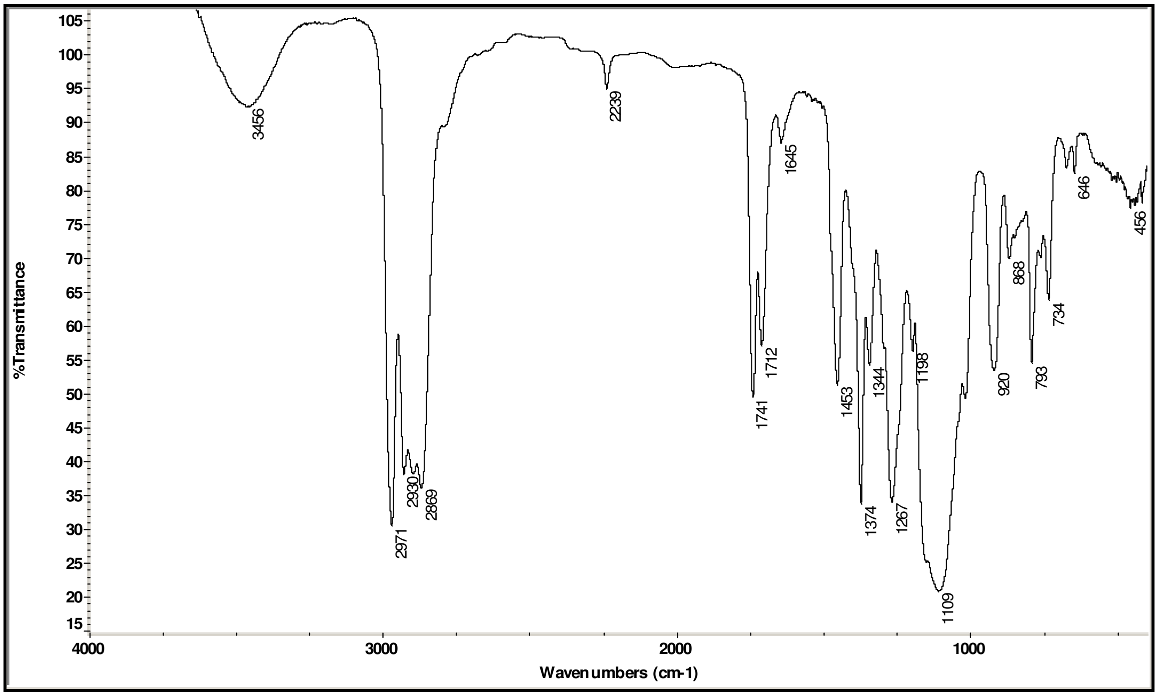


Figure 36: IR Spectrum of high fraction of experiment 4 (% S=11, f_2=0.266)

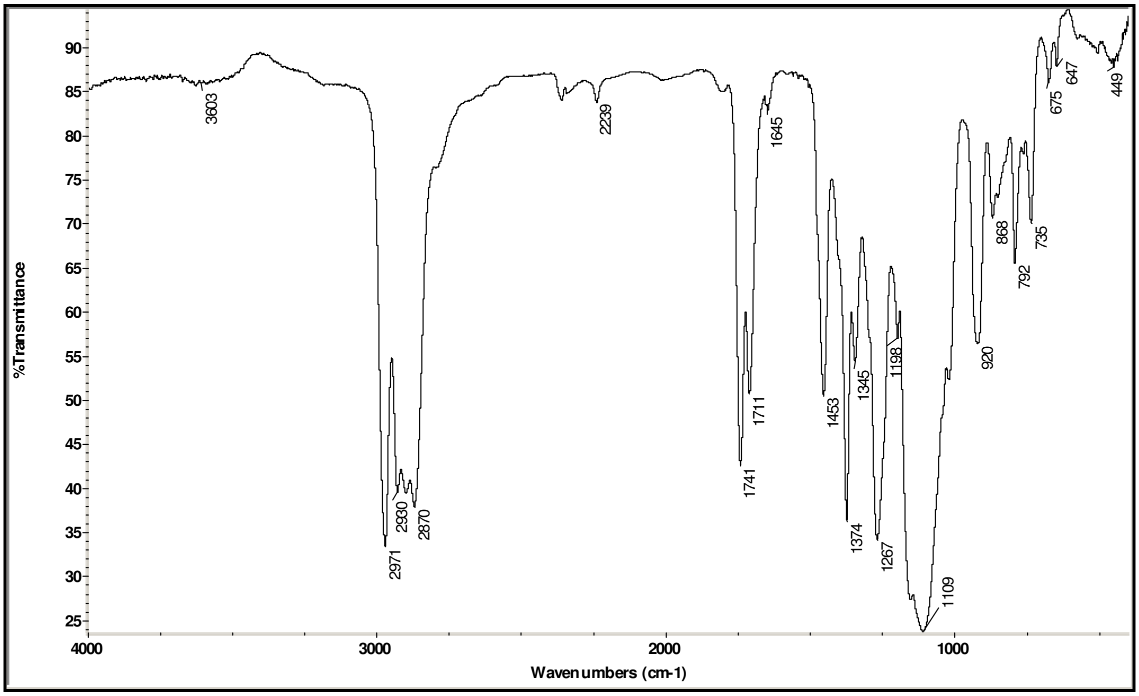


Figure 37: IR Spectrum of high fraction of experiment 13 (% S=13, f_2=0.266)

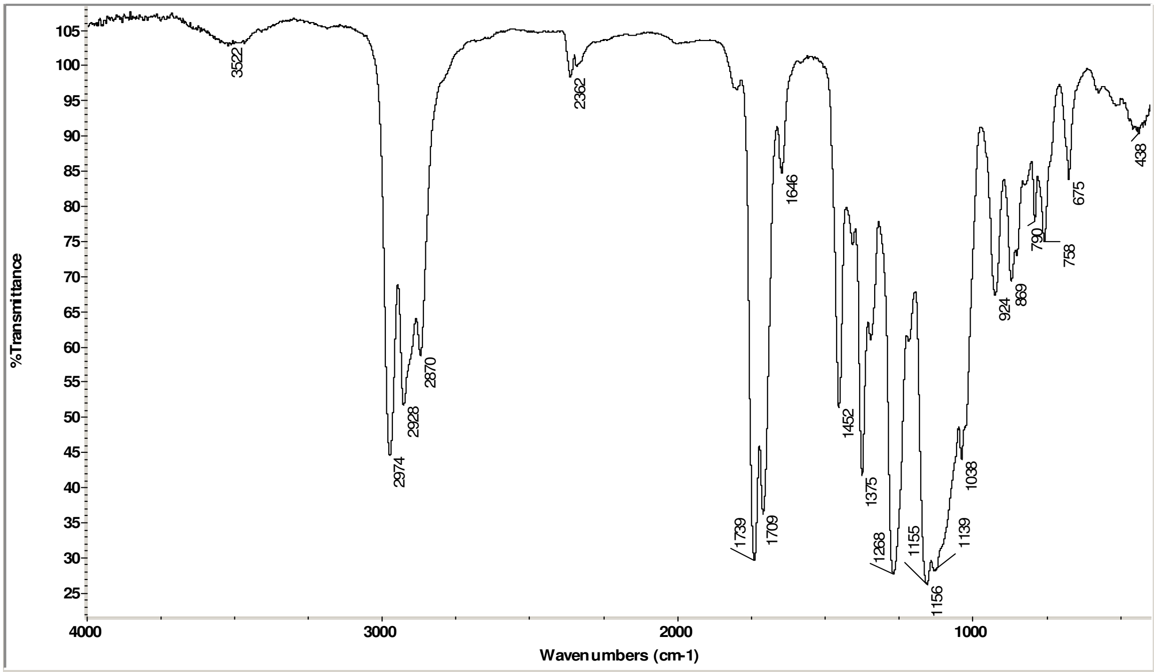


Figure 38: IR Spectrum of high fraction of experiment 14 (% S=21, f_2=0.266)

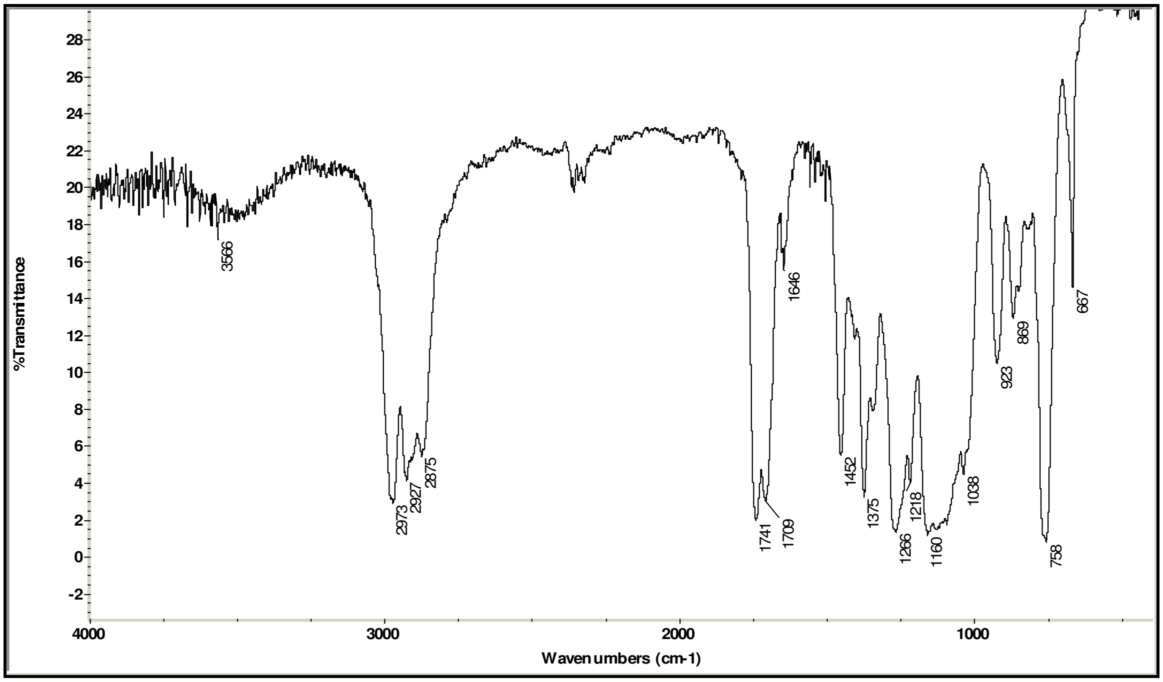
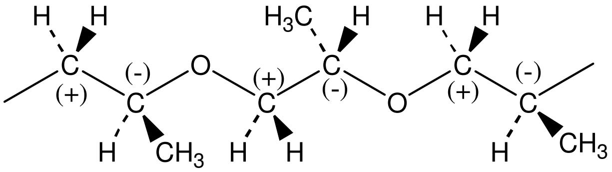


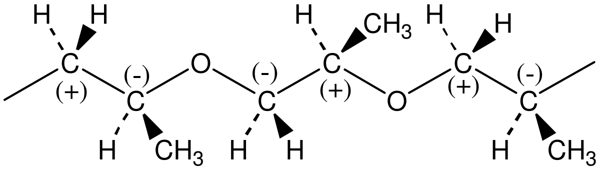
Figure 39: IR Spectrum of high fraction of experiment 18 (% S=19.7, f_2=0.266)

3.10 NMR Spectroscopy Results

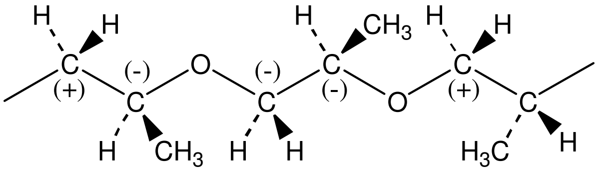
^{13}C-NMR spectroscopy was used to determine the degree of stereoregularity and the distribution of the steric irregularities in copolymers. Fischer projections of three possible stereochemical arrangements for poly(propylene oxide) are given below;



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 (Schaefer, 1969 and Oguni et al., 1979) and their assignments can be summarized as follows:

a) 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.

b) 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. The three methine carbon peaks (at 75.9, 75.8, and 75.7 ppm) were assigned to isotactic, heterotactic and syndiotactic triads.

i) In homo polymer of PPO ($Zn(Xt)_2$ catalysed), there are three methine peaks centered at 75.5 (isotactic), 75.3 (heterotactic) and 75.1 (syndiotactic) ppm with some splitting and two methylene peaks at 73.4 (isotactic) and 72.8 (syndiotactic) ppm in high fractions. The intensities of isotactic peaks are higher than the other peaks in all spectrums. It is also observed that methyl peak split into two peaks at 17.4 and 17.3 ppm. Uğur et al. (1989) 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. These results show that PPO synthesized by $Zn(Xt)_2$ catalysts is partially stereoregular. ^1H and ^{13}C NMR spectrum of PPO are given in Figure 40-41.

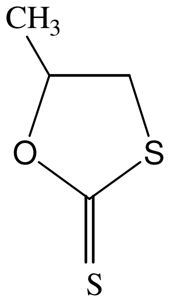
ii) In spectrums of copolymers, the characteristic methine, methylene and methyl peaks are observed but their values are shielded as sulphur percent increases (ie. as time of polymerization increases). Moreover, their intensities decrease as S content of copolymers increase (Figure 42-44).

iii) Cyclic structures for low fraction of copolymers and linear structures for high fraction of polymers were observed.

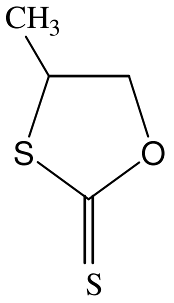
iv) For high fraction of f_2=0.487, small peaks nearly 40 (-CH_2-S) and 87 (O-CH (CH_3)-) ppm starts to appear but their intensities are small. These values increase in the other spectrums as sulfur content increases (Figure 45-46). These peaks are due to

-[O-CH (CH_3)-CH_2-S-(C=S)]- repeating unit

For low fraction, the spectrum is nearly the same as that of 1, 3-oxathioran-5-methyl-2-thione (I) (Bp 46 ^{o}C/3 mmHg) and 1, 3-oxathioran-4-methyl-2-thione (II) compounds and also characteristic PPO structure exist. For compound I, ^{1}H NMR (&, $CDCl_3$), 1.5 (d, 3H; CH_3), 3.5 (dd, 2H; CH_2S), 5.1(m, H; CHO); ^{13}CNMR(&, $CDCl_3$), 18.3 (CH_3), 39.8 (CH_2S), 86.8 (CHO), 211 (S-C=S-O, weak) and for compound II, ^{1}H NMR (&, $CDCl_3$), 1.5 (d, 3H; CH_3), 3.9 (dd, 2H; CH_2O), 4.5 (m, H; CHS); ^{13}CNMR(&, $CDCl_3$), 18.0 (CH_3), 49.1 (CH_2O), 54.2 (CHS), 211 (S-C=S-O, weak). These two compounds also exist in literature (Adachi et al., 1977). DEPT and HMQC spectrums show these peaks better (Figure 47-49). As a result, oily polymer shows presence of cyclic structures for low fraction.



(I)



(II)

v) As the f_2 value increases for 20 h polymerization time, characteristic sulfur peaks start to increase up to 0.487. However, when f_2=0.730, then it resembles to PPO structure because of dielectric constant of media. ^{1}H, ^{13}C NMR and DEPT-135 spectrum of this polymer are given in Figure 50-52.

vi) In confirming the IR results: carbonate peak O-(C=O)-O is observed in high fractions (Figure 53-54) on the other hand trithiocarbonate groups (S-C=S-S) were higher in concentration in the low copolymers (Figure 55-57). In addition, O-(C=O)-O group nearly 155, S-(C=O)-O group nearly 170, S-(C=S)-O group nearly 210 and S-(C=S)-S group nearly 225 ppm exist in the spectrum but their intensities are small (Figures 44, 53, 55, 56, 57).

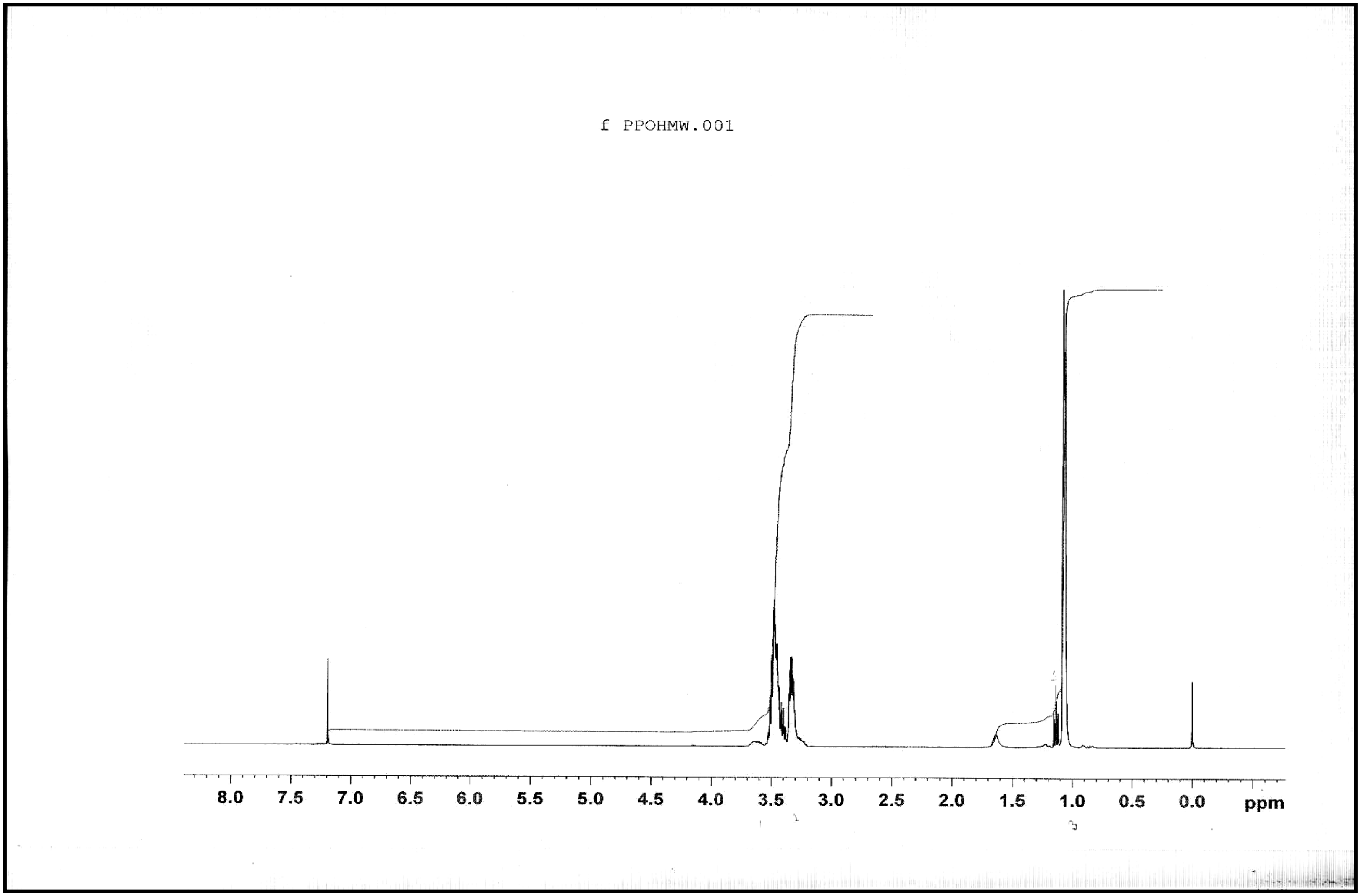


Figure 40: ^{1}H NMR Spectrum of high fraction of PPO

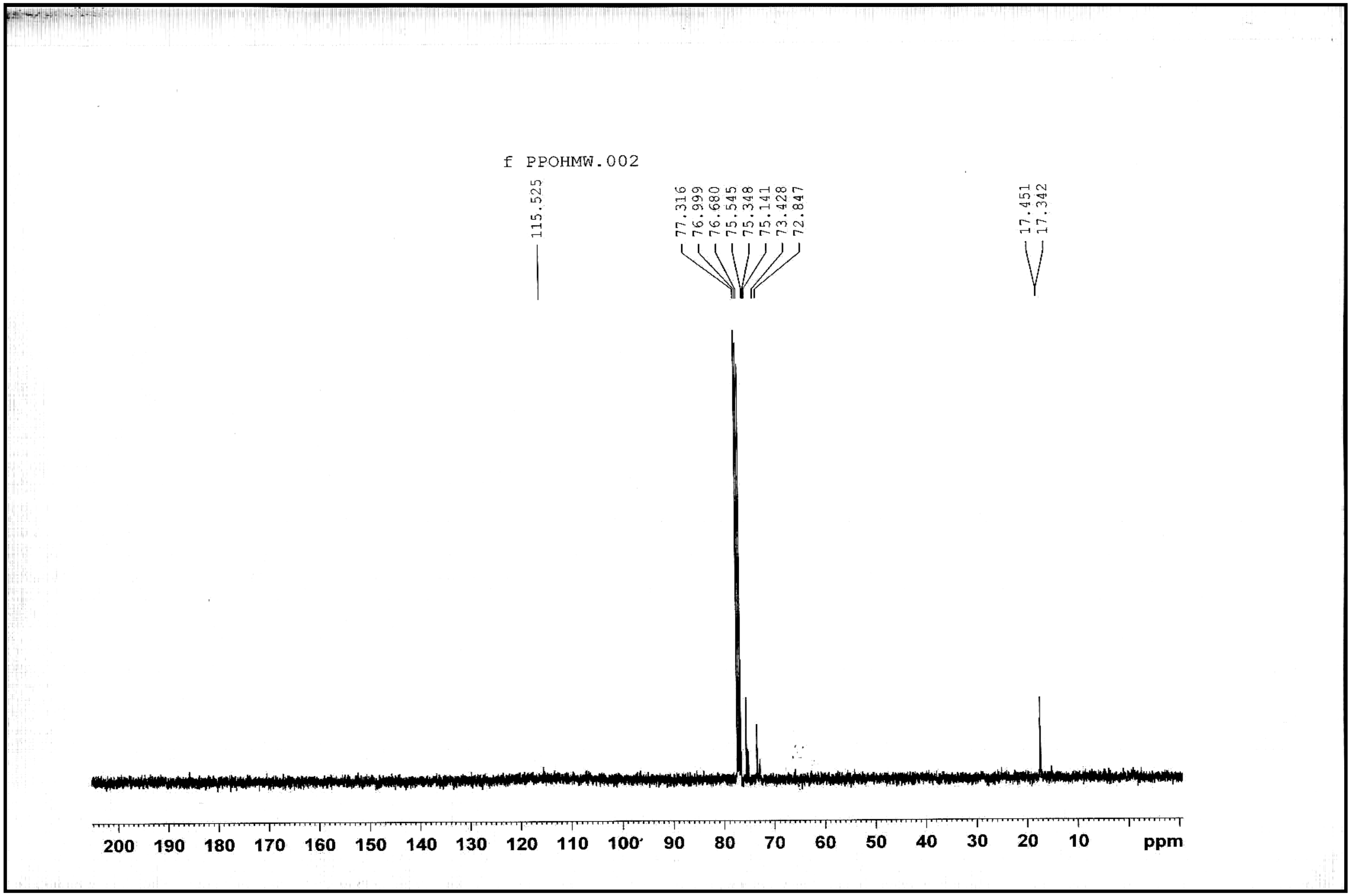


Figure 41: ^{13}C NMR Spectrum of high fraction of PPO

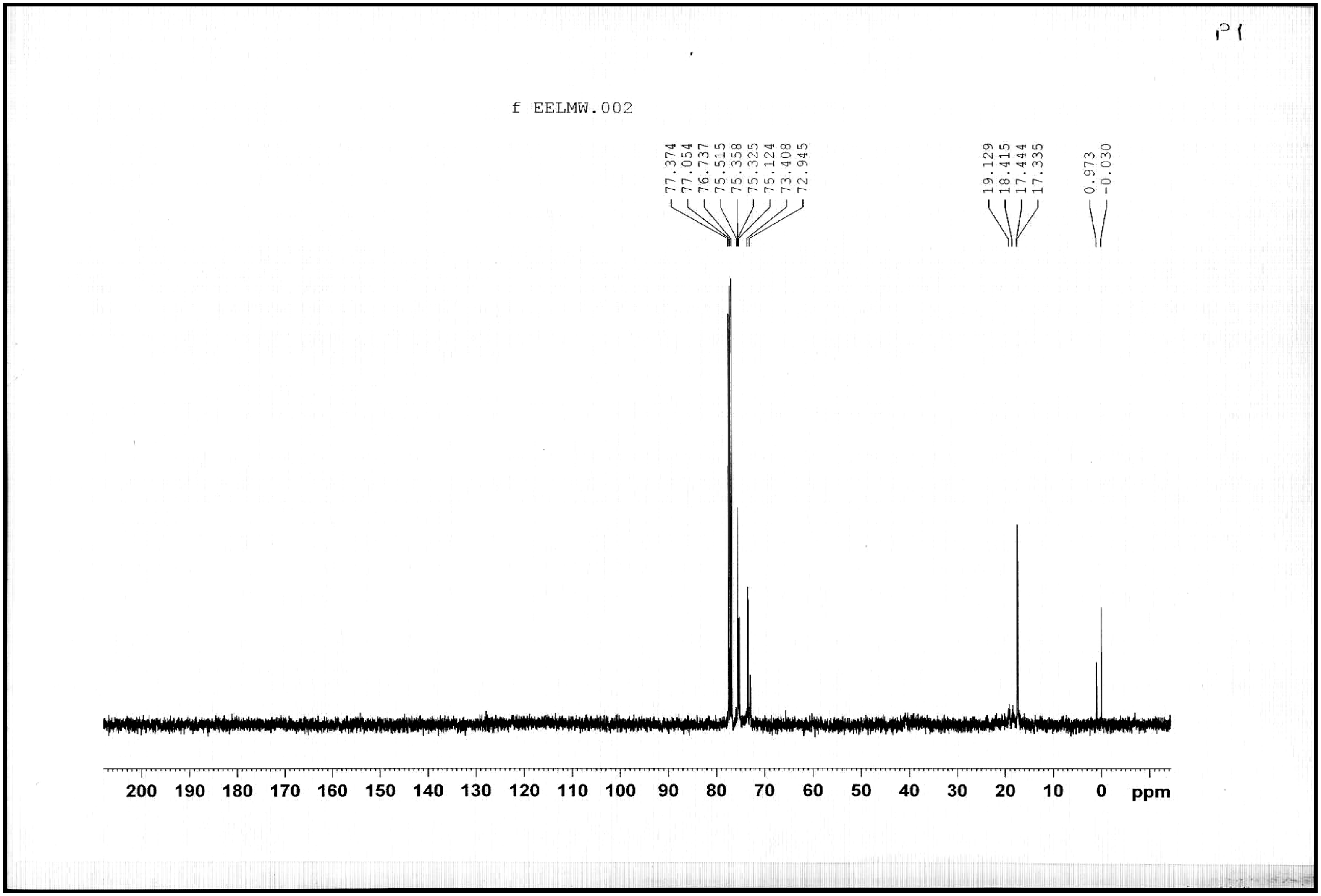


Figure 42: ^{13}C NMR Spectrum of low fraction of experiment 2 (%S=12.2, f_2=0.162)

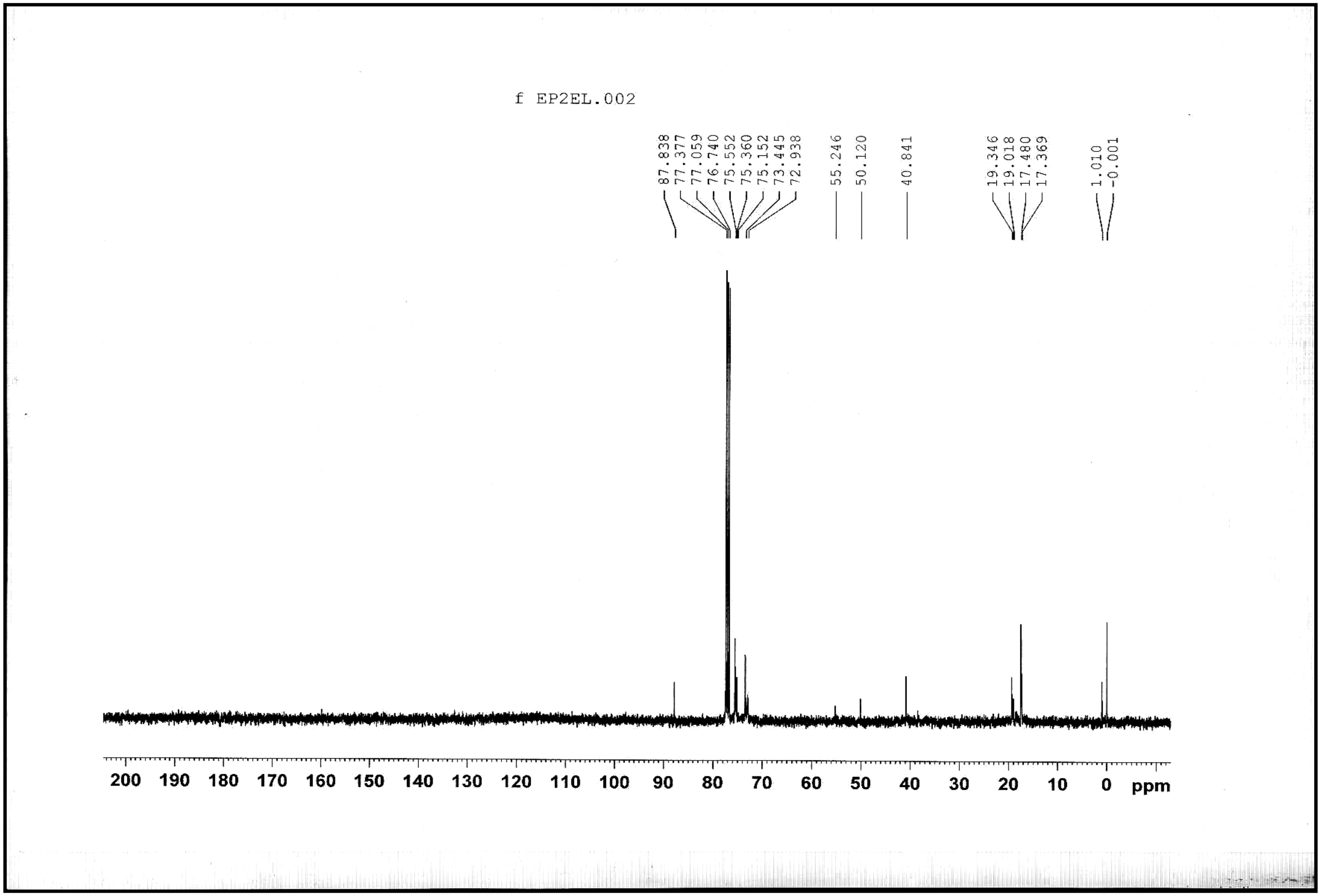


Figure 43: ^{13}C NMR Spectrum of low fraction of experiment 9 (%S=17.4, f_2=0.162)

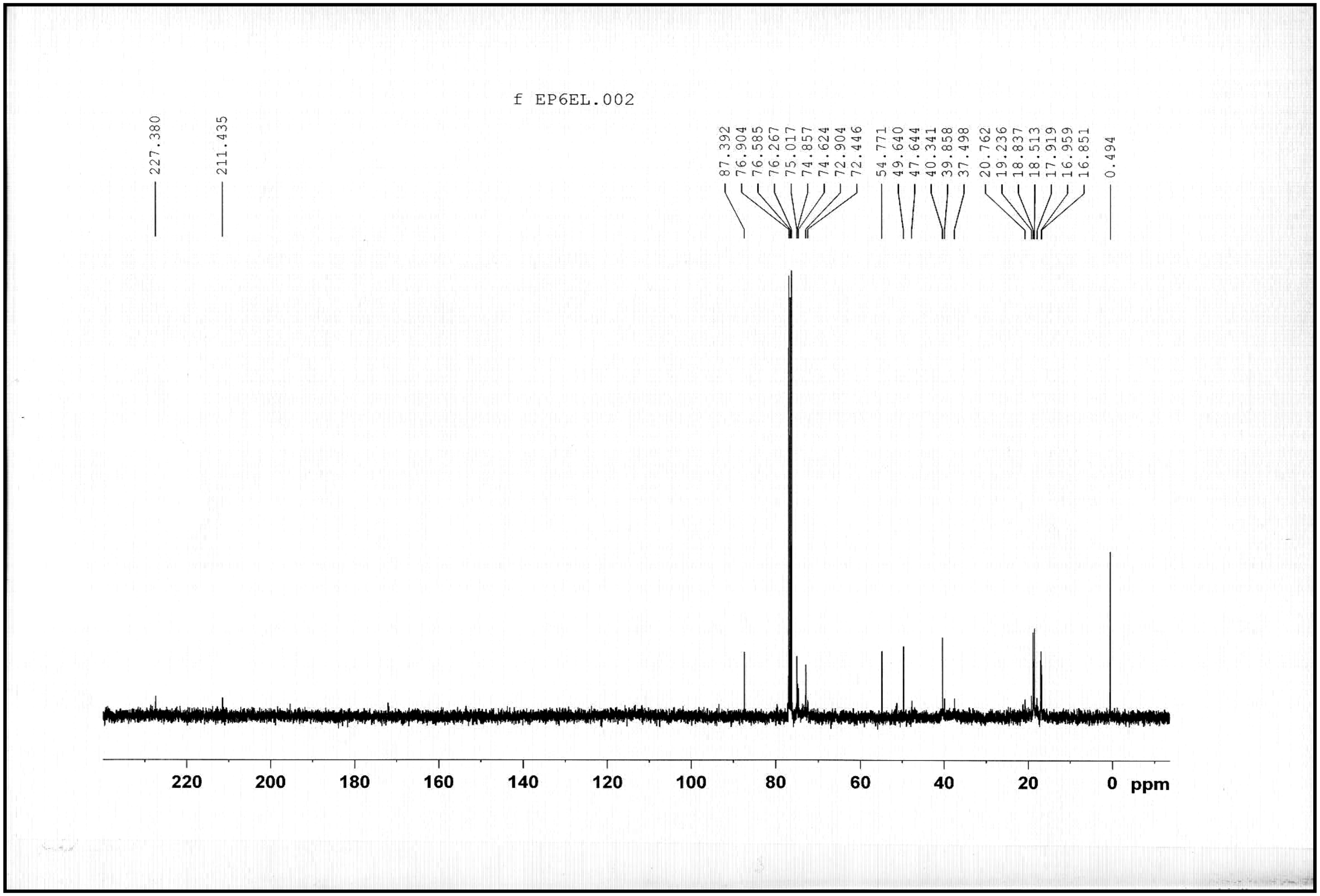


Figure 44: ^{13}C NMR Spectrum of low fraction of experiment 15 (% S=30.1, f_2=0.162)

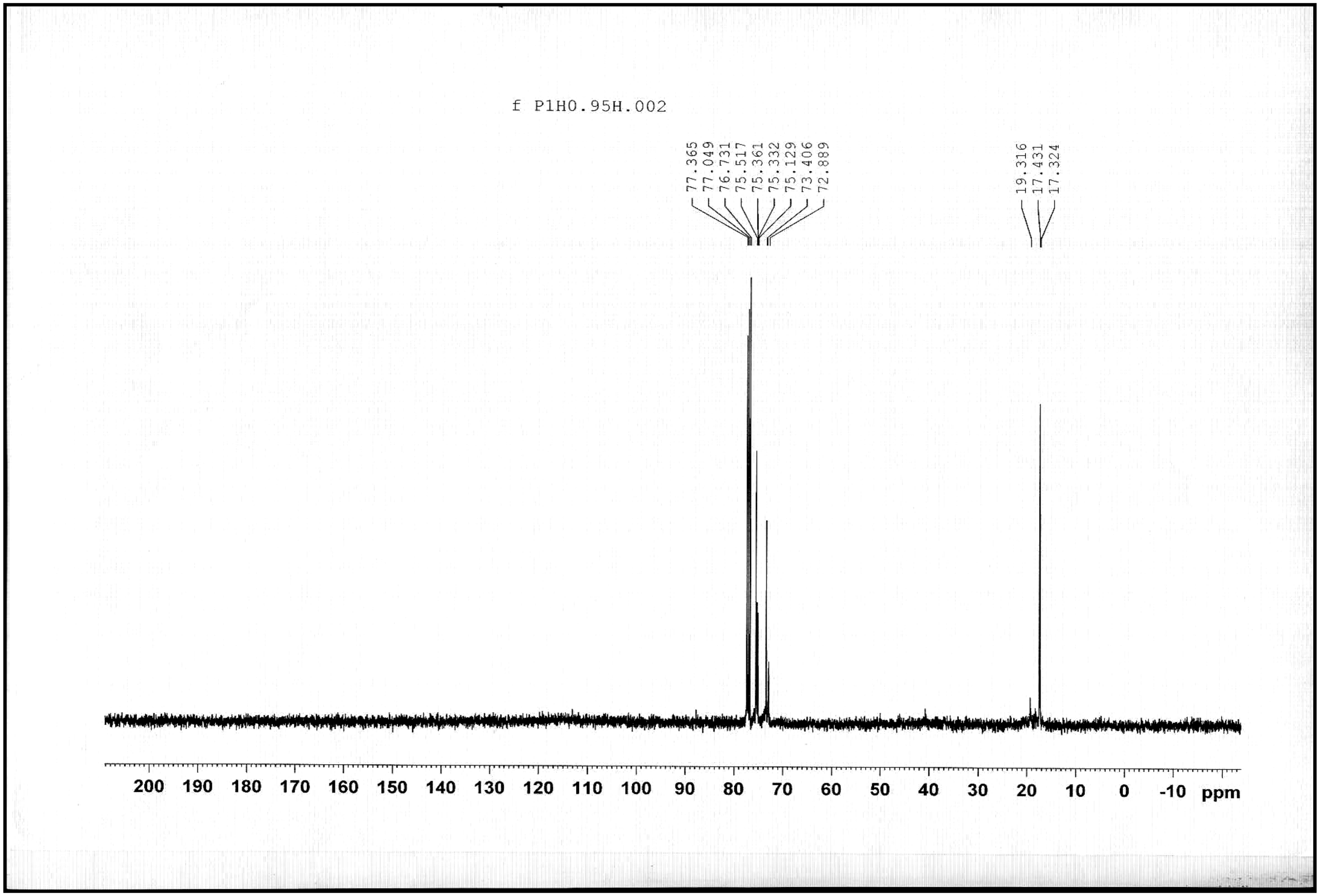


Figure 45: ^{13}C NMR Spectrum of high fraction of experiment 7 (% S=10.6, f_2=0.487)

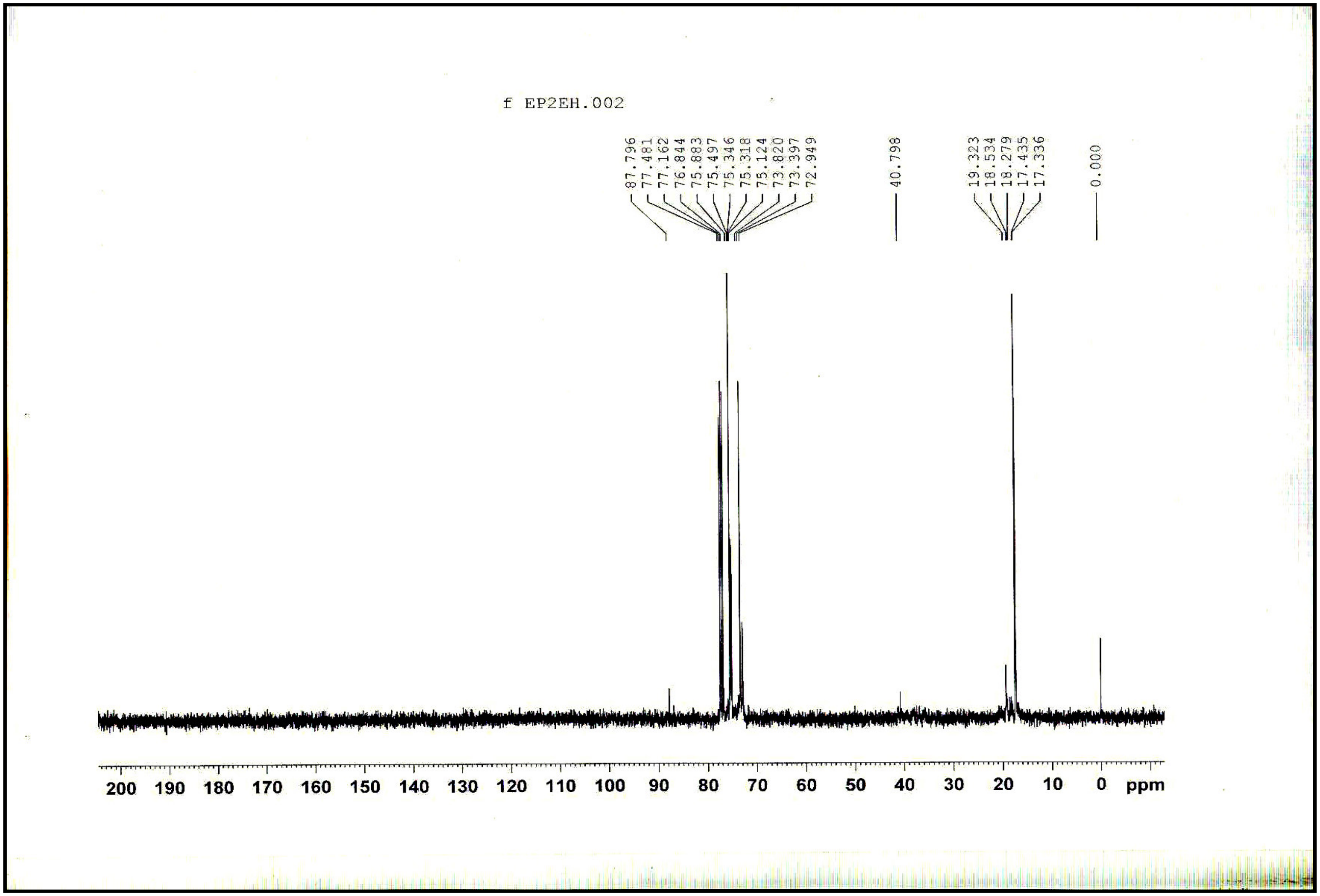


Figure 46: ^{13}C NMR Spectrum of high fraction of experiment 9 (% S=10.7, f_2=0.162)

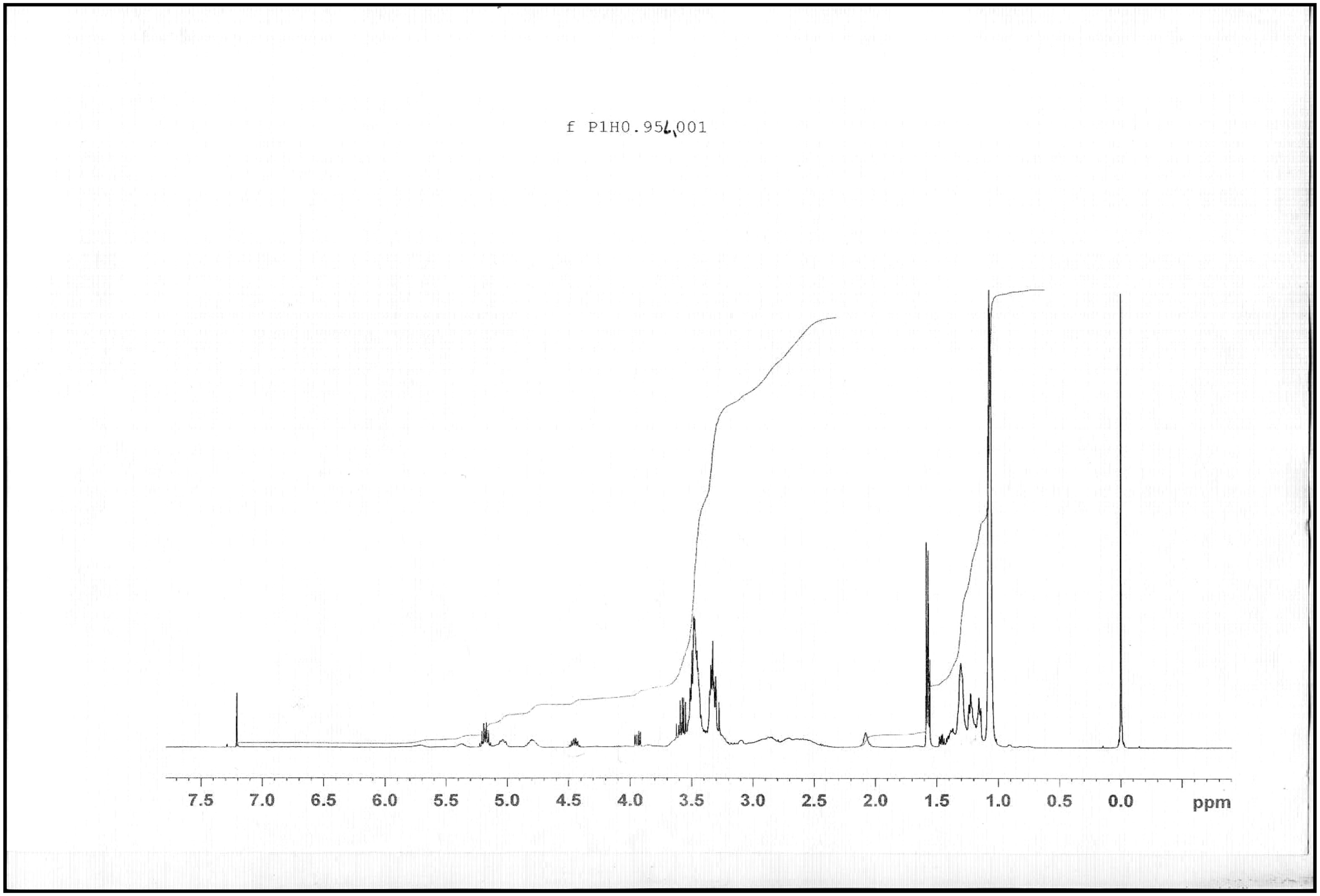


Figure 47: ^{1}H NMR Spectrum of low fraction of experiment 7 (%S=21.8, f_2=0.487)

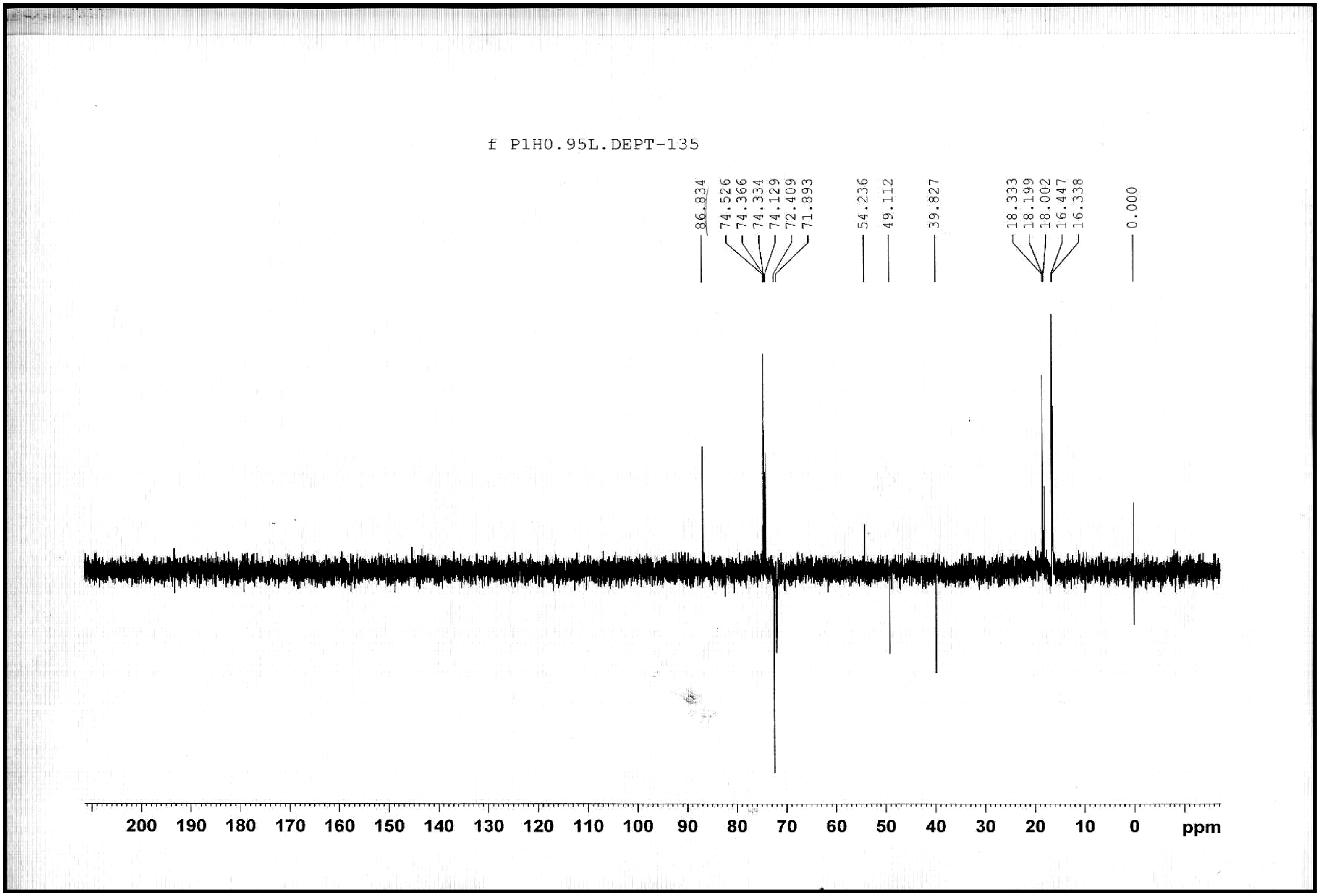


Figure 48: DEPT -135 Spectrum of low fraction of experiment 7 (%S=21.8, f_2=0.487)

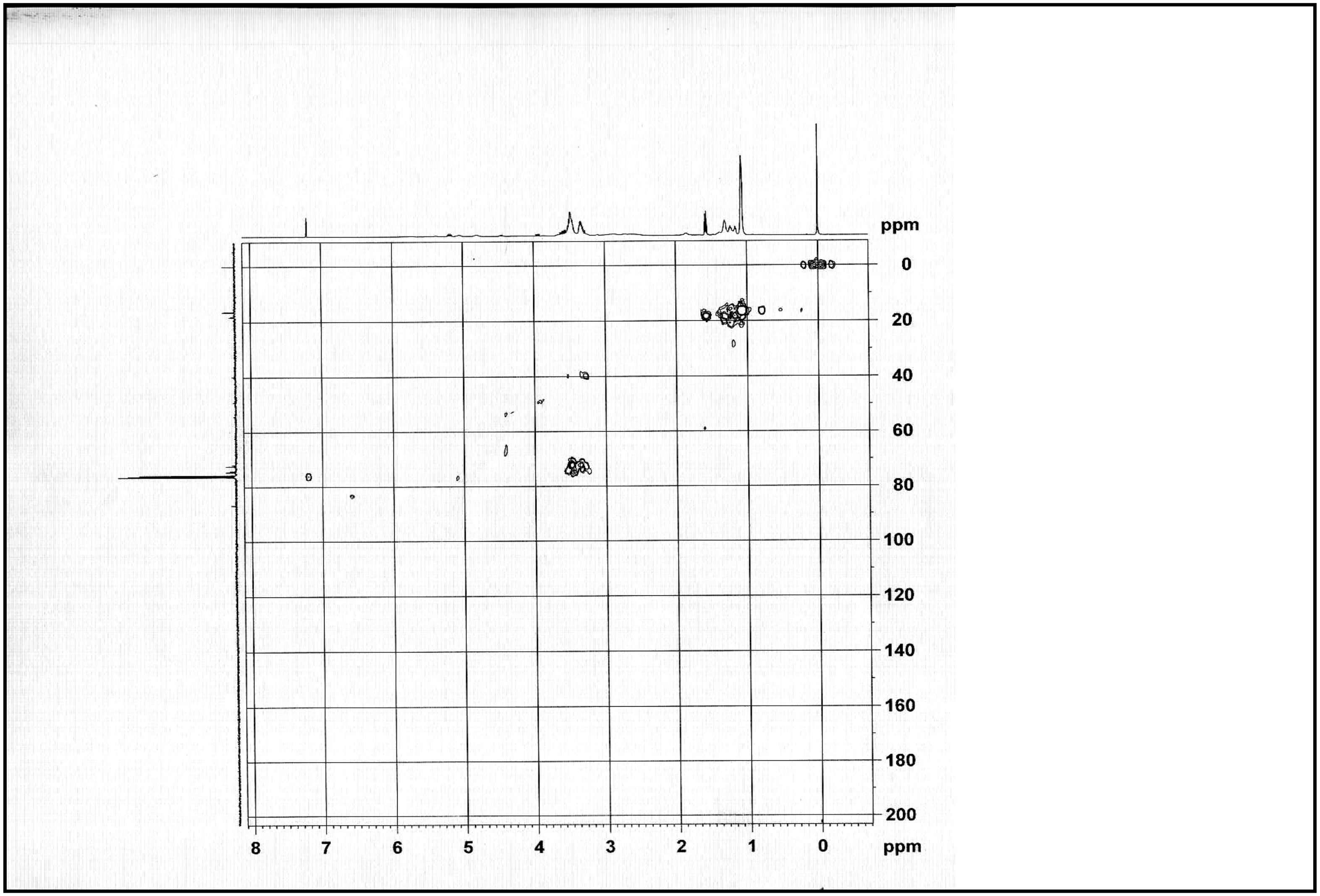


Figure 49: HMQC Spectrum of low fraction of experiment 7 (%S=21.8, f_2=0.487)

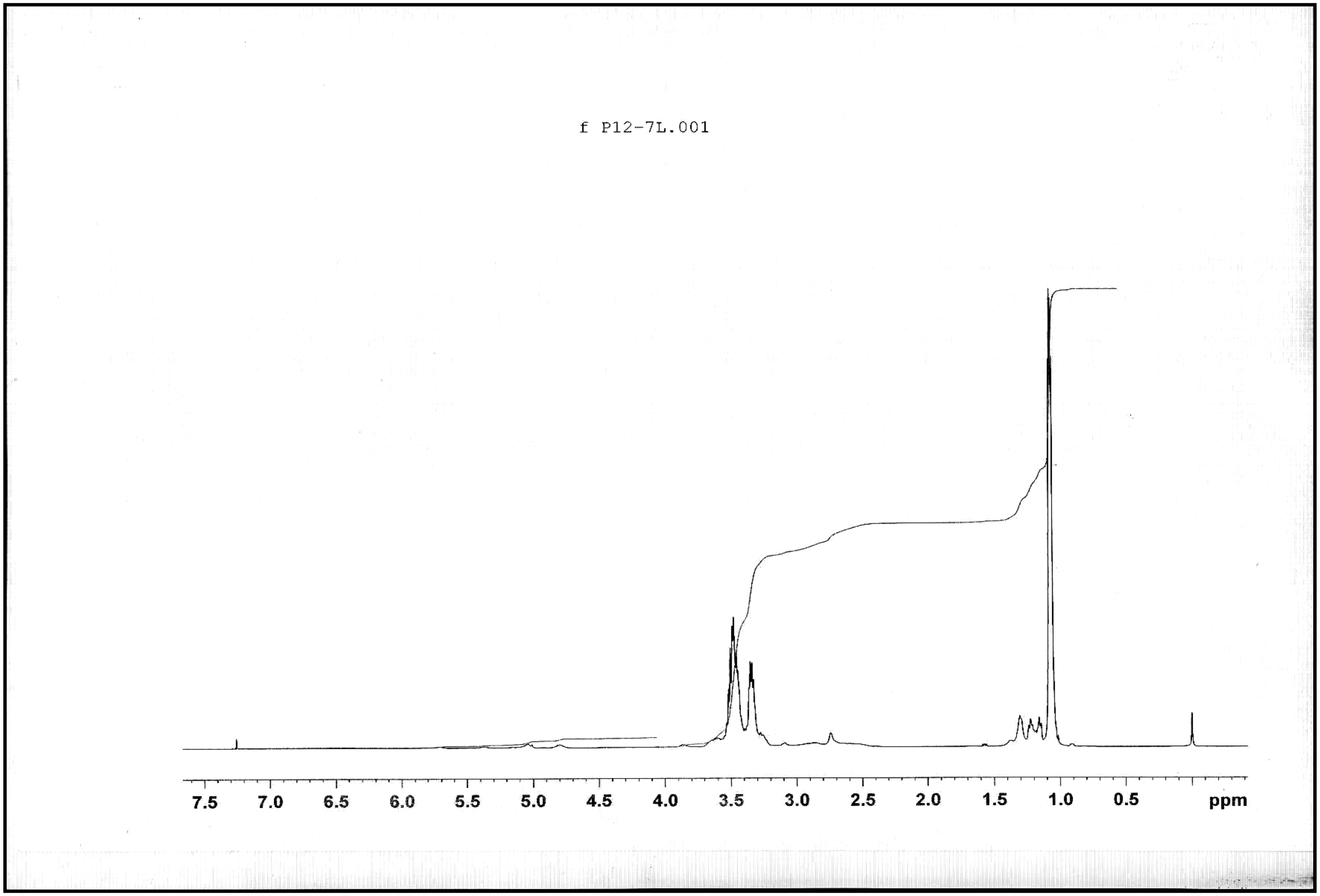


Figure 50: ^{1}H NMR Spectrum of low fraction of experiment 8 (%S=6.81, f_2=0.730)

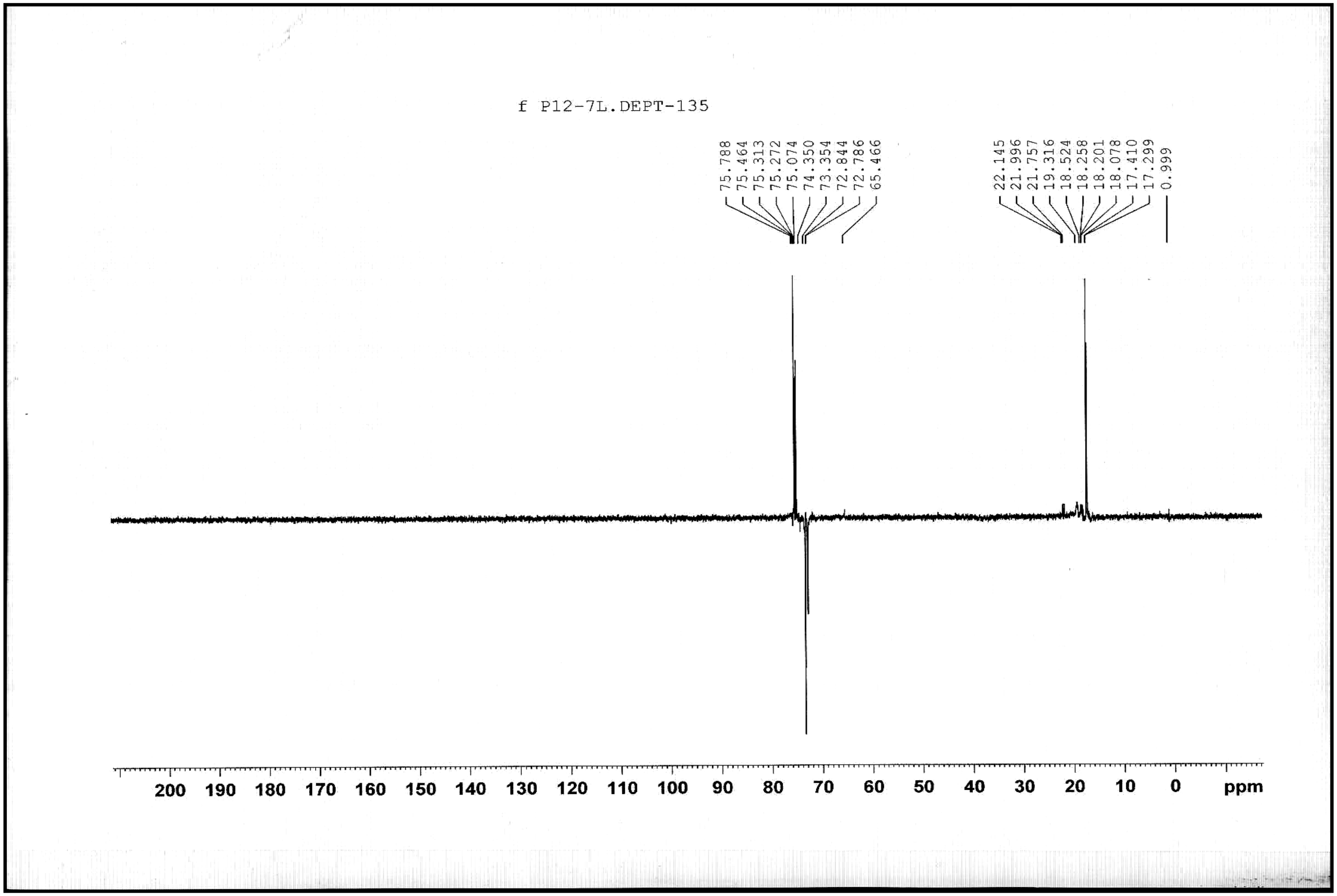


Figure 51: DEPT-135 Spectrum of low fraction of experiment 8 (%S=6.81, f_2=0.730)

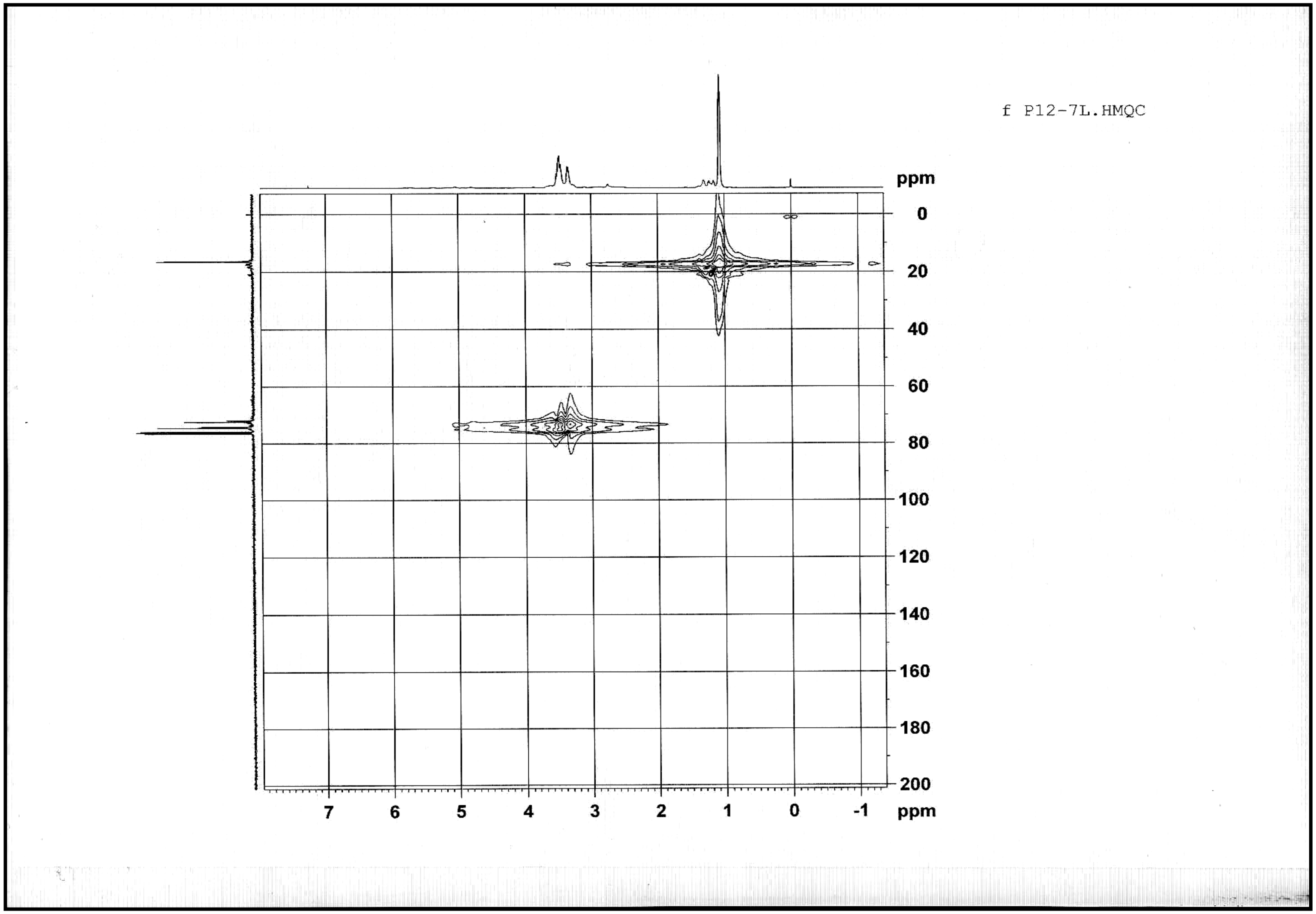


Figure 52: HMQC Spectrum of low fraction of experiment 8 (%S=6.81, f_2=0.730)

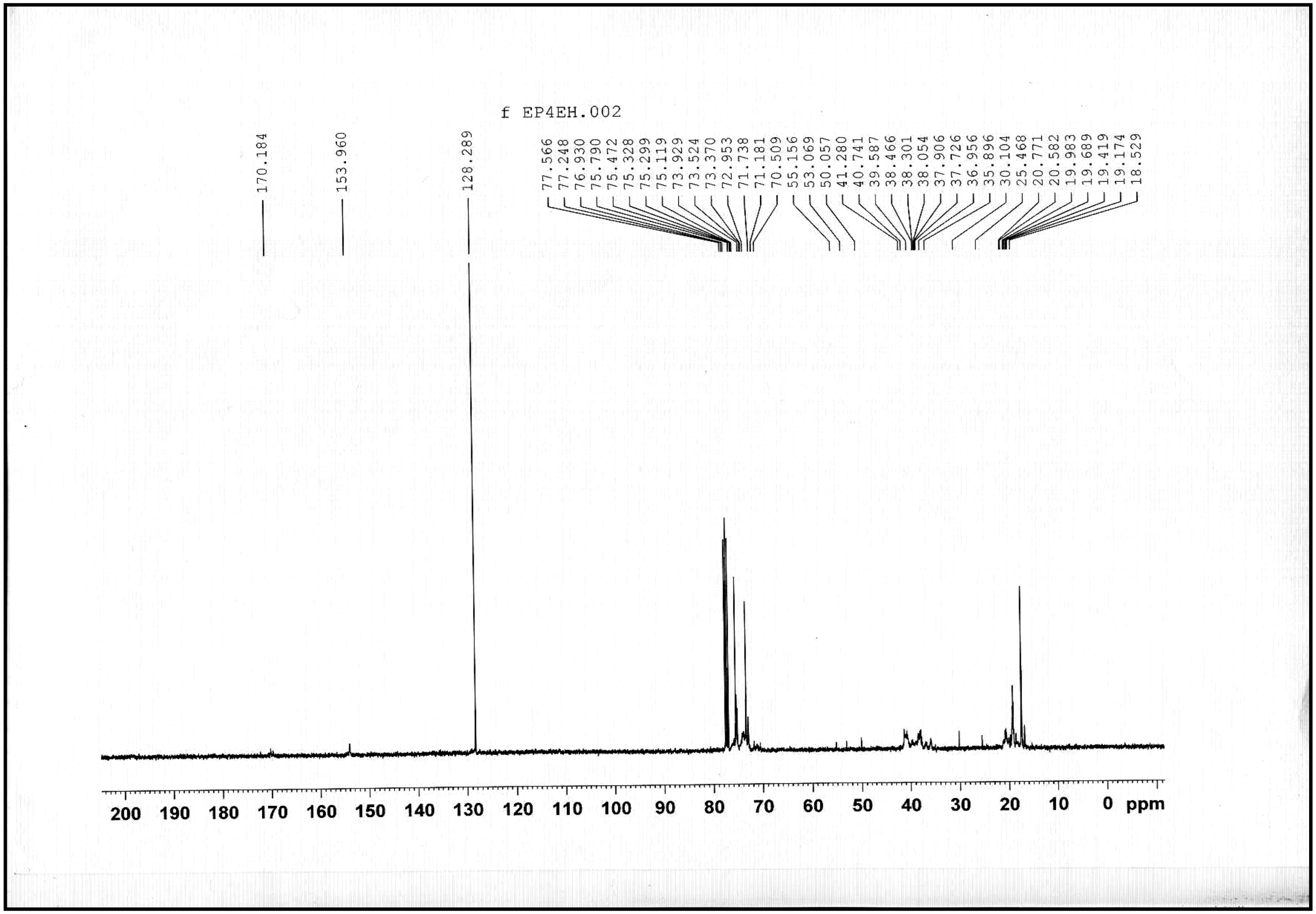


Figure 53: ^{13}C NMR Spectrum of high fraction of experiment 11 (%S=18.3, f_2=0.162)

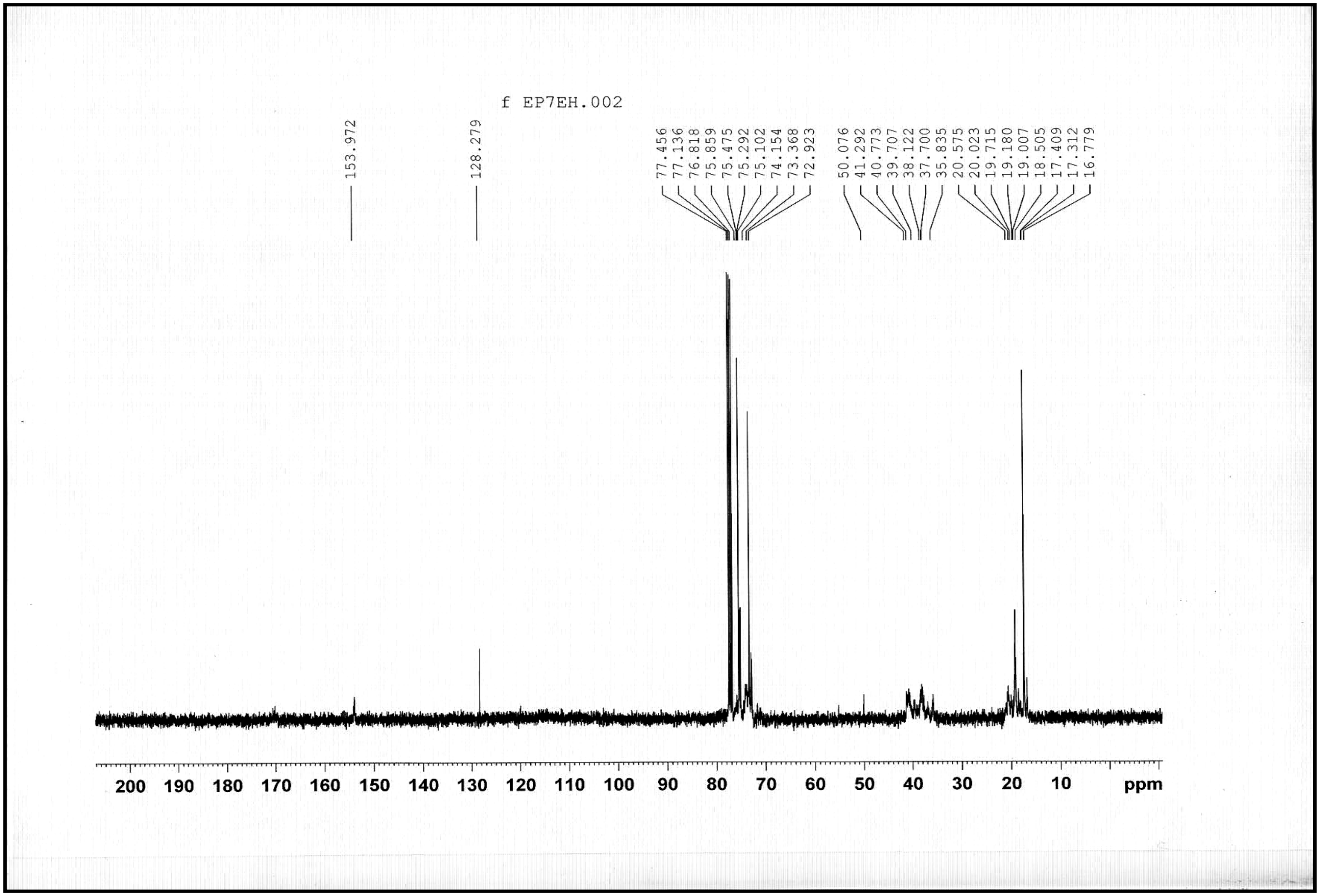


Figure 54: ^{13}C NMR Spectrum of high fraction of experiment 16 (%S=18.6, f_2=0.162)

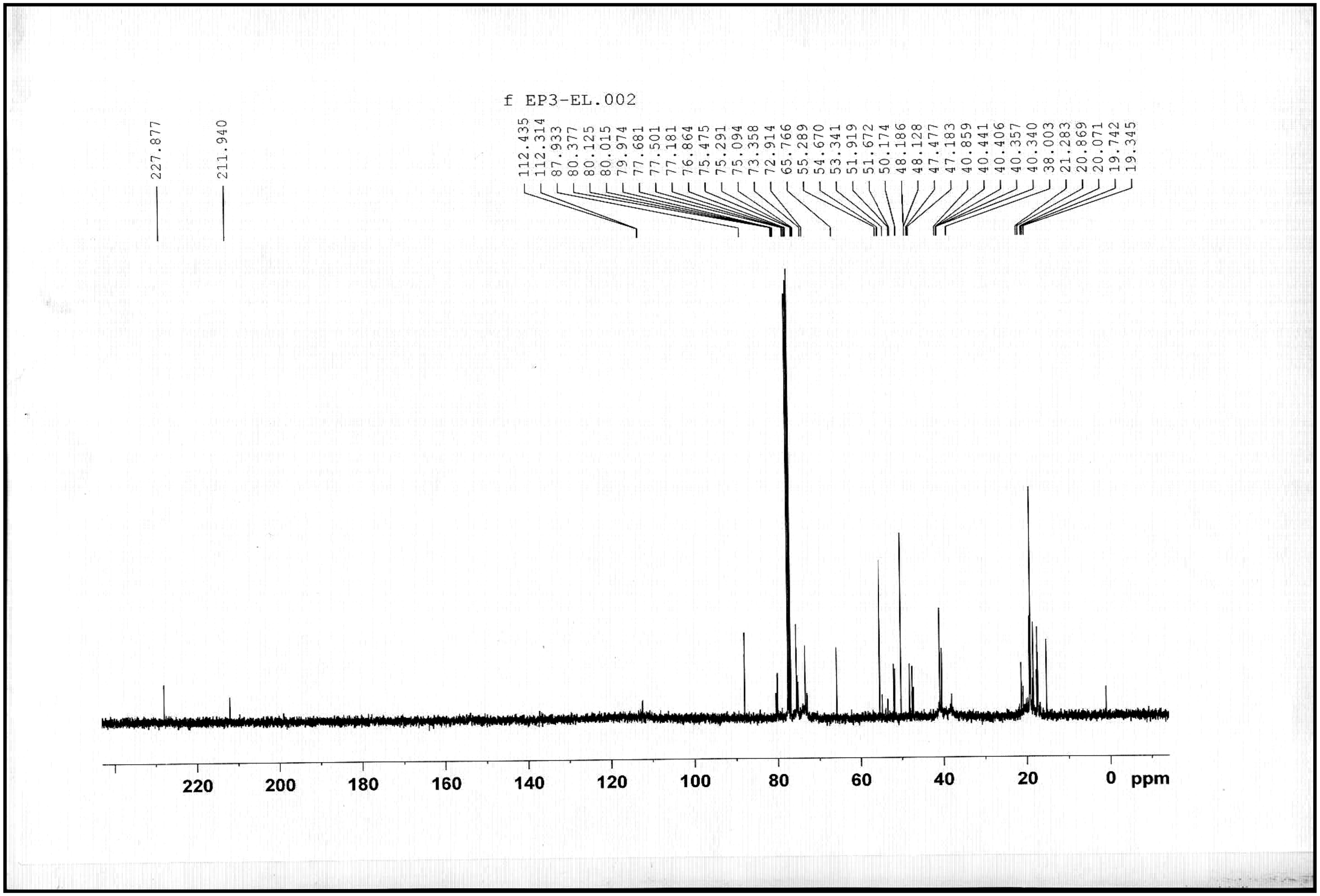


Figure 55: ^{13}C NMR Spectrum of low fraction of experiment 10 (%S=23.8, f_2=0.162)

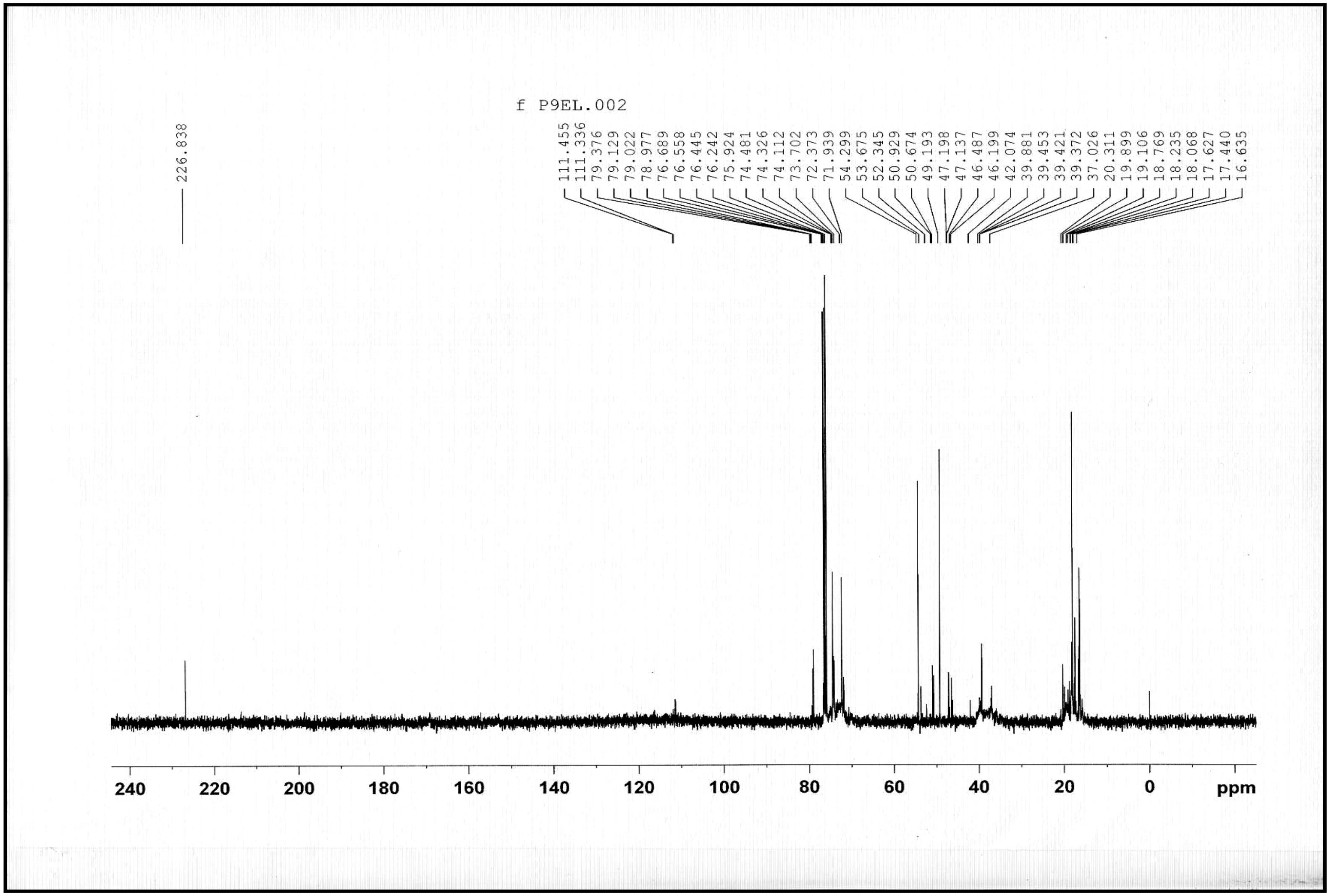


Figure 56: ^{13}C NMR Spectrum of low fraction of experiment 20 (%S=29.6, f_2=0.162)

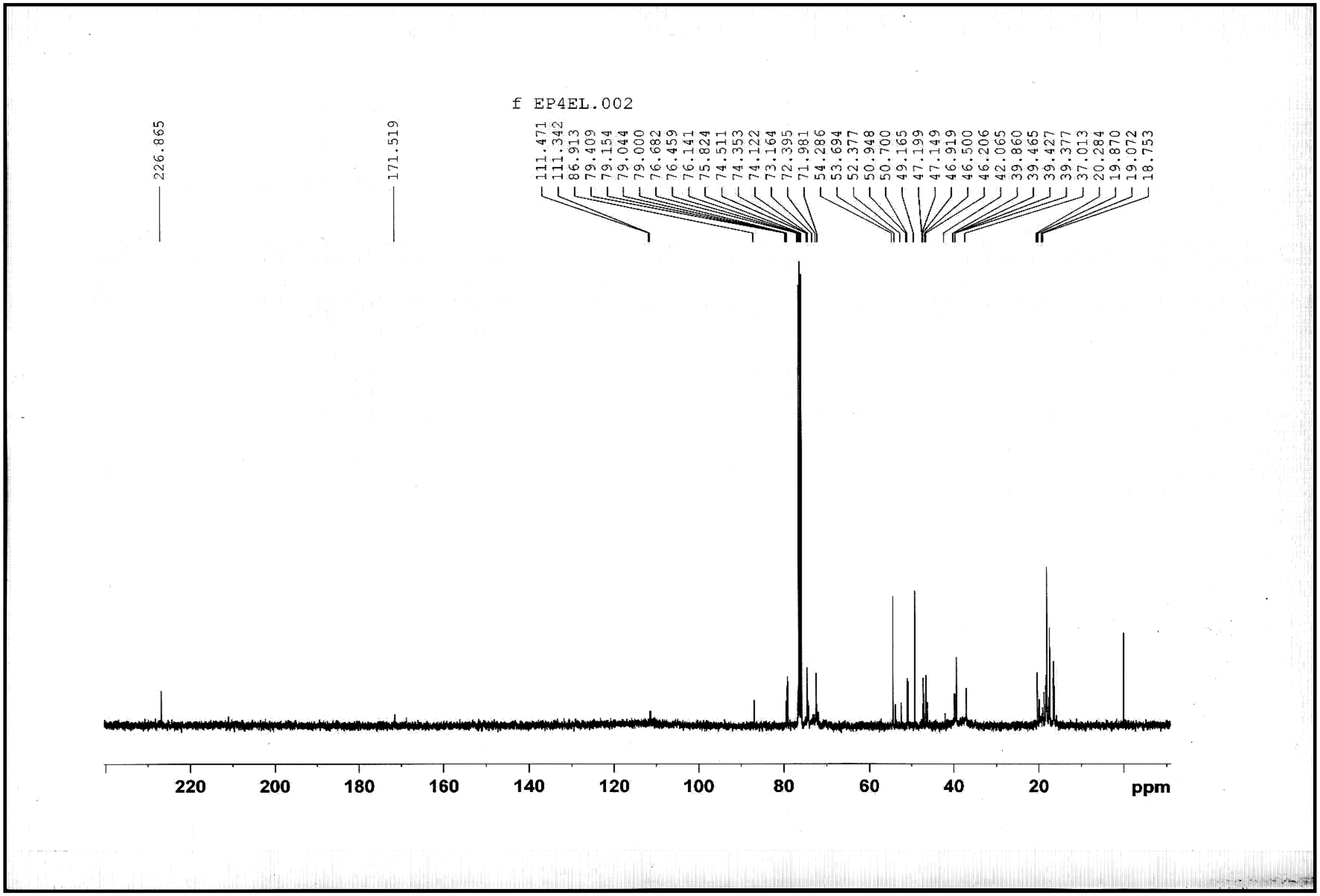


Figure 57: ^{13}C NMR Spectrum of low fraction of experiment 11 (%S=34.5, f_2=0.162)

3. 11 Results of Refractive Index Measurement

High molecular weight fractions of high sulphur content of polymers were taken and refractive indices were compared with high fraction of PPO that was synthesised with our $Zn(Xt)_2$ catalyst in Table 16. It appears that contribution of dithiocarbonate groups increases the refractive index of copolymers above the refractive index of PMMA (1.4893 at 20 ^{o}C (Brandrup, 1975)). Hence it would be interesting to copolymerise a phenyl group containing epoxide (such as styrene oxide) with CS_2.

Table 16: Results of Refractive Indexes

Ex	% S	Refractive Index
14	21.0	1.516
16	18.6	1.508
18	19.7	1.516
PPO*	-	1.457

Literature value of PPO is 1.4495 (Brandrup, 1975)
Note: Other values are in the Appendix A

3.12 An Attempt to Crosslink PO and CS_2 Copolymer

Copolymers with enriched hydroxyl functionality obtained from H_2SO_4 treatment were attempted to crosslink into three-dimensional network structures. For this purpose, gumstocks with a crosslinking ratio of 1.2 was prepared with Desmodur N-100 as cross-linking agent and put into the mould and into the oven. However, no crosslinking was observed due to low OH functionality.

3.13 General Discussion on the Mechanism of PO and CS_2 Copolymerization

In preceding sections some observations on the copolymerization and interpretation about these were given. The purpose of the present section is to combine these observations in order to explain the mechanism of the process.

a) UV spectrum shows that xhanthate groups in the Zn catalysts are not free anions like in potassium xhanthate, but they are ligands on the coordination sphere of Zn atoms. Therefore process is not terminated rapidly as in KXt but on the contrary it produces high copolymers.

b) As it's expected from coordination catalyst, products have some partial stereoregularity.

c) Process is not terminated (living) but suffers from a transfer reaction. Absence of a termination reaction evident from the zeroth order rate law of process. The zeroth order mechanism can be readily explained in following steps:

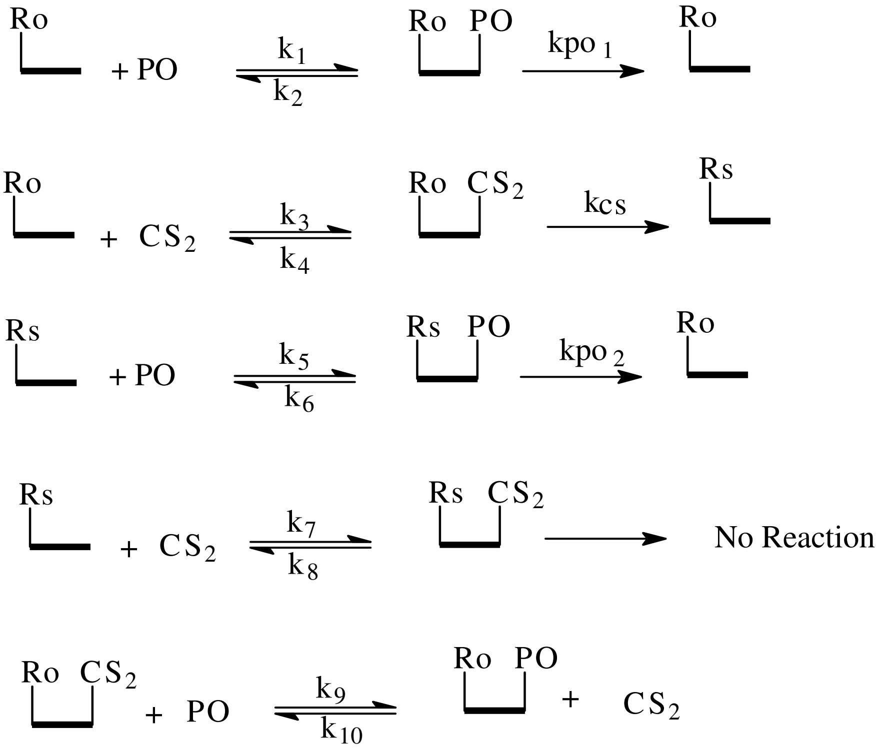
I) Active centers carry the growing polymeric anion as a ligand plus a coordinated monomer nearby. The active centers may exchange monomers reversibly in fast establishing equilibrium.

II) Polymeric (alkoxide) anion adds to both of the monomers those are activated by coordination on Zn. However addition of polymeric xhanthate anion to CS_2 monomer is impossible.

III) The addition of monomers into growing anions creates a vacancy on the coordination sphere and a new monomer is captured with a fast process.

IV) The addition of monomer to growing chain is rate determining, because of higher activation energy (since this step may involve some stereo chemical selections). However, the capture of a new monomer on to vacant coordination site is quite fast. Hence the concentration of active sites (saturated with coordinated monomers) will not change with the feed concentration. There is a competition between PO and CS_2 for empty coordination sites, but it appears that this competition mainly controlled by dielectric constant of medium rather than the feed composition.

The mechanism suggested is summarized in the following scheme (3.23). The active site, which is shown by a bold line, has a growing chain (Ro = polymeric ligand with alkoxide anion or Rs = polymeric ligand with xanthate anion) attached to it. On the active site there is also a vacant coordination site. For this site PO and CS_2 competes. Coordination of monomers on the vacant site is fast (all the rate constant k_1 to k_{10} are large). Hence concentrations of monomer-coordinated active sites are constant throughout reaction. But addition of incoming monomer on the growing chain (Ro and Rs) is slow (that is kpo_1, kpo_2 and kcs are small) due to higher activation of process. Over all mechanism leads to a zeroth order (or near zeroth order process).



(3.23)

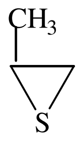
d) The stereo chemical control of process is likely controlled by the symmetry of the coordination sphere (octahedral or tetrahedral). Although zinc complexes are generally square planar, octahedral or tetrahedral geometries may form under the effect of a strong ligand. Another mechanism of stereo-selection might be due to symmetry of the last added PO residue on the terminal of growing chain (chain end control). The last mechanism seems less probable, as it is discussed already in DSC results (Section 3.7).

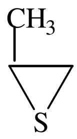
e) Although active sites are not destructed (a non-terminated zeroth order process) some competitive transfer reactions takes place leading to formation of S-(C=S)-S, O-(C=S)-O, O-(C=O)-O groups in the backbone of polymer and SH groups at the chain terminals.

f) Terminal OH groups are formed in reactions given in equations 3.14 and 3.16. On the other hand terminal double bonds are expected because of reaction 3.17 (Steiner et al., 1964). However, in equation 3.17, a double bond terminal is forming together with a potential OH terminal. In other words, the total amount of OH terminals would not decrease due to double bond formation. Therefore, majority of terminals should have OH groups. But end group analysis denies this expectancy (Table XII). Therefore, there must be some other type of end groups. These end groups are likely to be SH groups formed in following reactions:

Zn-S-(C=S)-O-P → Zn-S-P + COS (3.24)

ZnSP formed in Eq. 3.24 would produce SH terminal groups. However, ZnSP bonding may form in a two step reaction as Culvenor et al. (1946) proposed:

Zn-S-(C=S)-O-CH (CH_3)-CH_2-O-P→ Zn-O-P +  + COS (3.25)

Zn-O-P +  → Zn-S-CH (CH_3)-CH_2-O-P (3.26)

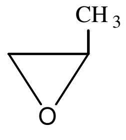
The condensed COS would react with a growing oxyanion to yield O-(C=S)-O groups attached on Zn. These groups may add on PO to yield O-(C=S)-O groups on the backbone of polymer as detected in IR and NMR. Another possibility is with similar reactions to 3.24 and 3.25 condenses to yield CO_2 (Eq. 3.27 and 3.28).

Zn-O-P + COS → Zn-O-(C=O)-S-P (3.27)

Zn-O-(C=O)-S-P → Zn-S-P + CO_2 (3.28)

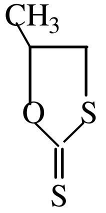
CO_2 in turn may add to a growing oxyanion to form O-(C=O)-O units in the back bone.

Zn-O-P + CO_2 → Zn-O-(C=O)-O-P (3.29)

Zn-O-(C=O)-O-P +  → Zn-O-CH (CH_3)-CH_2-O(C=O)-OP (3.30)

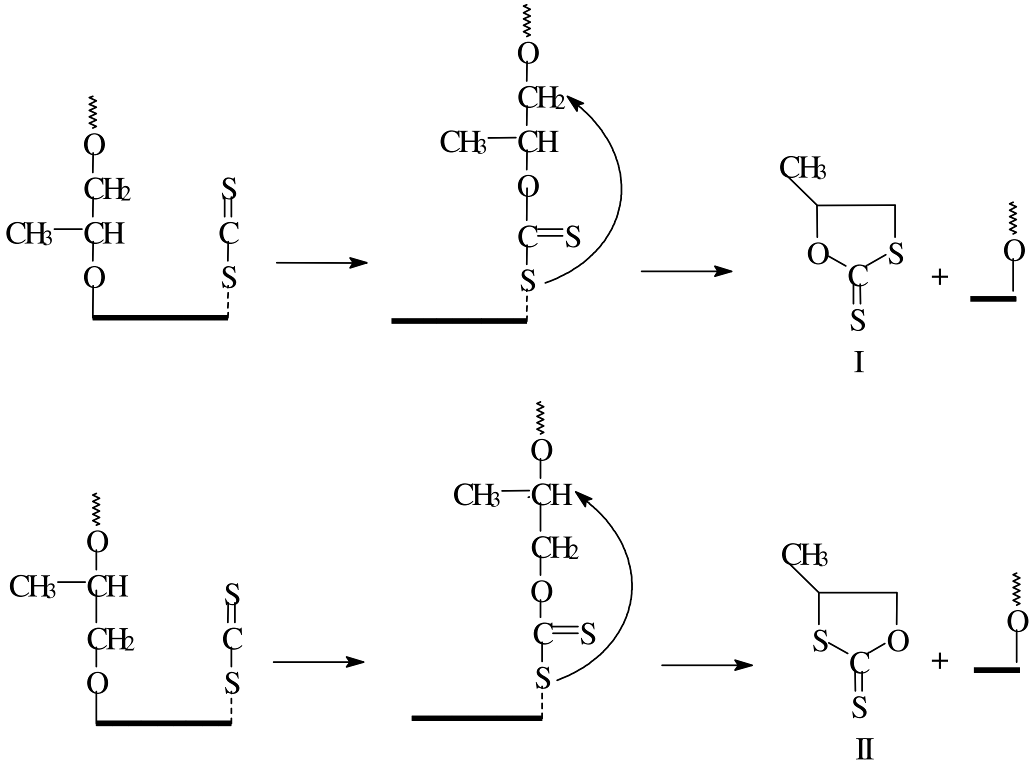
Obviously on hydrolysis Zn O-(C=O)-OP units formed in reaction 3.29 would produce CO_2 (g) and OH terminals.

g) The presence of dithio carbonates, and succeeding transfer reactions can be accounted for with a similar mechanism proposed by Durden et al. (1960) in Eq 3.31.

Zn-S-(C=S)-O-CH (CH_3)-CH_2-O-P → Zn-O-P +  (3.31)

These results imply that even CO_2 is copolymerisable with PO, with $ZnXt_2$ catalyst. This has been also tested in our laboratories in a research project of a fourth year undergraduate (Sezigen, 2005) but no signs of copolymerization could be detected. However the experiment performed almost open conditions. PO and $ZnXt_2$ (in milligram levels) and dry ice (CO_2(s)) are all enclosed in a steel bomb and system kept at 80 ^{o}C for few days. Condensation of atmospheric moisture on the surface of dry ice and air remained in the bomb would decompose $ZnXt_2$, since as stated in introduction chapter metal xhanthates are not stable in moist atmosphere.

h) Direction of attack on the coordinated PO occurs as follows: The growing polymeric chain (anion) on the coordination site may attack on the PO in two different directions: either on the methylene (CH_2) C atom without any inversion or on the methine (CH) C atom by the inversion of configuration. NMR results (Section 3.10-iv) have also shown that attacks on both directions do occur. However, attacks on CH_2 occur with much higher frequency. The presence of S-CH_2, -CH(CH_3)-O units in cyclic dithiocarbonate (Structure I) (or on the backbone) shows the attack on the CH_2 atom. Reaction 3.32 shows that the growing polymer with an oxyanion terminal formed by opening CH_2-O bond of PO. Coordinated CS_2 may add to this anion by copolymerizing or form a cyclic structure following the formation of five membered transition state (Structure I). But presence of cyclic dithiocarbonate (Structure II) can be only explained by ring opening of PO from CH-O bond (reaction 3.32)



(3.32)

In coordination polymerization of PO, the regular addition was found to be as ring opening at CH_2-O bond (Price et al., 1967 and 1972) but also ring opening at CH-O is also possible with lower probability. Since after a wrong addition (on secondary C) (Vandenberg, 1960), the more probable CH_2-O addition would succeed resulting in a head-head (or tail to tail) units. Therefore, presence of Structure I and S-CH_2, -CH (CH_3)-O units on the backbone is the result of attack on the primary C atom. Takrouri, Alyürük (1994) and also Öktem, Alyürük (1998) showed that as molecular weight increases the irregular additions occur at lesser extend. The same was observed in the present work: Structure II was much richer in low fractions. This structure become even richer as the S content of copolymer increased (Figure 43, 55, 56 and 57). In high fractions these structures were in trace amounts (Figure 46, and 53).

CHAPTER 4

CONCLUSIONS

1. $Zn(Xt)_2$ copolymerizes PO and CS_2 into high polymer. However the product can be fractionated into high and low molecular weight components. Difference in these fractions is not solely of molecular weight but they are also structurally different.

2. High copolymers are rubbery products, but low copolymers are oily products containing cyclic dithiocarbonates.

3. Spectral evidences and observed partial stereoregularity of products show that $Zn(Xt)_2$ is a coordination catalyst.

4. Apparent catalytic efficiency of $Zn(Xt)_2$ increases with aging or heating under vacuum at 80 ^oC for 24 h.

5. The mole fraction of PO residues in the copolymer is about 9 to 6 times greater than that of the CS_2 residues. This ratio decreases with increasing polymerization time.

6. Copolymerization is a non-terminated, zeroth order process with respect to both of the monomers.

7. Zeroth order process shows that the concentration of active species, formed from growing chain as a ligand on the coordination sphere and coordinated

monomer(s) are constant since after addition of monomer the resulting vacant coordination site quickly filled by a new incoming monomer.

8. Process, hence the composition of product controlled by the dielectric constant of reaction medium.

9. Although active sites are not destructed, some competitive transfer reactions takes place leading to formation of S-(C=S)-S, O-(C=S)-O, O-(C=O)-O groups in the backbone of polymer and SH groups at the chain terminals.

10. GPC result shows that copolymers show very broad distributions and high polymers have very high Mw components.

11. Contribution of dithiocarbonate groups increases the refractive index value of copolymers above the refractive index value of PMMA.

12. Tg values of copolymers increase as sulphur content of copolymer increases (From $-74^{o}C$ up to $-38\,^{o}C$).

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APPENDIX A

Table A.1: Copolymerisation conditions

Ex	**f_2**	**[Zn]×10^3 (M)**	**m_0 (g)**	**V_0 (ml)**	**$[PO]_0$ (M)**	**$[CS_2]_0$ (M)**	**T (^{0}C)**	**Time (h)**	**Py (g)**	**% Conversion**
1	0.113	6.03	8.73	10	12.86	1.655	80	20	1.190	13.6
2	0.162	5.73	9.36	10.5	12.25	2.362	80	20	0.566	6.05
3	0.225	6.01	9.16	10	11.43	3.310	80	20	0.519	5.66
4	0.266	5.73	9.79	10.5	10.89	3.940	80	20	0.554	5.66
5	0.332	6.01	9.59	10	10.0	4.964	80	20	0.563	5.87
6	0.403	6.44	9.39	9.5	9.026	6.097	80	20	1.037	11.0
7	0.487	6.12	10.2	10	7.860	7.447	80	20	1.051	10.3
8	0.730	6.12	11.3	10	4.287	11.58	80	20	0.542	4.80
9	0.162	5.73	9.36	10.5	12.25	2.362	80	48	1.176	12.6
10	0.162	5.67	9.36	10.5	12.25	2.362	80	120	2.941	31.4
11	0.162	5.67	9.36	10.5	12.25	2.362	80	240	7.518	80.3
12	0.266	5.73	9.79	10.5	10.89	3.940	80	48	1.038	10.6
13	0.266	5.67	9.79	10.5	10.89	3.940	80	120	2.475	25.3
14	0.266	5.67	9.79	10.5	10.89	3.940	80	240	7.124	72.8
15	0.162	11.3	9.36	10.5	12.25	2.362	80	48	3.755	40.1
16	0.162	20.0	9.36	10.5	12.25	2.362	80	48	7.430	79.4
17	0.266	11.3	9.79	10.5	10.89	3.940	80	48	3.113	31.8

Ex	**f_2**	**[Zn]×10^3 (M)**	**m_0 (g)**	**V_0 (ml)**	**$[PO]_0$ (M)**	**$[CS_2]_0$ (M)**	**T (^{0}C)**	**Time (h)**	**Py (g)**	**% Conversion**
18	0.266	20.0	9.79	10.5	10.89	3.940	80	48	7.081	72.3
19	0.162	11.0	9.36	10.5	12.25	2.362	60	48	1.998	21.3
20	0.162	11.0	9.36	10.5	12.25	2.362	100	48	7.713	82.4
21	0.266	11.0	9.79	10.5	10.89	3.940	60	48	1.172	12.0
22	0.266	11.0	9.79	10.5	10.89	3.940	100	48	7.261	74.2
23	0.266	16.9	19.6	21	10.89	3.940	80	240	16.67	85.0
24	0.266	16.9	19.6	21	10.89	3.940	80	240	17.1	87.2
25	0.487	17.8	20.5	20	7.860	7.447	80	240	12.63	61.6
26	0.487	17.8	20.5	20	7.860	7.447	80	240	12.02	58.6
27	0.162	5.83	9.36	10.5	12.25	2.362	80	48	2.061	22.0
28	0.162	5.83	9.36	10.5	12.25	2.362	80	48	2.288	24.4
29	0.332	6.03	9.59	10	10.0	4.964	80	20	1.198	12.5
30	0.730	6.03	11.3	10	4.287	11.58	80	20	0.662	5.86
31	0.730	3.02	19.2	20	2.144	5.792	80	20	0.078	0.41

Ex: Experiment number
f_2: Mole fraction of CS_2 in the feed
[Zn]×10^3 (M): Initial concentration of catalyst in molarity
m_0 (g): Initial mass of copolymerisation mixture in gram
V_0 (ml): Initial volume of copolymerisation mixture in milliliter
$[PO]_0$ (M): Initial concentration of propylene oxide in molarity
$[CS_2]_0$ (M): Initial concentration of CS_2 in molarity
T (^{0}C): Temperature of copolymerisation in centigrade degree
Time (h): Time of copolymerisation in hour
Py (g): Polymer yield in gram
% Conversion: Per cent conversion of copolymerisation

VITA

Elif Öztürk was born on 16th of December 1973 in Sakarya. She graduated from Middle East Technical University (METU), Faculty of Education in 1997. She began her MS studies at Faculty of Arts and Science in chemistry department of METU where she became a research assistant. During this time, she worked on energetic polymers which are used as rocket fuels under the supervision of Prof. Dr. Kemal Alyürük. She finished her MS studies on June 2000. She continued her doctorial studies with Prof. Dr. Kemal Alyürük in the field of synthesizing copolymers whose monomers were carbon disulfide and propylene oxide by using metal xanthate catalysts.

Within this time she has published one paper related her MS thesis.

- Synthesis, Crosslinking and Characterization of Energetic Polymers by Azidification of Glycidyl Ether Pre-Polymers (Journal of Applied Polymer Science, Vol: 91, Iss. 6, March 2004, p: 3785-3790)