SOLID STATE POLYMERIZATION OF ACETYLENEDICARBOXYLIC ACID INDUCED BY IRRADIATION

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ABSTRACT

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Radiation induced solid-state polymerization was carried out at room temperature, in open atmosphere and under vacuum condition. The gray color powder polymer obtained, was soluble in dimethylsulfoxide, but insoluble in most common solvents, such as water, methanol, acetone. The polymers were investigated by UV, IR, DP-MS and XRD, TGA and DSC to elucidate the mechanism of the polymerization and charecterization.

The radiation induced solid state polymerization of acetylenedicarboxylic acid is most probably a free radicalic polymerization.

The polymer was partially crystalline, and showed no melting up to 1200°C. The mechanism and assigned formulas of polymer was studied by direct pyrolysis mass spectrometry method.

The space group of the monomer and polymer was identified as P2, $P2_1$ respectively. The unit cell parameters for monomer and polymer formed were almost identical. It indicates that polymerization is topotactic type.

Key words: Solid state polymerization, acetylenes, disubstituted acetylenes, direct pyrolysis, space group, radiation polymerization.

ÖZ

ASETİLENDİKARBOKSİLİK ASİTİN RADYASYONLA BAŞLATILAN POLİMERLEŞMESİ

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Radyasyonla başlatılan katı haldeki asetilendikarboksilik asit'in polimerleşmesi oda sıcaklığında, açık havada ve vakum altında ışınlamayla yapıldı. Elde edilen gri toz halindeki polimerler dimetilsülfoksit'te çözündü. Fakat aseton, methanol ve su gibi genel çözücüler içinde çözünmediler. Polimer örnekleri; IR, UV, DP-MS, XRD, TGA ve DSC yöntemleriyle incelenerek polimerleşme mekanizması irdelendi ve polimer karekterizasyonu yapıldı.

Radyasyonla başlatılan katı haldeki asetilendikarboksilik asitin polimerleşmesinin büyük bir olasılıkla radikalik bir mekanizmayla oluştuğu gösterildi.

Elde edilen polimerlerin yarıkristal yapıda olduğu görüldü ve 1200°C'ye kadar ısıtıldığı halde erime görülmedi. Polimer mekanizması ve zincir yapısı, doğrudan kütle spektoskopi yöntemi ile çalışıldı.

Elde edilen kristal polimerin ve monomerin uzay grubu sırasıyla $P2_1$, P2 ve birim hücre boyutları yaklaşık olarak aynıdır. Bu polimerleşmenin topotaktik olduğunu gösterir.

Anahtar kelimeler: Katı hal polimerleşmesi, asetilendikarboksilik asit, radyasyonla polimerleşme, uzay grubu, doğrudan piroliz.

To my beloved parents

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[illegible] to [illegible] invention of Ziegler Natta catalyst. In solid state polymerization, polymer obtained was expected to be crystalline and well oriented, due to small molecular movements in the crystal lattice[1]. It was assumed that, in this case the, polymerization propagates along the crystallographic axis of that monomer. However, it was reported that only a few kinds of monomers could yield crystalline polymer by solid state polymerization.

The polymerization of solid monomers presents unique problems when compared with polymerizations in liquid states. Since mobility of molecules in solid state is severely restricted, the rate of reaction will be determined by local concentrations of reactants. Moreover, changes in the crystal lattice during course of reaction may influence the rate of polymerization.

The first study about solid state polymerization was done by Schmitz and Lawton[2] in 1951. They polymerized glycoldimethlacrylate explosively by ionization radiation.

Adler et al[3] found that acrylamide could be polymerized in solid state by high energy radiation. It was expected that a well-oriented crystalline polymer would be obtained after polymerization due to limited mobility of molecules in solid matrix. However, resulting polymer was amorphous. This drew attention of scientists to study the effect of crystal structure on solid state polymerization. Besides, polymerization continued after removing sample from irradiation source which is called post polymerization. ESR[3] studies showed that in the irradiated mixture of polymer and monomer trapped free radicals were present. When the residual monomer was not seperated precisely from polymer, these radicals lead to postpolymerization.

Many efforts have been made to clarify the characteristics of solid state polymerization of acrylamide after Mesrobian et al[4] succeeded, in 1954, producing in source and post polymerization by γ ray irradiation in crystalline state. These studies involved kinetics, ESR, broad line NMR, X-ray diffraction, optical and electron microscopic studies, pressure effects etc. Briefly, these results suggested: (1) the mechanism of polymerization was of a radical type (2) chain propagation started with the combination of a monomer molecule and initial radical in location e.g, a dislocation, which was still under the influence of lattice control (3) chain propagation proceeded at the interphases, where the monomer molecule, were released from strict lattice control; and (4) the resulting polymer was atactic and amorphous.

Restaiona et al[5] studied the polymerization of acrylamide and related monomers in 1956. The molecules of acrylamide in crystal lattice were in suitable location to form dimer. However, the addition of a third monomer to dimer molecule required an appreciable rearrangement. So crystal structure of monomer distrupted or polymerization enchainment did not proceed in crystallographic direction. Therefore, polymer obtained was amorphous. Some monomers have been found to polymerize faster in solid state than that in liquid state. For example, Chapiro[6] showed that 3,3 bis (chlorometyl)cycloxobutane was polymerized in solid but not in liquid state. This is probably associated with a favorable steric configuration in solid phase.

Kondo[7] have prepared the chloro, bromo, iodo derivatives of 3,3-bis(halogenometyl)cyclooxo butane and compared their rates of polymerization using ionizing radiation. All are polymerized faster in solid state than in liquid state, the rates being dependent on the orientation and size of crystals in the order of Cl>Br>I. Radiation induced polymerization of acrylonitrile[8] in solid state has been carried out around melting point of the monomer. The rate of polymerization of solid acrylonitrile was 30 to 40 times faster than that of liquid state. Acrylonitrile polymerizes between –83°C and –196°C. Polymer yield is higher for monomers recrystallized by slow cooling. Because, slow cooling leads to formation of large and well oriented monomer crystallites.

Morawetz and Rubin[8] observed polymerizatıon of alkali metals of acrylic acid and methacrylic acid. They showed that polymer conversion and polymer molecular weigths are dependent on the kinds of alkali metals. Therefore, different kinds of alkali metals salts of acrylic acid and metacrylic acid polymerized in different mechanism since they have different crystal structure.

1.2. Radiation Induced Solid State Polymerization

Polymerization is generally catalyzed with chemicals. However, radiation is used for some polymerizations. The reasons of radiation induced solid state polymerization studies concerning the researchers are as follows:

i) It was assumed that monomer crystal lattice is not distorted, and polymers of same crystal lattice will be obtained in the solid state polymerization.

ii) When monomers in the crystal lattice are oriented such as to make easy addition, the rate of polymerization is greater in solid state than that in liquid phase.

iii) Most of radioactive elements always irradiate by themselves, so getting irradiation is cheaper.

iv) In radiation induced polymerization, there is no need of chemicals to initiate or propogate the reaction. Therefore, there won't be any such impurities in the polymer.

v) The probability of polymerization termination by radical combination in solid state is low. Thus, in this case, high molecular weigth of polymers may be obtained.

vi) The probability of oxygen diffusion into crystal lattice is low, then the side effects resulted from oxygen are not common.

vii) When polymerization is induced by radiation, the reaction mechanism may be ionic or radicalic. So monomers having different properties may be polymerized.

viii) Monomers not copolymerized in liquid phase may be so polymerized in the crystal lattice, due to regular arrangements and orientation of both monomers together(forming solid solution).

Most of above assumptions were shown to be unvalid for many monomers. On the other hand, it was proved that these assumptions were correct for some monomers.

Solid state polymerization developed with the usage of high energy radiation, e.g γ rays, X-rays, UV radiation, electron beam etc. Since high energy radiation penetrates solids much better, the polymerization should take place easily. Solid state polymerization term is used in widest sense. In this polymerization, monomer used can be crystalline, liquid crystalline, that of glassy states. In addition to this, mixtures or complexes of monomers can be used to obtain polymer. In solid state polymerization , not only radiation is used as a source, but also thermal and chemical activators are also used.

Chemical reactions in solid state polymerization are accelareted at vacancies and imperfection sites. The crystal imperfections are commonly edge dislocations, screw dislocations, some kinds of point defects, etc. In addition to inherent imperfections in nonirradiated monomer crystal, imperfections may be produced by high energy radiation. Therefore, effects of impurities, crystallite size and perfectness of crystallites in solid state polymerization are important. These factors depend upon the crystal structure of monomer and the nature of crystallization .

Lando and Morawetz[9] showed that salts of calcium acrylate and dihydrate polymerized by irradiation, but salts of monohydrated monomers did not polymerize under similar conditions. This is also an indication for the crystal structure influence on polymerization.

Adler and Reams[10] indicated that polymerization would proceed at the interphase between monomer and polymer of acrylamide after some polymer formed. It was supported by an experiment in which acrylamide single crystal was divided into two parts, one part was wrapped with aluminum foil, other part was exposed to gamma radiation. After some time, the sample photographed under polarized microscope. In the photograph, the side polymerized was black, while other part was bright. Two sides were clearly different from each other. So, Adler believed that the crystal structure of acrylamide molecules exerted no influence on the polymerization because polymerization proceeded at the interphase between monomer and polymer. Adler et al[11] explained that the reason for the formation of amorphous acrylamide polymer, was due to the structure of monomer; the -C=C double bond (1.34 A) opened and transformed to –C-C- single bonds (1.54 A) during polymerization. However, intermolecular distance between molecules decreased from Van der Walls distance of about 3.75 A to 1.54 A, C-C single bond length. When both changes combined, overall volume of the system was decreased about 12%. That volume reduction created a strain in the crystal lattice. Therefore, the crystal structure broke down and caused the polymer to be amorphous.

Acrylic acid is also well known subject of solid state polymerization using γ rays[12] and UV[13] ligth. Eastmond et al[13] found that when polymerization was initiated with polarized UV radiation, the rate of polymerization in the initial stage showed strong dependence on the angle between the plane of electric vector of radiation and crystallographic axes, i.e the rate of polymerization is maximum when electric vector of radiation is parallel to a crystallographic axis. They suggested that this feature was in accordance with other data showing that absorbtion of radiation by vinyl groups was ultimately responsible for radical formation. These facts indicate that the molecular disposition has an important influence on the initial stage of polymerization. However, in the crystal lattice, dimers of acrylic acid are further from each other than the possible interaction which has intermolecular vinyl C.....C distance of 3.52 A. Therefore, all molecules have to be rearranged to be able for combination. The chain propagation are isotropic due to large movements. The resulting polymer is atactic and amorphous.

In general, vinyl monomers can not be crystallized except a few cases, such as poly(vinylalcohol)[14], poly(vinylchloride)[15], poly(vinylflouride)[16]. Atactic poly(vinylalcohol) is highly crystalline, because hydrogen bonds are formed and stabilize the crystal lattice even if the polymer chain is atactic. Poly(vinylflouride) in which the flourine atoms replaces hydrogen atoms randomly. Flourine atoms are small enough to permit polymer crystallization. In poly(vinylchloride), it seems likely that short syndiotactic-predominant sequences of far less than 50 A in length can be crystallized. Vinyl stearate[21] monomer permits to form crystalline polymer. Crystal structure is formed from side chains in the form of layers. The distance between layers are 25.4 A. So, polymer enchainment occurred along these layers and crystal structure of polymer didn't distrupt. This serves to yield crystalline polymer.

Okamura and his associates demonstrated that the structure of monomer lattice imposes an orientation on polymers obtained by γ irradiation of trioxane[17], β-propiolactone[18], diketene[19]. In the case of polyoxymetylene obtained by post polymerization irradiated large crystals of trioxane, the polymer was found to be highly ordered not only with respect to the orientation of the fiber axis, but also in the manner in which the polymer chains packed, so that the material resembled in a large single polymer crystal.

Cyclic monomers such as trioxane[17], diketene[19], β-propiolactone[18], 3,3bis(halogenometyl)cyclo oxobutane[20] and cyanuric chloride[21] polymerize easily by irradiation only in solid phase. The polymers formed by irradiation of single crystals of monomers have higher melting points and are better oriented than the polymers produced from aggregates of smaller crystals, indicating that monomer lattice affects the polymer structure.

In an attempt to clarify the polymerization kinetics and to investigate the role played by crystal structure, the solid monomer has been diluted with propionamide which was believed to be isomorphous. Solid solutions of propionamide and acrylamide[22] can be prepared over entire concentration range, giving a single phase mixture. If the polymerization are controlled by crystal lattice, then a change would be expected in the rate and degree of polymerization. Up to 10% mole ratio, propionamide produces no change in the rate of polymerization, but above this concentration a small decrease in the rate were observed. A drastic reduction in the molecular weigth is, however, obtained with small concentrations of propionamide, indicating that it acts as a surprisingly efficient chain transfer agent. With increasing of temperature the efficiency of propionamide decreases. According to this study[22], propionamide and acrylamide has similar molecular structure, which makes the propionamide molecules terminate the polymer chain. Therefore, the polymers moleculer weigths were low.

A typical example of lattice control polymerization can be seen in four center type of photopolymerization of 2,5-distyrlpyrazine studied by Hasegawa and Suzuki[23]. Distyrlpyrazine has two crystalline modifications; plate like crystals which are orthorhombic and needle like crystals which are monoclinic. Plate-like crystals undergo prompt photopolymerization in the crystalline state under influence of UV ligth or sunligth into high molecular weigth crystalline polymer. However, needle like crystals do not undergo any change with irradiation. Van der Walls distance of plate like crystals is lower than 4 A. So polymerization takes place with sligth rotations and translations. Therefore crystal structure of monomer is protected. This type of polymerization is topotactic.

Usanmaz and Melad[24] polymerized 3-Aminocrotonamide by radiation in solid state. Polymerization occurred by a condensation process with evalution of (2n-1)NH_3 molecules for each 2n monomer molecules. The polymer formed was similar in crystal structure to that of monomer. Thus, it gives a topotactic polymerization by condensation.

Structure and properties of polyurathane and acrylate prepolymer films, obtained by electron beam (EB) and UV, in solid state polymerization examined[25] to reveal the charecteristic of these radiation polymerizations. Although polyurathane and acrylate films from EB and UV solid state polymerizations mainly consisted of amorphous and crystalline phases, it was proved that the film obtained by 10 Mrad of EB radiation at 25°C had higher crystallinity and larger crystallite size than film from UV irradiation. This is assumed to be due to the reason that EB irradiation below melting point of polyurathane-acrylate can lead to crosslinking without the destruction of original crystal structure. On the other hand, the UV polymerization procedeed around melting point of crystalline structure by absorbing electromagnetic radiation other than the UV absorber by a photoinitiator.

The mechanism of polymerization is greatly influenced by monomer crystal geometry in the solid state. The change in the crystal structure most probably orients the molecules in a more favorable arrangements for polymerization of allylthiourea[26] leading to a higher maximum conversion. When IR spectrum of partially polymerized monomer was investigated, it was seen that, although monomer peaks were partially covered by broad amorphous polymer peak, the monomer molecules still retained their crystalline structure at 46% conversion. The changes in relative intensities of monomer peaks during polymerization were most probably due to distortion of crystal morphology. The polymer was amorphous and isotropic; it always looked dark between crossed polarizers, where the monomer was anisotropic and looked brigth except at extinction positions in polarizing microscope. The results proved that polymerization did not proceed by a two phase mechanism like the monomer-polymer interphase polymerization.

The effect of oxygen on the polymerization of allylthiourea was investigated by Usanmaz and Yılmaz[26]. The accelarating effect of oxygen was clear at conversions above 40%. This suggests that the crystal structure becomes distorted with the formation of polymer to allow easier diffusion of oxygen.

The solid state polymerization of acrylamide[27] showed that an inhibiting effect of oxygen on the polymerization process were observed. The strongly inhibiting effect of oxygen proves that the reaction has free radicalic mechanism.

Radical polymerization of dialkyl muconates was investigated in crystalline state by Matsumoto et al.[28]. They discovered that diethylcis muconate underwent highly stereospecific polymerization in crystalline state by UV radiation via a topochemical mechanism. The resulting polymer was ultrahigh molecular weigth with high stereoregularity and crystallinity. This polymer has been clarified to be tritactic polymer. Usanmaz and Baytar[29] made solid state polymerization of acenapthylene by radiation. The induction period shows that, the monomer molecules are not initially in favorable orientation for an addition reaction. After receiving a certain amount of energy the molecular orientation by rotation in their plane rearrange them to take position for a possible addition reaction. There is a correlation between crystal structure of monomer and polymer that is an indication of topotactic polymerization mechanism under given conditions.

1.2.1 Proposed Mechanism for Solid State Polymerization

The proposed mechanism for solid state polymerization is an addition polymerization. It is usually produced by a chain mechanism involving active centers of one short or another. Addition polymerization reaction involves essentially three steps;

i) Initiation
ii) Propagation
iii) Termination

Initiation: The first step is the activation of a monomer molecule to form a free radical.

$$M \xrightarrow{k_i} R^{\bullet}$$

Also if a catalyst ,such as peroxides,is present it'll be activated to give radicals.

$$Cat \xrightarrow{k_d} 2R^{\bullet}$$

$$R_i = fk_i[Cat] \qquad (1)$$

Where f is the efficiency factor and k_i is the initiation rate constant.

Propagation: A free radical add on to a double bond of a monomer molecule, thereby regenerating another free radical etc.

$$R + M \xrightarrow{k_p} RM^{\bullet}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$RM_n^{\bullet} + M \xrightarrow{k_p} RM_{n+1}^{\bullet}$$

Where R is a primary radical, M is the monomer and RM_n is a growing polymer chain. The propagation rate equation used in conventional homogenous polymer kinetics.

$$-d[M]/dt = k_p[M][R] \qquad (2)$$

where k_p is the propagation rate constant, [M] is the monomer concentration and [R] is the total concentration of radical. Usually a steady state concentration of [R] is assumed at low conversions where [M] is high, that can be considered to be constant and decreases at higher conversion as [M] decreases. The following reaction scheme was proposed by Baysal[30] for the in the source polymerization of acrylamide initiated by Gamma radiation. If one considers the S shaped kinetics curves of percent conversion vs time for solid state polymerizations, it can be seen that the rate is not constant even at low conversions. The rate actually increases linearly with time up to about 20% conversion at which point accelaration occurs, it was assumed that k_p is a constant, at least at low conversions, the increasing rate can only be explained by increase in [R], thus eliminating steady state kinetics. Here, [R] may be related to the radiation intensity I by expression.

$$[R] = fk_i = fk_i\, I = K.I$$

where K is a constant composed of an initiation rate constant k_i ,and also efficiency factor f. Instead of equation(1) we can write;

$$-d[M]/dt = k_p.k_i.f.I_t.[M] \qquad (3)$$

which in integrated form is

$$\log([M_0]/[M]) = k_p.k_i.f.I_t^2/4.606$$

where I is a constant for any one series of experiments. Then a plot of $\log[M_0/M]$ versus t should give a straigth line with the slope of k_p . k_i . f.I/4.606. (M_0 is initial concentration of monomer)

Termination: The termination step involves the mutual annilation of activity of two radicals. This can take place in two ways. The two chains may terminate by combination.

$$RM_n^\bullet + RM_m^\bullet \rightarrow P_{n+m}$$

or they may undergo disproportionation with the transfer of a hydrogen atom and the formation of an unsaturated end group.

arrangement of the monomer molecules in the crystal matrix. This arrangement is determined by the rest group R of the monomer molecules R-C≡C-C≡C-R. The reaction can be induced by radiation (γ orUV) or thermally.

Many workers[32, 33, 34, 35] studied solid state polymerization of acetylene monomer (-C≡C-C≡C-) in 1970. The experiments e.g; X-ray, electron reflection, optical and mechanical properties showed that polymer formed had the same structure with that of monomer. These types of rections are called topotactic solid state polymerization.

Hirschfeld and Schmidt[36] polymerized disubstituted diacetylenes and the resulting polymer chain was conjugated. The product crystals have been continued to attrack interests as model materials. The relatively perfect crystal structure contrasts sharply with the amorphous and microcrystalline morphologies of other conjugated polymers. Polymerization of diacetylenes attracts the attention of scientists because of expected high electrical conductivity.

They observed from these topographic studies[36] that defect free regions of the crystal were uniformly polymerized and was supported by no change in defect density during polymerization. It indicated that dislocations were not the only dominant reaction site in diacetylene crystals. Thus, solid state polymerization in diacetylene must be topochemical reaction. This distinguishes it from many other topochemical reactions which can occur only in the vicinity of lattice defects. They considered a model of solid state polymerization of diacetylenes. That is a reaction in which diacetylene units are able to undergo 1,4 addition polymerization simply by rotation with centers of gravity on fixed lattice sites. Under such conditions emprical criterion was suggested that reacting carbons must have a seperation of less than 0.4 nm in the monomer lattice.

Baughman[37] suggested a second model that allows both rotation and translation of diacetylene units which were assumed to behave as rigid rods. It is assumed that a simultaneous translation, rotation and a pure translation (a shearing motion of reacting units) are present to calculate root mean square distance. In both cases, the motion was constrained to the plane containing the diacetylene units. Experimantally, polymer chains are observed to coincide with the axis of the monomer stack in accord with this result. A reaction path involving out of plane motion is suggested by calculation of least energy paths for methylene radicals[38]. A low lying phone mode has been also shown to be important in the polymerization of one diacetylene though its exact nature has not been idendified[39]. Both these facts indicate that molecular deformation occurs during reaction so that a model involving planar motion of rigid rod is not realistic.

Roxy et al.[40] polymerized diacetylene monomers having the bulky substituent. The diacetylene has two phases having the chiral substituent group as ($-CH_2HC^*(CH_2CH_3)OCNHC_6H_5$). The bis(phenylurathane) of 5,7-dodecadiyne-3,10diol (UDD) is an unresolved mixture of R-C≡C-C≡C-R, S-C≡C-C≡C-S and R-C≡C-C≡C-S molecules. This mixtures of isomers was seperated into two crystalline phases via selective crystallization. Phase which crystallizes first from methanol is phase I (m.p136.0-138.2°C). Precipitation of uncrystallized material via water addition followed by recrstallization from a methanol/water mixture from that obtained phase II. Packing of monomers phase I, the molecules form chains along the c-direction and the chains are stabilized by NH...O=C hydrogen bonding. In phase II, monomer molecules pack such that the a-axis is the direction of polymerization. It is also stabilized by hydrogen bonding. The X-ray study on phase I crystals of the UDD indicates that polymerization occurs by reaction of R-C≡C-C≡C-R and S-C≡C-C≡C-S molecules related by c-glide plane. Consequently, the polymer structure is [=(R)C-C≡C-C-(R)=(S)C-C≡C-C(S)=]$_n$ rather than the alternative halved or doubled repeat structures. This unusual synthesis of a polymer with regularly alternating substituents of different chirality evidences the power of solid state reactions as a synthetic method. The structure of UDD phase II reveals that the polymerization reaction take place between translationally related (along a-axis) R-C≡C-C≡C-S molecules. Thus, the polymer formed is [=(R)C-C≡C-C(S)=]$_n$. The phase I polymer appears to be isomorphous with the starting monomer phase, while the phase II polymer has only a liquid crystal-degree of order. It may be resulted from larger molecular movements of monomer molecules.

The reactivity of diacetylene can be related to the their crystal structure. In the case of UDD, neither phase is extremely reactive, but phaseI is significantly more reactive than phase II. It forms a much more ordered crystalline product. Another possible explanation for the difference in reactivity considers, the arrangements of the side chains.When polymerization occurs there must be movement of the side chains toward the center of the molecule along the main axis of the side chains. In phase I, the side chain is virtually extended. There would appear to be little hinderence for cooparative movement of the side chains toward the center with the preservation of the hydrogen bonding. In phase II, the molecule adopts a much more zig-zag shape with the substituent ethyl groups protruding into a crevice in the adjacent molecules. Thus, there could be more resistance to a cooparative contraction in the direction normal to polymer direction.

Prock et al.[41] carried out a detailed study of the solid state UV polymerization of highly radiation sensitive diacetylene. The diacetylene chosen for this study is 4BCMU, RC≡C-C≡CR, where R is $((CH_2)_4\ OCNHCH_2COO(n\text{-}C_4H_9))$ for solid state polymerization . BCMU stands for [(butoxycarbonylmethyl)urethane]. The polymerization rate for irradiation of thin diacetylene films is found to decrease markedly as film thickness increases. While polymerization proceeds, quenching may be occured by irradiation. Quenching of the monomer excited state by polymer chains presents in the partially polymerized samples is shown to provide a resonable explanation for this behavior. Quenching is probably an important limiting factor in determining overall polymer conversion in the photopolymerization of diacetylene. UV spectra of partially polymerized samples showed that there was some broadening of the monomer absorbtion peaks. An intrinsic source of this broadening could be life time reduction of radicals due to nonradiative quenching

The dimer of 1,11 dodecadiyne, $HC\equiv C\text{-}(CH_2)_8\text{-}C\equiv C\text{-}C\equiv C\text{-}(CH_2)_8\text{-}C\equiv CH$, (1,11,13,23-tetracosatetrarayne) was first reported by Thakura and Lando[42-44] claimed that this dimer polymerized upon irradiation by γ-rays to form an inherently electrical conducting polymer resulting from the polymerization of both diacetylene and terminal diacetylene groups to form the structure composed of sheets of alternating polydiacetylene and polyacetylene chains.

Nezu and Lando[45] found that 1,11,13,23-tetracosarayne(dimer of 1,11 dodecadiyne, hereafter referred to as monomer) showed polymorphism. The X-ray powder diffractograms for the melt crystallized monomer and its polymer formed by exposure to 20 Mrad of γ-irradiation, also a partially polymerized sample by UV were investigated. The UV polymerized sample underwent polymerization only at the surface. Thus, the diffractograms of UV polymerized sample shows peaks due to remaining monomer and new peaks due to the polymer. It was shown in these diffractograms that unit cell dimensions sligthly changed upon polymerization. The X-ray diffractograms of polymer treated at several temperatures showed that upon annealing at 70°C, new peaks at $2\theta=3.35°$ and $2\theta=21.7°$ appeared on the diffractogram. The color of the sample changed to sligthly reddish green. Upon treatment at 90°C, the monomer peaks at $2\theta=8.5°$ and at $2\theta=9.48°$ seen in unannealed sample disappeared and the intensity of peak at $2\theta=23.55°$ markedly decreased. A new peak appeared at $2\theta=9.79°$. At 130°C, the peak at $2\theta=23.55°$ almost disappeared. Peak broadening can be seen in the diffractogram for the sample annealed at 160°C, indicating the start of disordering of the crystal structure. It is completely lost at 200°C. These results indicated that the black to red color change originated in the crystalline phase transition which may be due to the changes in electronic state of the conjugation system.

They[45] polymerized a sample by exposure to 3 Mrad of γ radiation. Its IR spectra indicated that the sample contained a substantial amount of the monomer. The X-ray diffractogram of the partially polymerized sample was very similar to that of the completely polymerized greenish black polymer. Thus, it has been judged that the monomer and polymer did not exist in separate phases, but as a solid solution.

The polymerization of solution-crystallized monomer was studied under similar conditions. The X-ray diffractograms of monomer, polymer and subsequently annealed sample at 90°C for 10 min following the γ irradiation were investigated. It was seen that the unit cell dimensions did not change through polymerization, unlike the case of melt crystallization. The polymerizability of solution crystallized monomer is lower than that of melt crystallized monomer. The melt crystallized sample polymerizes spontenously to completion. Consequently, the diffraction pattern of melt crystallized polymorph is obtained.

Aoki et al[46] polymerized acetylene at high pressure. They obtained Raman spectrum of the polymer. The reaction product consisted of two kinds of conjugated polymers, trans-polyacetylene and cis-polyacetylene. Acetylene molecules form planar zig-zag patterns in the ab plane of the unit cell. Polymerization reactions accompany opening triple bonds and crosslinking of the polymer molecules. It was expected that polymerization occured in the bc plane rather than ab plane. There are two possible reaction paths for polymerization in the bc plane. One is linear path running along diagonal of the bc plane (path A). The reaction was procedeed by trans opening of the triple bonds and crosslinking of the adjacent molecules to form a trans polymer. The other is zig zag path, leading to a cis polymer by cis opening of the triple bonds and succesive crosslinking reaction of the molecules (path B). The polymerization reaction along path A involves less molecular motions than along path B. The molecules located along path A form a molecular plane inclined somewhat with respect to the b axis of the unit cell. The molecular orientation in this plane is very favorable to a topochemical polymerization. A trans polymer can be formed simply by crosslinking of the adjacent molecules with C-C single bonds. On the other hand, chain propagation along path B involves molecular rotations prior to crosslinking reactions. The axes of the molecules at cis geometry sites along path B are not in the same plane, canting sligthly with respect to the backbone plane of the cis polymer to be formed. Therefore, rotations of the molecules into suitable reactive sites in the bc plane are required to form a cis polymer. In molecular solids, reactions involving the least changes in molecular positions are favored. This least motion principle suggest that path A is more preferable to path B for solid state polymerization.

1.4. Disubstituted Acetylenes

Acetylene and monosubstituted acetylenes can be polymerized to linear polymers by Ziegler Natta catalysts. For instance, $Ti(O\text{-}n\text{-}Bu)_4\text{-}Et_3Al$ catalyst is used for stynhesis of polyacetylene film[47]. Iron chelates- Et_3Al show high reactivity for polymerization of monosubstituted acetylenes such as phenylacetylene,[48] 1-hexyne,[49] and isobutoxyacetylene.[50] However, these Ziegler-type catalysts fail to polymerize sterically hindered, disubstituted acetylenes such as 3-hexyne.[51]

There have been only a few papers on the polymerization of aliphatic disubstituted acetylenes owing to their low reactivity: A linear oligomer (M_n=724, m.p 90°C) of 2-hexyne was obtained at high pressure and temperature (23.5 kbar, 255 °C)[52] . A mixture of polymer and cyclic trimer was formed in the reaction of 3-hexyne catalyzed by diarylcobalts[53]. Cotton et al reported that 3-hexyne and 4 metyl-2hexyne are polymerized by Nb(III) and Ta(III)- based catalysts[54].

It was reported that 2-hexyne[54] was polymerized in toluene by equimolar mixture of $MoCl_5$ and WCl_6 provided an extremely high polymer (avM_w>1.10^6). All polymerization procedures were carried out under dry nitrogen. IR spectrum of polymer has the absorbtion at 1650-1580 cm^{-1} is due to the stretching of conjugated

C=C bonds along main chain. The reason that this absorbtion is very small every main-chain carbon is substituted by alkyl groups, resulting in good symmetry. Absorbtions in the 1150-980-cm^{-1} region varied sligtly, depending on the kind of catalyst. Its NMR spectra were measured in a mixture of C_6D_6 and $CDCl_3$. These NMR spectra are consistent with the expected polymer structure, $-(CCH_3=C_3H_7)-_n$. In the UV spectrum of poly(2-hexyne) obtained with $MoCl_5.Ph_4Sn$ exhibited a maximum around 290nm, while those produced with $WCl_6.Ph_4Sn$ did not. As a result, the elemental analysis of data indicate that no side reactions such as hydrogenation, dehydrogenation, and oxidation take place during polymerization. The ^{13}C and ^1H NMR spectral data clearly indicate that the polymers have the $-(CCH_3=CR)-_n$ structure. The IR absorbtion at 1650-1580 cm^{-1} supports the polyene structure along main chain. The avarage extent of conjugation in solution , however, is presumed to be no more than several C=C bonds, according to UV spectra. This is explained in terms that the main chain is considerable twisted owing to the presence of two substituents per repeating unit. No definite informaion was obtained concerning geometric structure and head-to-head structure. The poly(2-hexynes) were all white solids. The polymers were soluble in less polar solvents such as benzene, toluene, cyclohexane, n-hexane, and tetrahydrofurane, partly soluble in carbontetraflouride, chloroform, and insoluble in more polar solvents, acetone, ethyl acetate, nitrobenzene, and acetonitrile.

In the polymerization of 1-phenyl-1 propyne[55] by $TaCl_5$, the polymer formed underwent degradation after all the monomer had been consumed. In contrast, no polymer degradation occurred when suitable organometallics (e.g., tetra-n-butyltin, trietylsilane) were added as cocataysts at 1:1 ratio to $TaCl_5$. Consequently, polymers with weigth avarage molecular weigths exceeding 1.10^6 could be obtained. 1-phenyl-1-propyne polymerizes in the presence of group 6 transition metal cataysts, that is, $Mo(CO)_3$. Toluene and 1:1 WCl_6-Ph_4Sn.

$CH_3C\equiv CC_6H_5 \rightarrow -(C(CH_3)=C(C_6H_5))-_n$

Masuda et al[55] indicated that cocatalyst effect of polymerization of 1-phenyl-1-propyne by $TaCl_5$ and $NbCl_5$. So, it was found that they did not only accelerate polymerization but also effectively inhibit polymer degradation.

3-Octyne,disubstituted acetylene, polymerized by using group 5 transition metal[56]. Since poly(3-octyne) is a new polymer, its structure and properties were studied using polymer sample prepared with $TaCl_5$. The spectral data are as follows: IR(KBr) 2950(s), 2850(s), 1650-1600(w), 1470(s), 1380(m), 1120(w), 920(w) cm^{-1} ; ^{13}C-NMR ($CDCl_3$, 22.5Mhz) δ 136 (C_3, C_4), 23,-12 (others);UV max(cyclohexane) 279nm(ε810), transparent above 370 nm. These data support the main-chain structure comprising alternating double bonds[i.e., $-(Cet{=}C\text{-}n\text{-}Bu)-_n$] but taking a twisted conformation. This polymer is a white solid soluble in low polarity solvents such as carbon tetrachloride, cyclohexane, and a polymer film could be prepared by solution casting. The softening point was 210-220°C, the electrical conductivity was lower than 10^{-18} $S.cm^{-1}$.

Niki and Masuda[57] studied the effects of organometallic catalysts on the polymerization of disubstituted acetylenes. For example, the structure and properties of the poly(diphenyl acetylene) obtained with Ta catalysts were studied and compared with those of the polymer with W and Mo catalysts. The present polymer was yellow solid insolible in any organic solvent and infusible below 400°C. IR spectrum of this polymer was identical to that of the polymer obtained with WCl_6-Ph_4Sn.[58] An exothermic peak due to cis-to-trans isomerization was observed at 280°C in the DTA of the polymer obtained with $MoCl_5$-EtOH-Et_3Al(1:2:1).[58] This polymer did not lose weigth in air below 500°C in TGA, indicating its very high stability. The electrical conductivity (25°C) was $1.2\times10^{-17}Scm^{-1}$, the polymer being a typical insulator.

1-(p-t-Butylphenyl)-2-phenylacetylene[59] were polymerized in catalytic systems based on $TaCl_5$ to give new polymers in high yields. These monomers were more reactive than diphenylacetylene(DPA) in copolymerization. Unlike poly(DPA), the present polymers were soluble in toluene, $CHCl_3$, et. Owing to the high configurational entropy induced by the para-substituents. Their relative weigth avarege molecular weigths determined by GPC were in the range of $6x10^5$-$3.6x10^6$, and films could be obtained by solution casting. These polymers were fairly thermally stable, as seen from their high on set temperatures (320°C-380°C) of weigth loss in TGA in air. The elemental analysis data of poly(p-t-BuDPA) and poly(p-n-BuDPA) was carried out by Kouzai and Masuda [59] IR spectra of poly(p-t-BuDPA) and poly(p-n-BuDPA) showed no absorbtion due to the C≡C stretching observed in the monomers. The ^{13}C NMR spectra of the monomers showed two peaks due to acetylenic carbons at δ 89.5, 88.7 (p-t-BuDPA), and at δ89.6, 88.7(p-n-BuDPA), which disappeared in the polymers. All these spectral data support the alternating double bond structure for main chain of present polymers.

1.5. X-Ray Diffraction

An electron in the path of unpolarized X-rays beam vibrates with the frequency of the incident radiation, periodically absorbing energy and emitting it as X-ray of same frequency. The original X-rays are unmodified in λ by interaction but are radiated in all directions.

The electron has the effect of scattering the incident radiation and acts as a secondary X-rays. The nucleus because of high mass, makes a negligible contribution to the radiation scattered by an atom.

The intensity of radiation scattered by an atom depends on not only number of electrons associated with nucleus, but also their distribution, on the angle of scattering and on the temperature.

X-ray analysis[60], in crystalline polymers, can lead to obtain the identification of sample, its crystallinity and the geometry of crystallites.

An ideal crystal may be defined as generated by stacking infinite numbers of copies of the the contents of a parallelpiped in three dimensions. The simple repeating unit is the unit cell, and its dimensions a, b, c. (cell edges) and α, β, γ (cell angles). Different orientations of these six cell parameters give seven different types of unit cell called crystal system. The fourteen different types of unit cells can be generated which are called Bravaias Lattice[61]. It can be primitive cell which has only one lattice point per unit cell and nonprimitive unit cell which has more than one lattice point. In primitive unit cells, lattice points are on the corners. But if lattice points are in the two parallel faces or on faces is nonprimitive.

Any operation that can be applied on a repeating unit can give an equavelant or the same repeating unit is called symmetry operation. It can be divided into two groups point group symmetries, space group symmetries. The application of point group symmetries to lattice points in 14 Bravias lattice give 32 unique unit cells. The space group can be defined as combination of fourteen Bravias lattice and 32 point groups with two more symmery operations namely screw axes and glide planes (space group symmetries), 230 unique unit cells are generated. Screw axes of rotation is a rotation followed by a translation is a fraction of the axes that translation takes place parallel to it. A symmetry operation which is a reflection across a plane follows by one half translation parallel to specify axes in the plane is Glide plane.

Space group gives information about crystal structure and position of molecules with respect to each other. Molecular structural parameters which are bond length and bond angles can be calculated from experimental positional coordinates of atoms obtained from intensities of X-ray reflections.

The equation used for X-ray reflections is called Bragg's equation which is;

$$2d\mathrm{Sin}\theta = n\lambda$$

Where d is interplanar distance, θ Bragg's reflection angle, n order of reflection and λ wave length of X-ray employed. The reciprocals of the fractional intercepts which the plane makes with crystallographic area is called the Miller indices and designated by three letters in brackets (h k l). A general expression which can be used to calculate reciprocal d spacing may be deduced from the geometry of the reciprocal lattice and Bragg's equation:

$$d^{*2} = a^{*2}h^2 + b^{*2}k^2 + c^{*2}l^2 + 2hla^*b^*\mathrm{Cos}\alpha^* + 2hka^*c^*\mathrm{Cos}\beta^* + 2klb^*c^*\mathrm{Cos}\gamma^*$$

Where d^* is 1/d in order to obtain direct relation with sinθ, in monoclinic system, $a^*=1/a\mathrm{Sin}\theta$, $b^*=1/b$, $c^*=1/c\mathrm{Sin}\beta$ and $\beta^*=180-\beta$

The X-ray instrumentation are designated to determine crystal structure of the sample, single crystal or powdered samples can be used. In these two ways photographic and counter method can be used to obtain complete information on crystal and molecular structures.

In diffraction, information is directly related with type of compound and amount of compound, however, in spectroscopy, information is about an element not compound.

X-ray diffraction is divided as, photographic method and counter method. Former registers the refraction on the film giving more information than counter method. It can be found symmetries, direct cell parameter on the film. So indexing is easier and direct space group can be deduced. Counter method counts the data, results in digital number and plotting the spectra. Both methods are supporting each other.

Diffraction can be done by single crystal or powder method. When the structure of sample is crystallized in single crystal, the single crystal method is used. When sample is in polycrystal form, powder method is used.

Powder diffractograms of thousands of samples were taken, they are present in literature. These are involved certain d values, intensities and cell parameters. The crystal structure of sample is found comparing observed d values, intensities with theoretical ones.

In this work counter method of powder samples were studied. This method is very important and useful in qualitative phase analysis because every crystalline material has its own charecteristic powder pattern. There are two main factors[62] which determine powder patterns.

i) The size and the shape of unit cell.
ii) The atomic number and position of the various atoms in the cell.

θ's are used to find cell parameters. The d^* are calculated using Bragg equation. When d^{*2} values are known, comparing with theoretical values for different combination of hkl, indexing can be done i.e. cell parameters of sample can be determined. The indexing for monoclinic and triclinic unit cells are almost impossible if cell parameters are not known but for cubic unit cell, it's very easy. Intensities are used to find molecular structure of sample. I(hkl) is related to electron density in unit cell matrix. Electron density is used to find coordinates of atoms i.e, bond lengths, bond angles. So molecular structure is determined with intensity.

1.6.Application of X-ray in Polymer Studies

It's possible to determine the degree of crystallinity[60] by using the X-ray spectrum of an unoriented polymer. In many cases, it has been possible to distinguish differences between the X-ray intensity diffracted from amorphous and diffracted from crystalline regions with X-ray sectrum of polymer.

The mechanism of solid state polymerization is described by X-ray diffraction analysis[63]. By X-ray diffraction analysis crystal and molecular structure can be studied, defect sites, phase seperation during solid state polymerization and direction of the chain propagation can be studied[60].

1.7.Mass Spectroscopy

In mass spectroscopy, a substance is bombarded with an electron beam having sufficient energy to fragment the molecule. The positive fragments which are produced (cations and radical cations) are accelerated in a vacuum through a magnetic field and are sorted on the basis of mass to charge ratio. Since the bulk of ions produced in the mass spectrometer carry a unit positive charge, the value m/e is equivalent to the molecular weight of the fragment. The analysis of mass spectroscopy information involves the reassembling of fragments, working backwards to generate the original molecule.

A very low concentration of sample molecules is allowed to leak into the ionization chamber (which is under a very high vacuum) where they are bombarded by a high energy electron beam. The molecules fragment and the positive ions produced are accelerated through a charged array into an analyzing tube. The path of the charged molecules is bent by an applied magnetic field. Ions having low mass (low momentum) will be deflected enough and will collide with analyzer wall. Ions having proper mass-to- charge ratio, however, will follow the path of the analyzer, exit through the slit and collide with the collector. This generates an electric current, which is then amplified and detected. By varying the strength of the magnetic field, the mass-to-charge ratio which is analyzed can be continously varied.

The output of the mass spectrometer shows a plot of relative intensity vs masss-to-charge ratio(m/e). The most intense peak in the spectrum is termed the base peak and all others are reported relative to its intensity. The peaks themselves are typically very sharp, and simply represented as vertical lines.

The process of fragmentation follows simple and predictable chemical pathways and the ions which are formed will reflect the most stable cations and radical cations which that molecule can form. The highest molecular weight peak observed in spectrum will typically represent the parent molecule, minus an electron, and is termed the molecular ion(M+). Generally, small peaks are also observed above the calculated molecular weight due to the natural isotopic abundance of ^{13}C, ^{2}H, etc.

1.8. Properties of Acetylenedicarboxylic Acid

The crystal structure of anhydrous acetylenedicarboxylic acid[64] has been solved from 1031 independent three dimensional counter data and refined by least square methods to R 0.045. Crystals are monoclinic, space group $P2_1/n$, Z=4, unit cell dimensions: a= 14.894, b= 6.420, c= 4.862 A, β=90.90°. the molecules are nonplanar: dihedral angle between the carboxy groups is 57.8°. The four C=O bond lengths are nearly equal 1.254 ± 0.01A. The experimental value of the -C≡C- bond is 1.168A.

Polyanhydride of acetylenedicarboxylic acid[65] was produced by addition of phosgene in PhMe to a solution of $HO_2CC{\equiv}CCO_2H$ and Et_3N in chloroform. $Et_3N.HO[COC{\equiv}C]_n[COC{\equiv}CCO_2COC{\equiv}C]_mCOC{\equiv}CCO_2H.-\ NEt_3^{\cdot}$. The polymer molecular weigth was smaller than 1000. It was soluble in $HCONMe_2$, Me_2SO, concentrated H_2SO_4. Its color, ESR spectrum and analomous solution viscositiy indicated the polyconjugated structure. During the polymerization the keto groups were formed from anhydride by CO_2 elimination.

1.9. The Aim of this Study

Solid state polymerization of acetylene monomers generally gives topotactic and conductive polymers. Markedly, the monomer which is monosubstituted acetylene gives conductive polymer. Then, we thought that there may be a possibility of forming conductive polymer from disubstituted monomer. Acetylenedicarboxylic acid, used in this study, is disubstituted. Polymers normally can not be conductive unless they are doped. But the active centers may be formed spontenously because of the effect of irradiation. It was expected that the polymer formed from acetylenedicarboxylic acid may be conductive even if it is not doped. Then, we discussed the effect of monomer crystal structure on solid state polymerization.

CHAPTER II

EXPERIMENTAL

2.1 Purification of Chemicals

Acetylenedicarboxylic acid: It was a product of Aldrich Chemical Co. Ltd and purified by recrystallization in diethyl ether. The melting point was179 °C.

Water: It was distilled by physical chemistry labarotoy.

Dietylether: Technical grade diethylether obtained from Kimya Sanayi A.Ş.

Dimetylsulfoxide: It was obtained from Kimya Sanayi A.Ş used without further purification.

Carbon tetrachloride: It was a product of Merck and used without further purification.

Tetrahydrofurane: It was product of Merck and used without further purification.

2.2. Instrumentation

Irradiation Tubes: Pyrex tubes of 11 mm in diameter and 10 cm in length were used.

High vacuum system: High vacuum system was used to evacuate the irradiation tubes in which the solid monomer was present, down to 10^{-4}-10^{-5} mmHg pressures. It was composed of the following parts.

a) Rotary Oil Pump: It was a product of General Electric Company CO. , Model 5X BIODH and has ability to reduce the pressure down to $1.5x10^{-2}$ mmHg.

b) Mercury Diffusion Pump: It was a water-cooled one stage diffusion pump with approximate capasity of 200 mLHg. Mercury was heated by a 143w metallic band and resistive heater operating at 115 V.

c) Main Mainfold: It was made up of a pyrex glass tube with diameter of 4.59 cm and length of 113cm carrying one outlet tube with high vacuum stockcock for the connection of irradiation tube.

d) Liquid Nitrogen Traps: Irradiation tube was connected a trap through a high vacuum stopcock. To protect the pumps from the chemicals evaporated at low pressures, two pyrex traps were used. One of the traps was connected between the mercury diffusion pump and the other was connected between the main and mercury diffusion pump.

Co-60 Gamma Ray Source: 220 Model Gamma cell of Atomic Energy of Canada Limited CO. was used as radiation source. In this unit the cobalt is in the form of rigid cyclinder rods and 24 Co rods are put around hollow cyclinderical chamber. Samples to be irradiated were hold in a cyclinder chamber that could be automatically lowered to the irradiation source. The dose rate during the experiment was 0.015 Mrad/h.

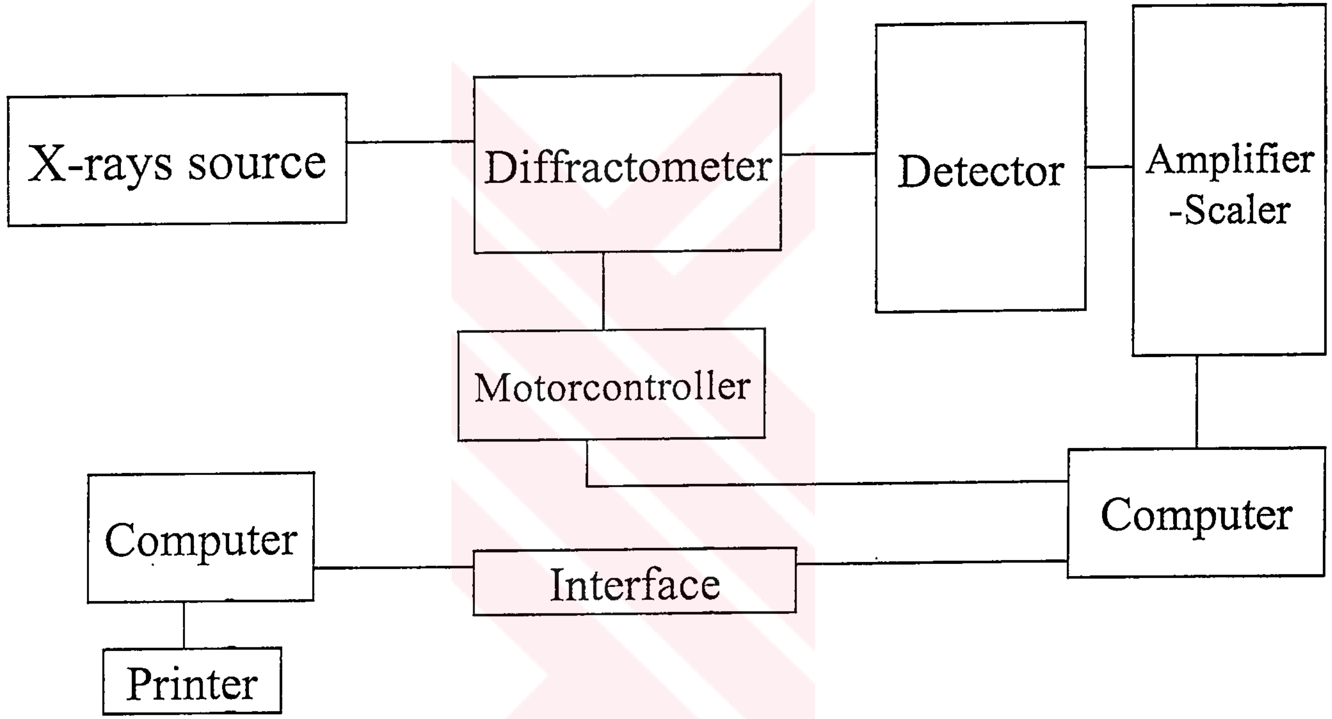


Figure2.1. Block diagram of X-ray diffractometer

X-ray diffractometer: The block diagram of X-ray diffractometer is shown in Figure 2.1. It is Enraf-Nanics diffractometer of FR 582 equipied with Huber SMC 9000 goniometer using CuK_{α} (40kV, 20mA, λ= 1.54178A) radiation.

a) X-ray Source: X-rays are produced when electrons are accelerated in an electric field(35-50kV) and impiringe on a metal target. For the copper as target material, there are two sharp peaks at wave-lengths 1.542 A and 1.392 A where the radiation having λ= 1.542 A is called the K_{α} radiation, and the radiation having λ=1.392 A is called K_{β} radiation. A nickel filter absorb most of the K_{β} and the continous radiation. In this work 40 kV voltage and 20 mA current was used to produce X-ray with CuK_{α}(λ=1.54178A)

b) Diffractometer: In the diffractometer, the intensity of a diffracted beam is measured directly by electronic counter.

c) Detector: A semiconductor detector(scintillation counter) was used to convert radiant energy to electrical signal.

d) Amplifier and Scaler: Amplifier has the ability to amplify the signals produced from detector by a factor up to 10000. A scaler is introduced between the signal source and the counter.

e) Motor controller: It's connected between diffractometer and computer1. The direction of diffractometer and the speed of rotation is affected to motor controller

f) Computer: An HP computer was used for instrumental control, intensity collection and data processing.

FTIR

Infrared Spectra of monomer and polymer were obtained from Mattson 1000 spectrophotometer, using KBr pellets.

Ultra-Violet Spectrophotometer (UV)

Shimadzu 160 was used to obtain UV spectra of monomer and polymer. Dimetylsulfoxide is used as a solvent for both monomer and polymer.

Direct Pyrolysis- Mass Spectrometry (DP-MS)

The mass spectrometer used for direct pyrolysis experiment was Balzers QMG 311 qudrupole mass spectrometer via a personel computer for the control of the MS data acquisition and analysis.

Differential Scanning Calorimeter (DSC)

910S type (DSC) was used to invetigate the melting point of the monomer and polymer under nitrogen atmosphere. Rate of heating is 10°C/min.

Thermal Gravimetric Analysis (TGA)

Dupont 951 type TGA was used to investigate the decomposition temperature of the monomer and polymer under nitrogen atmosphere. Rate of heating is 10°C/min.

Gel Permeation Chromotogrophy (GPC)

Water 160 type GPC was used to investigate molecular weight of the polymer.

Viscometer

Ubbelohde type of glass viscometer was used to determine the intrinsic viscosity of the polymer at 25°C, using DMSO as a solvent.

2.3 Procedure

2.3.1.Radiation Induced Solid State Polymerization of Acetylenedicarboxylic acid

The solid state polymerization of acetylenedicarboxylic acid initiated by Co-60 γ rays was done under vacuum and in atmospheric air at room temperature. About 3-5g of monomer sample was put into irradiation tube made up of pyrex glass and connected to high vacuum system 4-5 hours. During the evacuation liquid nitrogen trap was removed from frozen monomer for a period of 5-10 minutes to prevent encapsulation of oxygen, this process was repeated two times for each sample. At the end of the evacuation; the tube was sealed and they were irradiated by γ rays for desired period of time at room temperature. For the polymerization in open air, similar amount of monomer samples in the fist set were placed in the tubes and put into irradiation source without evacuation of air from sample tubes.

After the irradiation for the desired time, the tubes were broken, the irradiated samples were dissolved in a small amount of water which is solvent for monomer and nonsolvent for polymer. The polymer was filtered and dried to constant weight. The percent conversion of the monomer to the polymer was calculated gravimetrically.

2.3.2.X-ray Powder Diffraction Analysis

The samples (monomer and polymer) were grounded to a fine powder at mesh size of about 325 in a small ceramic mortar, then the diffractogram of samples were taken.

2.3.3. Viscosity Measurements

The basic viscometric relations are as follows:

$$\eta_{sp} = \eta_r - 1 = (\eta - \eta_0)/\eta_o = (t - t_0)/t_o$$

$$\eta_{red} = \eta_{sp}/c = (\eta_r - 1)/c = (\eta - \eta_o)/\eta c_o$$

where η_{rel}, relative viscosity; η_{sp}, specific viscosity

η_{red}, reduced viscosity

Relative and specific viscosities are dimensionless, while the dimension of reduced and intrinsic viscosities is that of inverse concentration. If specific viscosity over concentration η_{sp}/c is plotted against concentration, the straight line gives the intrinsic viscosity.

The viscosity of samples were measured in a glass type Ubbelohde viscometer using DMSO as solvent at 25°C.

CHAPTER III
RESULTS AND DISCUSSION

3.1 Solid State Polymerization of Acetylenedicarboxylic Acid

Solid state polymerization of acetylenedicarboxylic acid by Co-60 gamma ray was carried out under air and vacuum conditions at room temperature.

The results for radiation induced polymerization under air condition at room temperature are given in Table 3.2. The percent conversion against irradiation time are plotted in Figure 3.1.

The curve shows that polymerization in atmospheric air follows autocatalytic kinetics. The rate is slow initially,showing an induction period, after about 15 days of irradiation only 0.4 % of the monomer is polymerized. The percent conversion increases almost linearly up to about 2.3%, then it stays constant near the limiting conversion of about 4.5%. The polymer is soluble in Dimethylsulfoxide, tetrahydrofurane; but insoluble in methanol, water, chloroform, acetone, etc.

The results for irradiation induced polymerization under vacuum condition at room temperature are given in Table 3.3. The percent conversion against irradiation is shown in Figure 3.2.

The polymerization in vacuum shows an autocatalytic type with almost no observable induction period. The induction period is very short since after about 10 days of the irradiation the conversion is about 2.7%. The percent conversion increases linearly with respect to irradiation time up to about 5.20% which is higher than that under air condition.

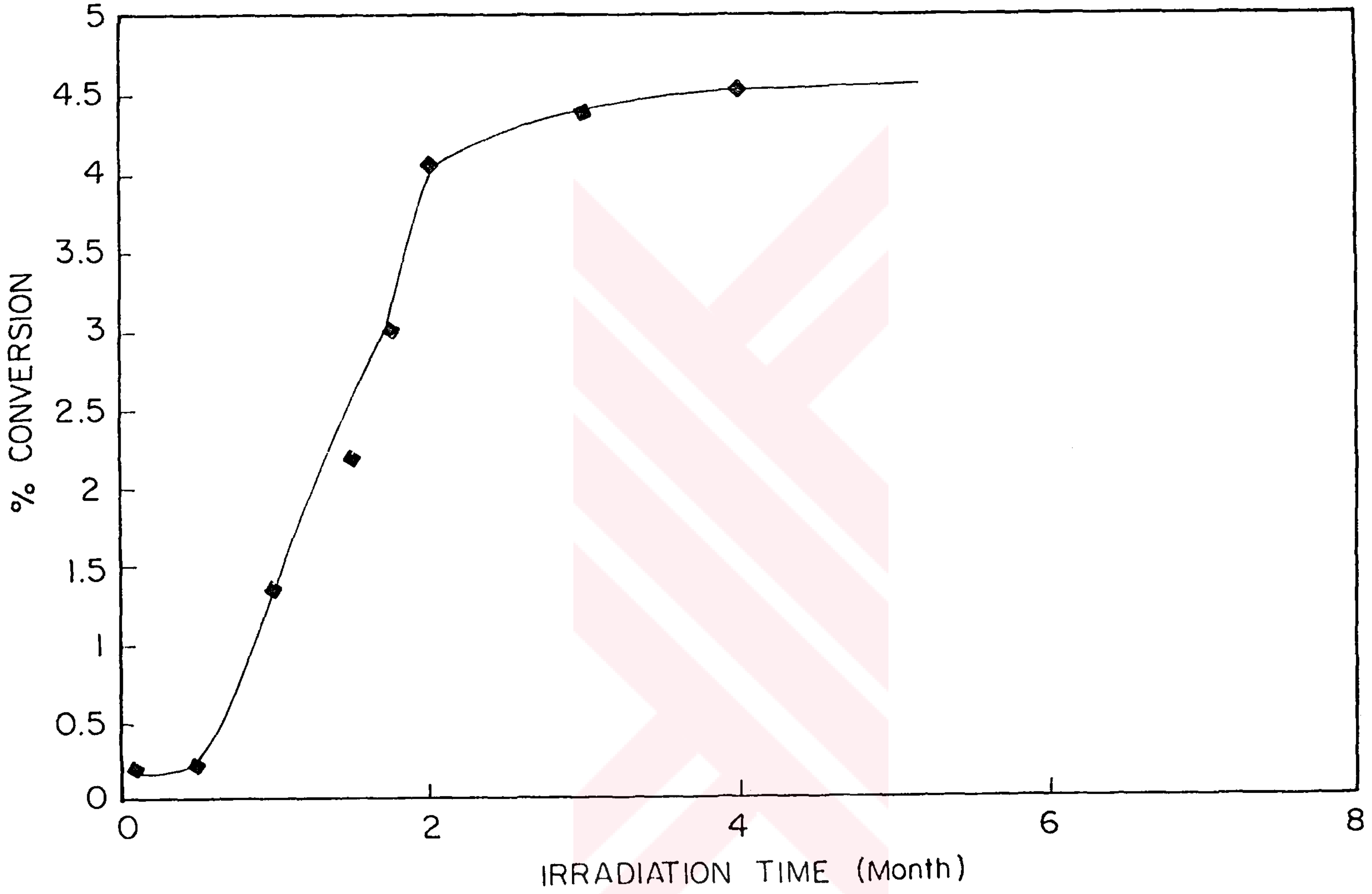


Figure 3.1 Percent Conversion vs irradiation time plot of polymer obtained under air condition

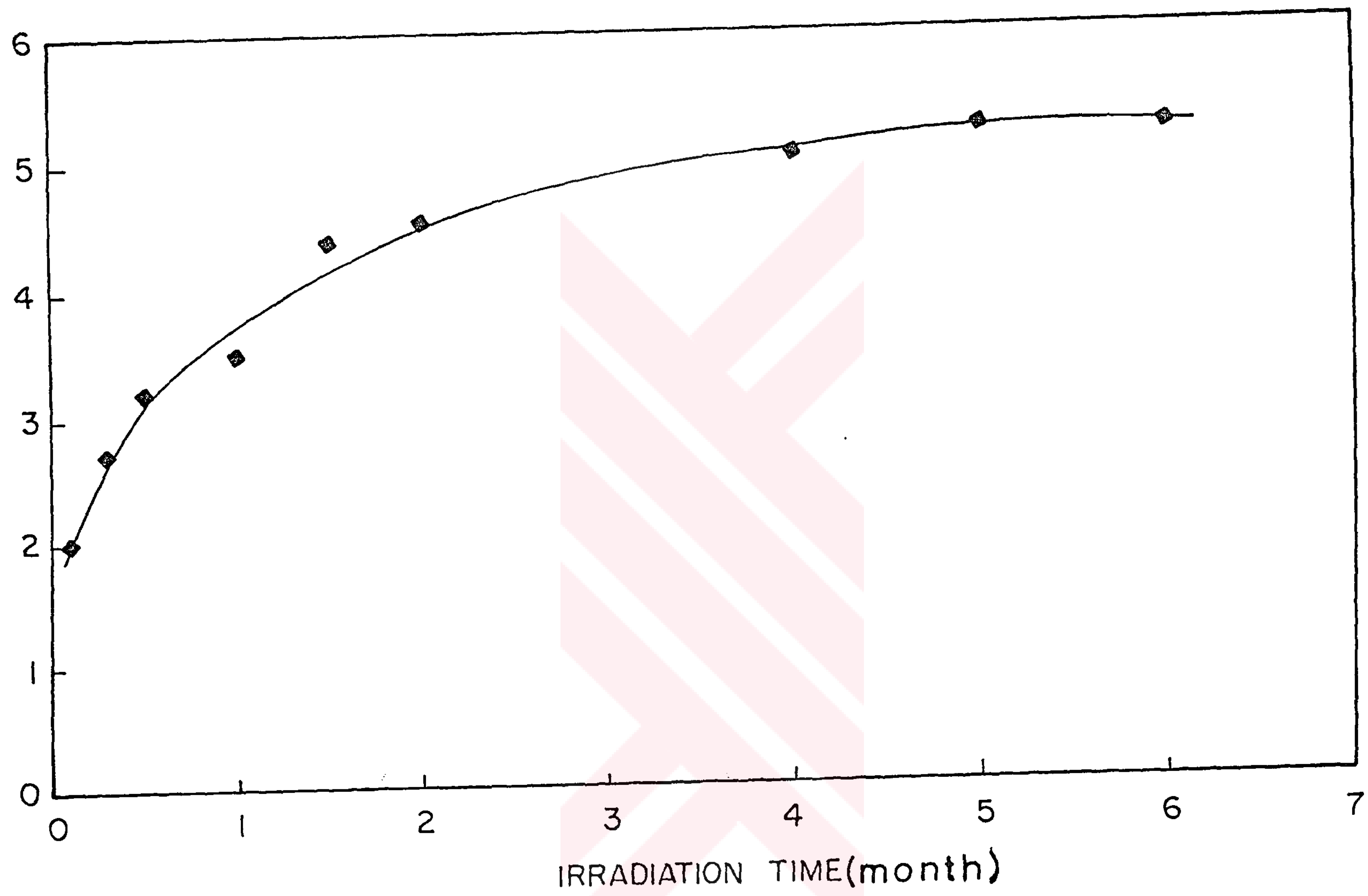


Figure 3.2 Percent Conversion vs irradiation time plot of polymer obtained under vacuum condition.

In Figure 3.2, the induction period is not observable because of axis-scaling. The time is given in month which is much longer time. The low limiting conversion is a result of crystal structure of monomer. For the polymerization process, the monomer molecules has to be in locations that will be suitable for addition reaction. If the active end of monomer molecules are more than Van der Waals distance apart from each other, the addition will not be possible. In this case, the energy has to be given to change the location of molecule by overcoming lattice energy and put the monomer in more favorable position for addition reaction. Therefore, it seems, in our case, the molecules are arranged in such a way that will not give easy addition reaction. These resulted in low limiting conversion.

In the presence of oxygen, the rate of polymerization is decreased and polymerization kinetics shows an induction period, therefore there is a retarding effect of oxygen on limiting conversion, a large effect of oxygen on limiting conversion can not be observed. Still, the result indicates a free radicalic mechanism, due to the retarding effect of oxygen.

3.2 Infrared Spectral Investigation

The FTIR spectra of (a) monomer and (b) polymer obtained by irradiation are given in Figure 3.3 in the region of 2000-400 cm^{-1} for corresponding samples. Table3.1 summarizes peak assignment to the wave number.

In the monomer spectrum, the C=O is observed at about 1600 cm^{-1}, C≡C peak at 2200 cm^{-1}, carboxylic acid peak at 2800-3200 cm^{-1}. In the polymer spectrum, the cyclic etheric carbon strecthing is observed at about 1100 cm^{-1}, the overlapped C=O and C=C strecthing at 1600 cm^{-1}, C≡C peak at 2200 cm^{-1}. The C=O peak intensity in polymer spectrum is smaller compare to that of monomer. This is due to evolution of CO or CO_2 in the reaction. The C≡C bonds that exist as end groups in the polymer chain are observed in the spectrum, because the polymer

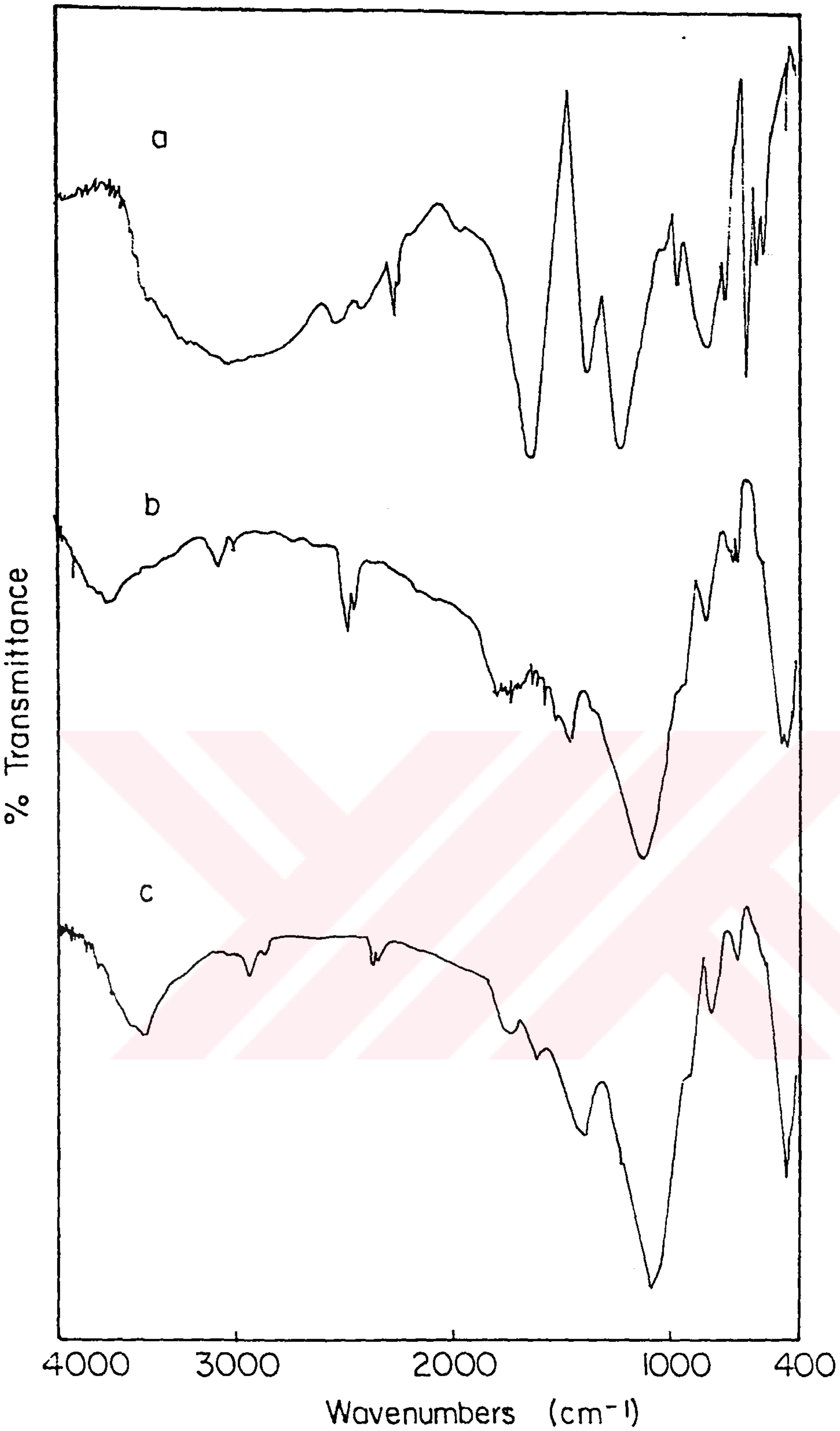


Figure 3.3. Infrared spectrum of a) monomer, b) polymer obtained under air condition c) polymer obtained under vacuum.

Table 3.3. Infrared absorbtion values for monomer, polymer obtained from air condition, polymer obtained vacuum condition.

Wavenumber(cm^{-1})	Monomer	Polymer (under air condition)	Polymer(under vacuum condition)
2797-3644	-OH, -C≡CH	-OH, -C≡CH, $=CH_2$,AromaticAr-H	OH, -C≡CH, $=CH_2$,AromaticAr-H
2644	COOH		
2500	COOH		
2932			COOH, CH_2 asymmetric
2864			COOH, CH_2 asymmetric
2938		COOH, CH_2 asymmetric	
2800		COOH, CH_2 asymmetric	
2373	C≡C		
2355	C≡C		
2381			C≡C
2364			C≡C
2369		C≡C	
2348		C≡C	
1711	C =O		
1559	C =C		
1440	OH bending, CH_2 scissor in plane		
1754			C =O
1610			C =C
1381			C-O-C asymmetric, OH bending
1677		C =O, C =O	
1415		-OH bend, -COO-	
1000	C-O-C, $RCH=CH_2$		
1092		Cyclic C-O-C, $RCH=CH_2$, C=C=C	
1101			Cyclic C-O-C

molecular weight is low and their concentration is high enough to be observed. After CO is broken, C≡C can also be formed, because of conjugation in C=C=C ↔C-C≡C. Cyclic C-O-C bond absorbtion is more intense in the polymer spectrum at about 1000cm^{-1}. This gives evidence for the presence of cyclization in the polymer chain.

The expected chain propagation is the addition reaction through acetylene groups forming =C=C=C or –C=C-C=C- type of bonding. However, the experimental results showed that firstly one of the CO or CO_2 is broken, and then polymerization takes place through acetylene groups.

3.3. Molecular Weight Determination

The results of the change in intrinsic viscosity [η] with percent conversion of polymers obtained under air and vacuum conditions are shown also in Table 3.2 and Table 3.3.

Table 3.2. Change of intrinsic viscosity and percent conversion with irradiation time under atmospheric condition.

Time(month)	%Conversion	[η]
0.17	0.4	-
0.5	0.4	-
1	1.6	-
1.5	2.3	0.540
2	3	-
3	4.45	0.066
4	4.51	0.170

Table3.3. Change of intrinsic viscosity and percent conversion with irradiation time under vacuum condition.

Time(months)	% Conversion	[η]
0.17	2.05	
0.33	2.75	0.076
0.5	3.35	
1	3.51	
1.5	4.38	0.698
2	4.49	
3.5	4.51	0.026
5	5.25	
6	5.20	0.308

The viscosity of some samples are not measured, because enough polymer samples could not be obtained due to low conversions. Since samples are insoluble in most of the solvents, other methods such as light scattering or other cryscopic methods for molecular weight determination could not be carried out to find K and α values used in viscosity-molecular weight relation. However, the intrinsic viscosities are relatively high for these types of polymer. The molecular weight seems to be higher for the polymers obtained by irradiation under vacuum condition.

The gel permeation chromotogram result of the polymer obtained from irradiation under vacuum is shown in Figure 3.4. The chromotogram indicates that the molecular weight distribution is monomodel. Since molecular weight of polymer is relatively low, and we didn't have suitable standart to obtain calibration curve for the polymer, the number avarage, weight avarage molecular weight could not be calculated from chromotogram.

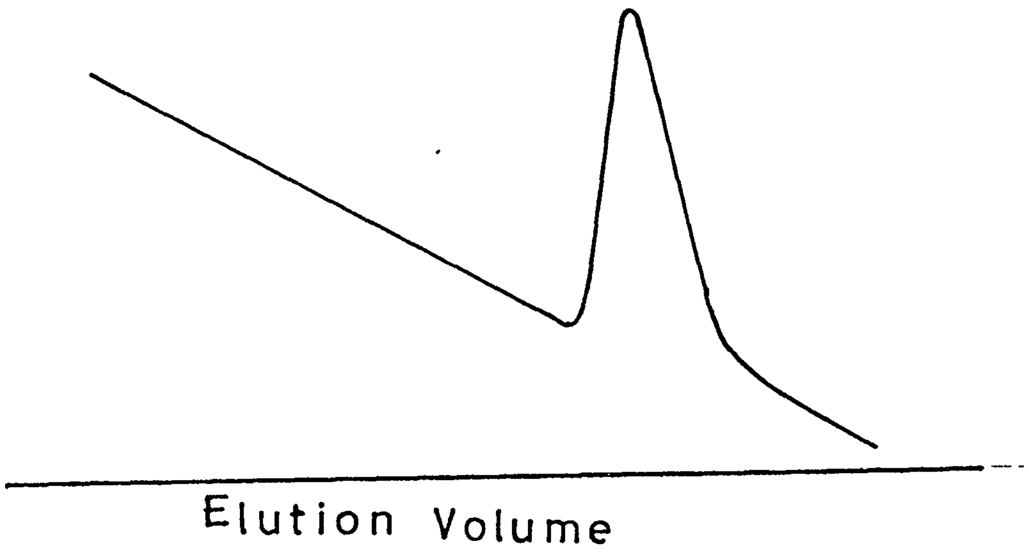


Figure 3.4 Gel permeation chromotography spectrum of polymer obtained from Irradiation under vacuum.

3.4. Ultra Violet-Spectral Investigation

The UV spectrum of (a) the monomer (b) the polymer obtained by irradiation are given in Figure3.5. The spectrum of monomer is similar to that of polymer. In the monomer spectrum, maximum absorbance observed at 291 nm for monomer. This peak corresponds to C≡C bond. However, maximum absorbance of polymer is 293 nm. There is a shoulder in the polymer spectrum and also the maximum absorbance shifted at higher wavelength. These are very similar with poly(2-hexyne) whose max. absorbance is observed at 290 nm[54].

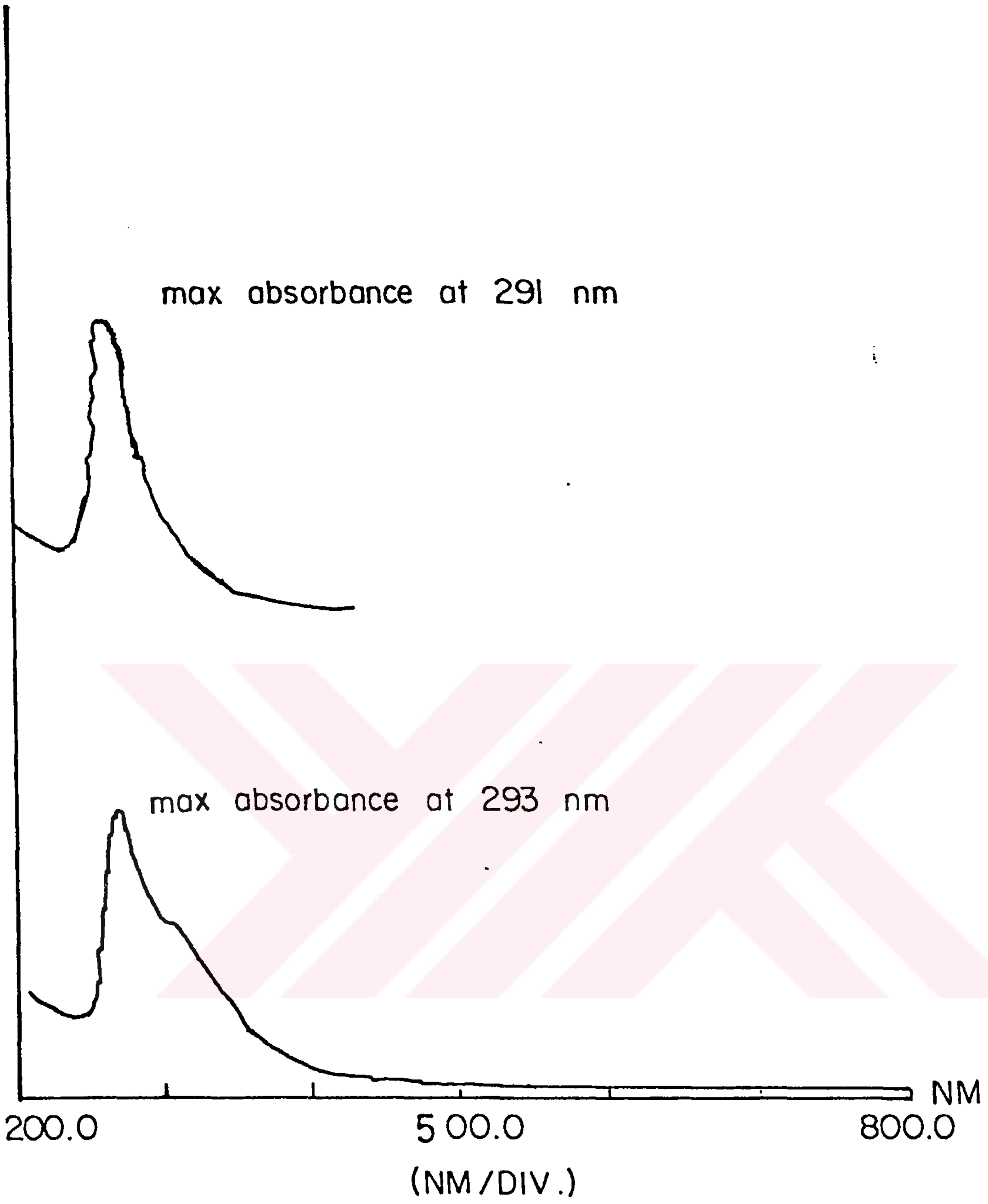


Figure 3.5. Ultra violet spectrum of a) monomer
b) polymer obtained by irradiation.

3.4. Thermal Investigation

The DSC thermograms of the monomer and polymer obtained by irradiation are given in Figure 3.6, Figure 3.7 respectively. Thermograms of monomer shows an exothermic peak at 204.84°C. The softening followed by decomposition temperature of acetylenedicarboxylic acid in the literature [64] is 175°C. Benghiant and collaborators prepared crystals of anhydrous aceylenedicarboxylic acid from nitromethane solution by slow evaporation. In this study, the crystals are obtained by recrystallization in dietylether. The exothermic peak in this study is most probably due to breaking of CO or CO_2 fragments with a phase change to a new crystal structure. The DSC thermograms of polymer (Fig 3.7) gives a T_g value of 157.08°C with no melting or observable decomposition up to 350 °C, The high T_g value for polymer is due to the rigid structure of it.

The TGA thermograms of the monomer and polymer obtained by irradiation are given in Figure 3.8, Figure 3.9 respectively. The first weight lost in the monomer starts at about 80°C and accelerated at 170°C. At this stage, the weight lost is about 10%. The peak decomposition from differential thermograms is observed at 226.05°C. The residual monomer left after about 250°C is 11%. This weight did not change up to 350°C that was studied. Most probably the initial weight lost (~10%) is due to the –OH, CO and/or CO_2 evolution which is about 1 mole per 3 moles of monomer. The second decomposition is due to further fragmentation of monomer. However, some of the monomer is also thermally polymerized. This is the fraction (~11%) that remained as residual after heat treatment.

The TGA thermogram of polymer is shown in Figure 3.9. In this case the initial decomposition is not observed as it did for monomer. The decomposition starts at about 125°C and accelarates at 150°C. From differential thermogram, the maximum decomposition temperature is observed as 214.77°C. Decomposition almost completed at 220°C and continue with a slower rate when temperature increased further. The weight remained at about 370°C is 91.3%. This shows that the polymer loses some side groups which is most probably in the form of CO molecules and the side groups are aromatized to give a more stable rigid chain.

In order to understand the decomposition behavior of monomer and polymer better, a sample of polymer was heated in a muffle furnace up to 1200 °C. The weight lost of polymer was checked at each of 50 °C temperature increments and the IR spectrum at each increment were also taken to observe any structural change. The weight lost of polymer was about 12% at temperature range of 200-300°C, then remained constant up to 1200 °C. No noticable change were observed in the sample. The IR spectra taken at temperatures of 1050 °C, 1100°C and 1200 °C are given in Figure 3.10. The etheric streching peak at about 1000 °C in the spectrum of polymer is almost disappeared at higher temperatures. This is most probably due to the breaking of a second CO or CO_2 group from side cyclic group of polymer chain, that was formed during polymerization. The corresponding 12% weight lost shows about one CO lost in about 2-3 monomer units. Therefore the recyclization of side groups has taken place toward an aromatic structure.

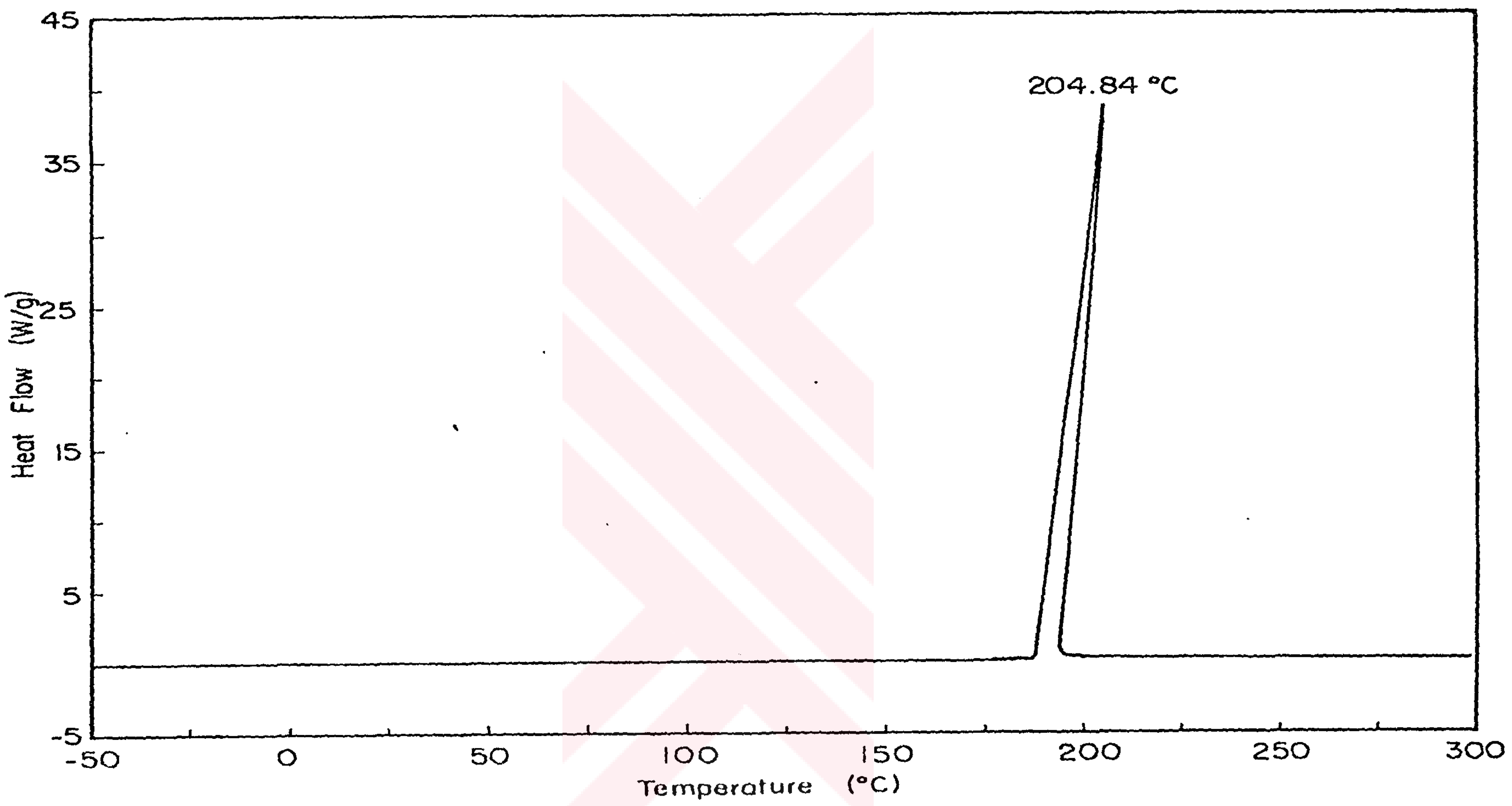


Figure.3.6. DSC Spectrum of monomer

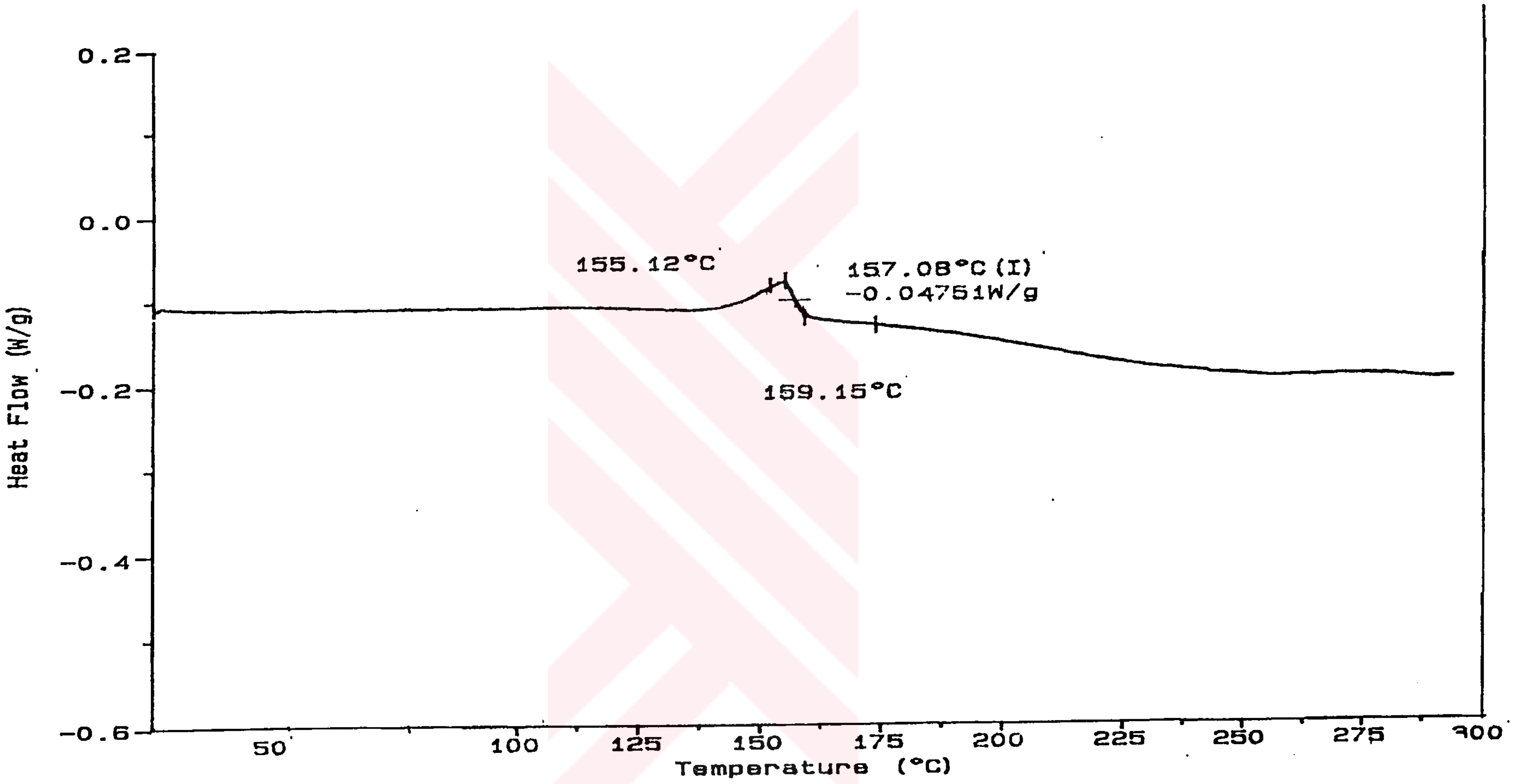


Figure 3.7. DSC Spectrum of polymer obtained by irradiation.

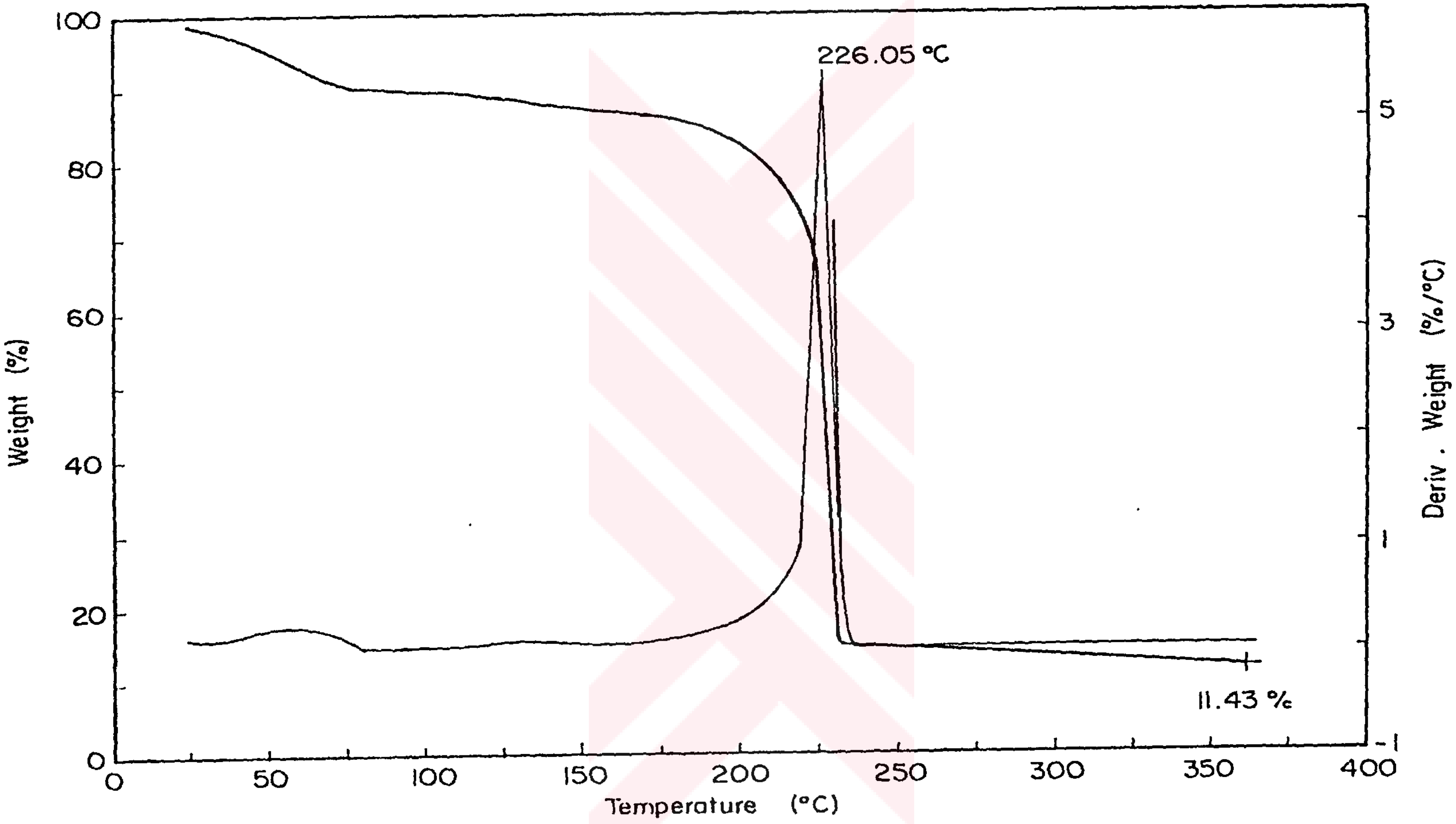


Figure 3.8. TGA spectrum of monomer

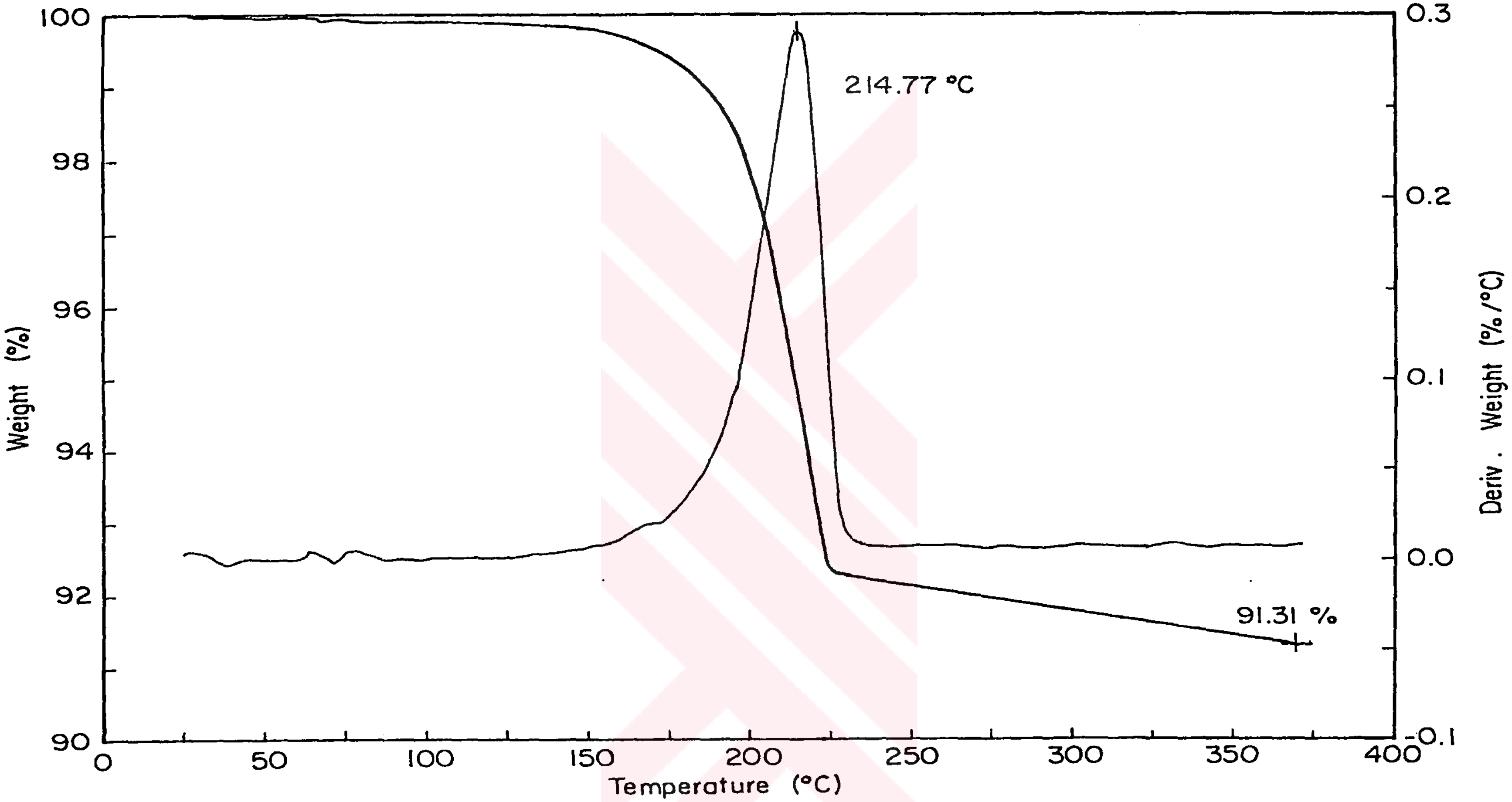


Figure 3.9.TGA spectrum of polymer obtained irradiation

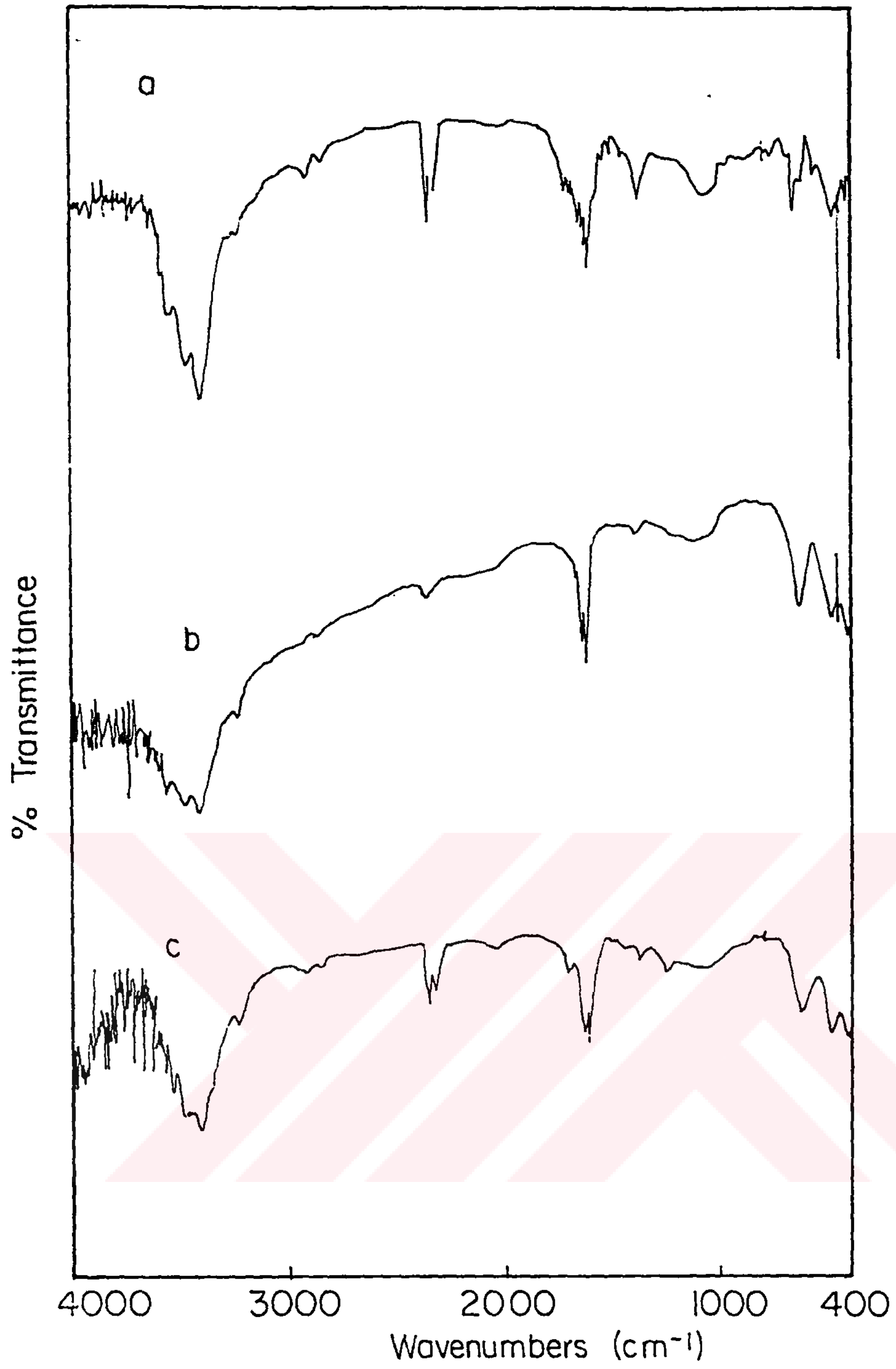


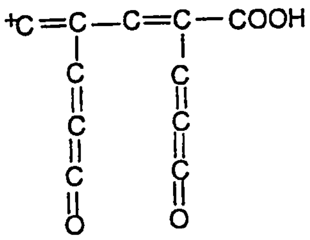
Figure 3.10. IR spectra of polymers treated a) 20 min, at 1000°C b) for 20 min, at 1050°C, c) for 20 min at 1200°C.

3.6. Mass spectral Investigation

Direct pyrolsis mass spectrometry(Dp-Ms) is clearly an appropriate instrument for both studying the mechanism of thermal degradation and chain structure determination of the polymer sample under investigation[66]. Direct pyrolysis results are used to identify the polymer and to elucidate the mechanism of polymerization.

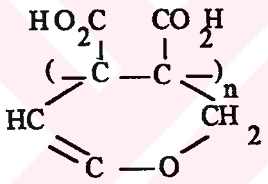
The mass spectra were recorded as a function of temperature continously. The monomer spectrum and polymer spectrum are shown in Figure 3.11 and Figure3.12 respectively. The assigned formulas of the most abundant monomer and polymer fragments are shown in Table 3.4, Table 3.5. The monomer spectrum indicated that there is a CO evolution when irradiation is applied and polymerization initiated after evolution of this group. Since the monomer fragment in the mass spectrum is not observed the monomer can easily decomposed giving CO to assume the the proper orientation for polymerization reaction. In the monomer spectrum, the peaks at 71.83, 75.83, 77.09 amu are the monomer fragments after CO_2 evolution. The peak of 93.84 amu indicates that it is the monomer fragment after CO evolution.That is indicated that if decomposition is continued, the fragments of cyclic side group is obtained. So, polymerization propagates by opening C≡C bond and side groups goes to cyclization. In the polymer spectrum, the assigned formulas of the most abundant ions having intensities 10-30 % of base peak are collected. However, it is impossible to conclude whether these fragments were produced during thermal decomposition or produced after ion formation due to dissociative ionization of thermal degradation products by 70eV electrons. In the polymer spectrum, the presence of peak at 17 amu showed that OH evolution. That group indicated that it most probably shows the oxygen in the side group cyclization. The base peak of 44 amu shows CO_2 evolution. Due to intense peak of CO_2 fragments in the mass spectrum of polymer, the COOH side group breaks up mostly as CO_2. The results are supporting the the conclusion derived from thermal investigations. When polymer is annealed at high temperature, etheric bond disappeared from IR spectrum. Since the monomer fragment exist in the polymer mass spectrum at 114 amu, this assigned to end group of polymer chain.

The 153, 197, 241 amu, are attributed to a different end groups. Some examples of end group are shown as



$HOOC-C\equiv C-COOH$

Furthermore presence of peak at 142, 194, 208, 221 amu can be attributed to the structure of the polymer as



The assigned structure can only be formed by CO or CO_2 elimination during irradiation of monomer. The mass spectrum of polymer and monomer showed that there is side group cyclization on polymer chain.

Table3.4. The assigned formulas of most abundant monomer fragments under 70eV.

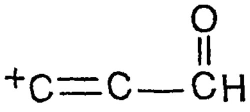
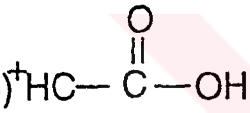
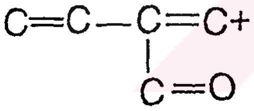
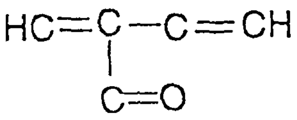
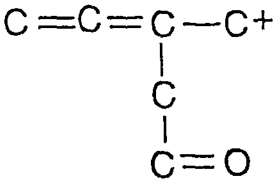
Assignedformulas	Peak Intensity
1) $C\equiv O$	28
2) $^{+}HC{=}O$	29
3) $O{=}C{=}O$	43
4)  $^{+}C{=}C{-}\overset{\overset{O}{\|}}{C}H$	53
5)  $^{+}HC{-}\overset{\overset{O}{\|}}{C}{-}OH$	60
6)  $C{=}C{-}\underset{\underset{C=O}{\vert}}{C}{=}C^{+}$	76
7)  $HC{=}\underset{\underset{C=O}{\vert}}{C}{-}C{=}CH$	78
8)  $C{=}C{=}\underset{\underset{\underset{\underset{C=O}{\vert}}{C}}{\vert}}{C}{-}C^{+}$	89

Table 3.5. The assigned formulas of most abundant polymer fragments under 70eV.

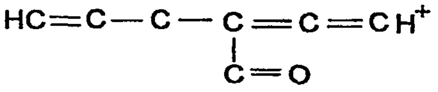
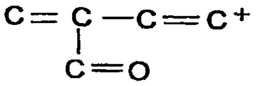
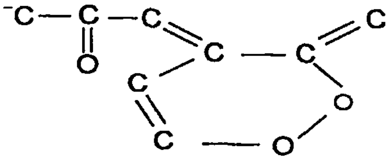
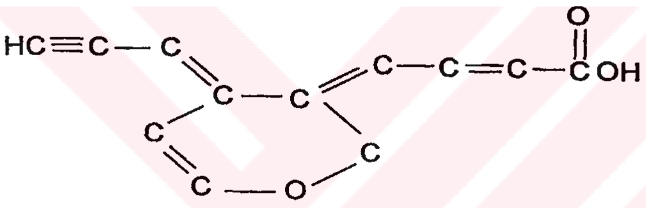
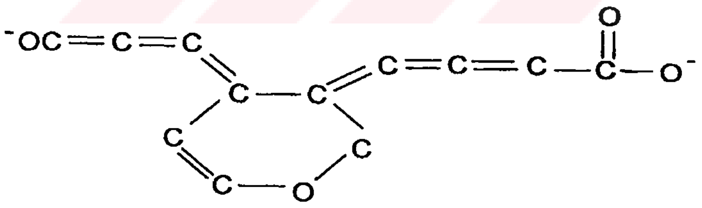
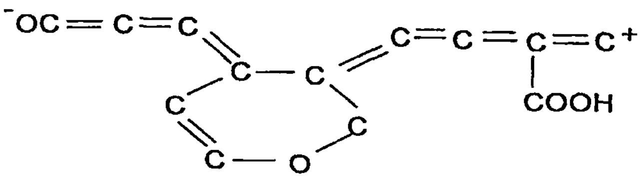
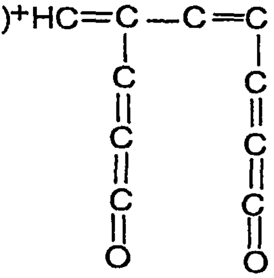
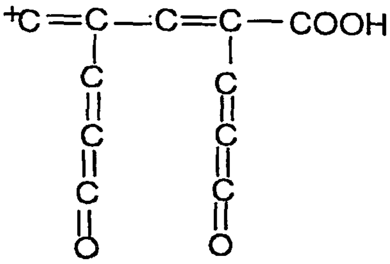
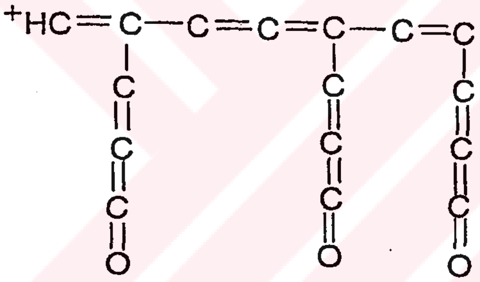
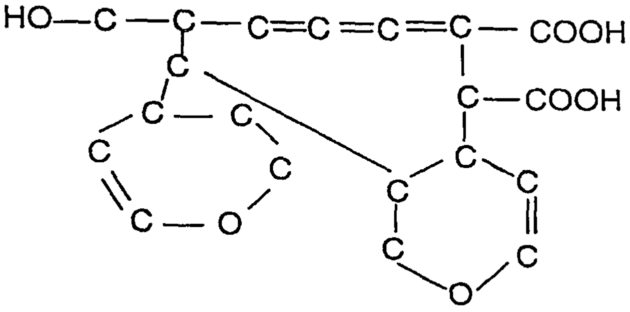
Assigned formulas	Peak Intensity
1) $O=C=O$	44
2)  $HC=C-C-\underset{\underset{C=O}{\mid}}{C}=C=CH^{+}$	91
3)  $C=\underset{\underset{C=O}{\mid}}{C}-C=C^{+}$	77
4) 	142
5) 	194
6) 	208
7) 	221

Table3.5 continued

8) 	153
9) 	197
10) 	241
11) 	355

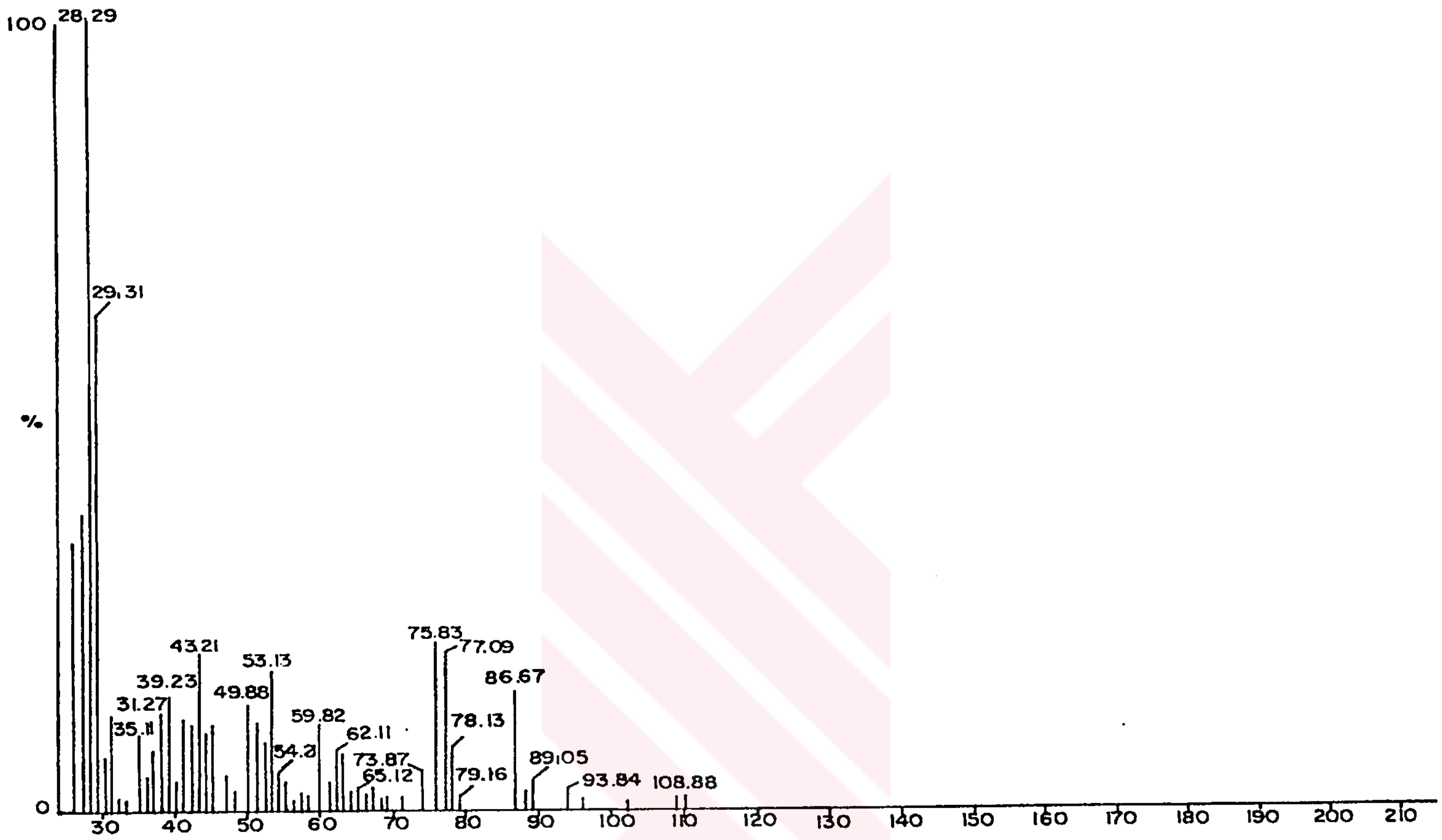


Figure 3.11. Mass Spectrum of monomer under 70eV

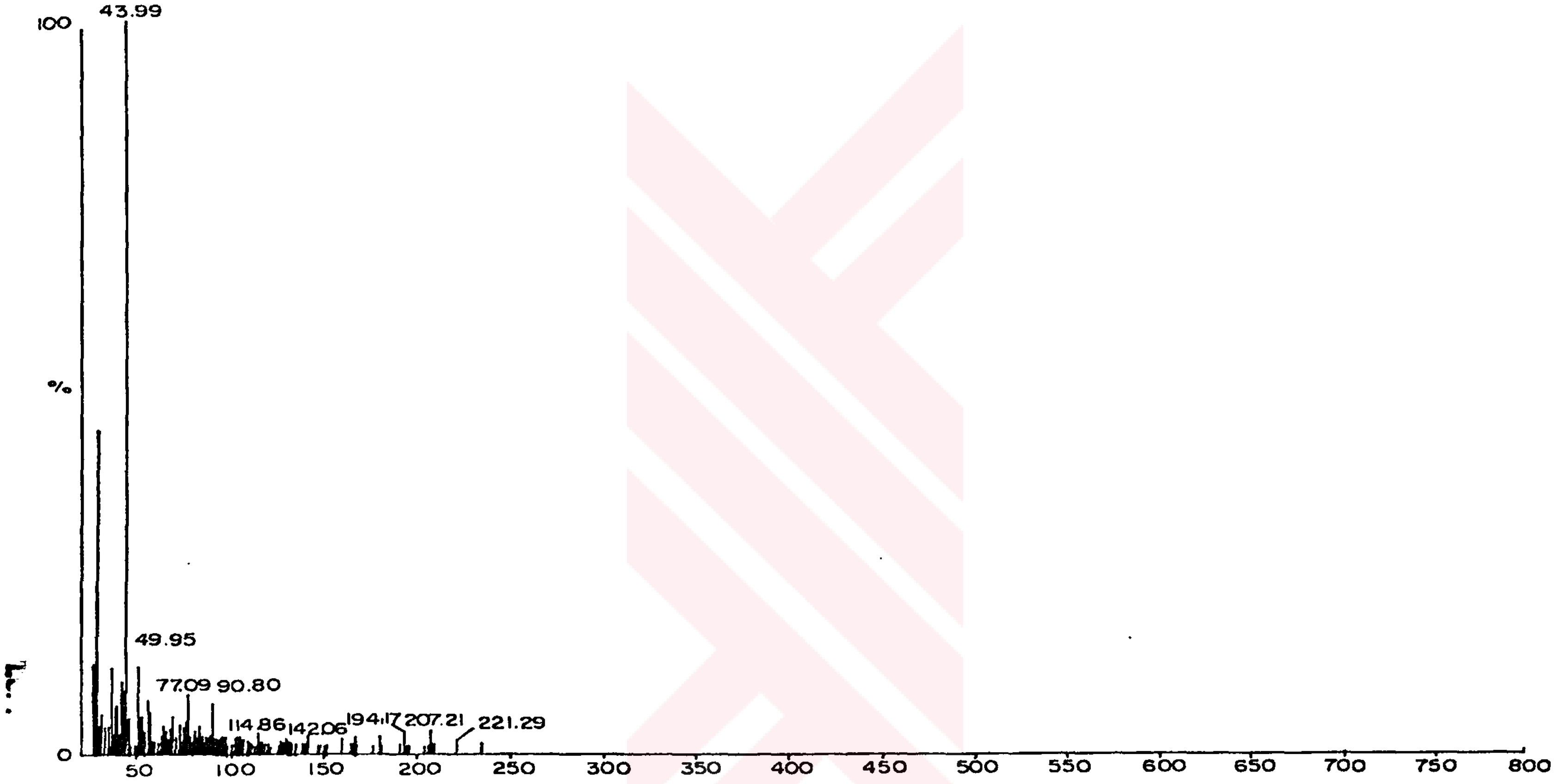


Figure 3.12.The Mass Spectrum of polymer under 70 eV

3.5. X-Ray Investigation

The powder X-Ray pattern of acetylenedicarboxylic acid is given in Figure 3.13. The Bragg angle θ, and relative peak intensities are tabulated in Table 3.6. From the square reciprocal d-spacing for monoclinic unit cell:

$$d^{*2}=a^{*2}h^2+b^{*2}k^2+c^{*2}l^2+2a^*c^*hl\cos\beta^*$$

The calculated and observed d-spacing were compared by least square analysis of 23 observed reflection and indexing of reflections were carried out by a computer programme. The found h k l indices with observed d_{obs}, and calculated d_{cal} values are also tabulated in Table 3.6.

The cell parameters are:

a= 15.185A°
b= 6.468A°
c= 4.858A°
β=91.84°
z=4
$D_{x\text{-}ray}$=1.59
$D_{reported}$=1.63

From the present reflections:

h k l all orders,

The space group of monomer is P2.

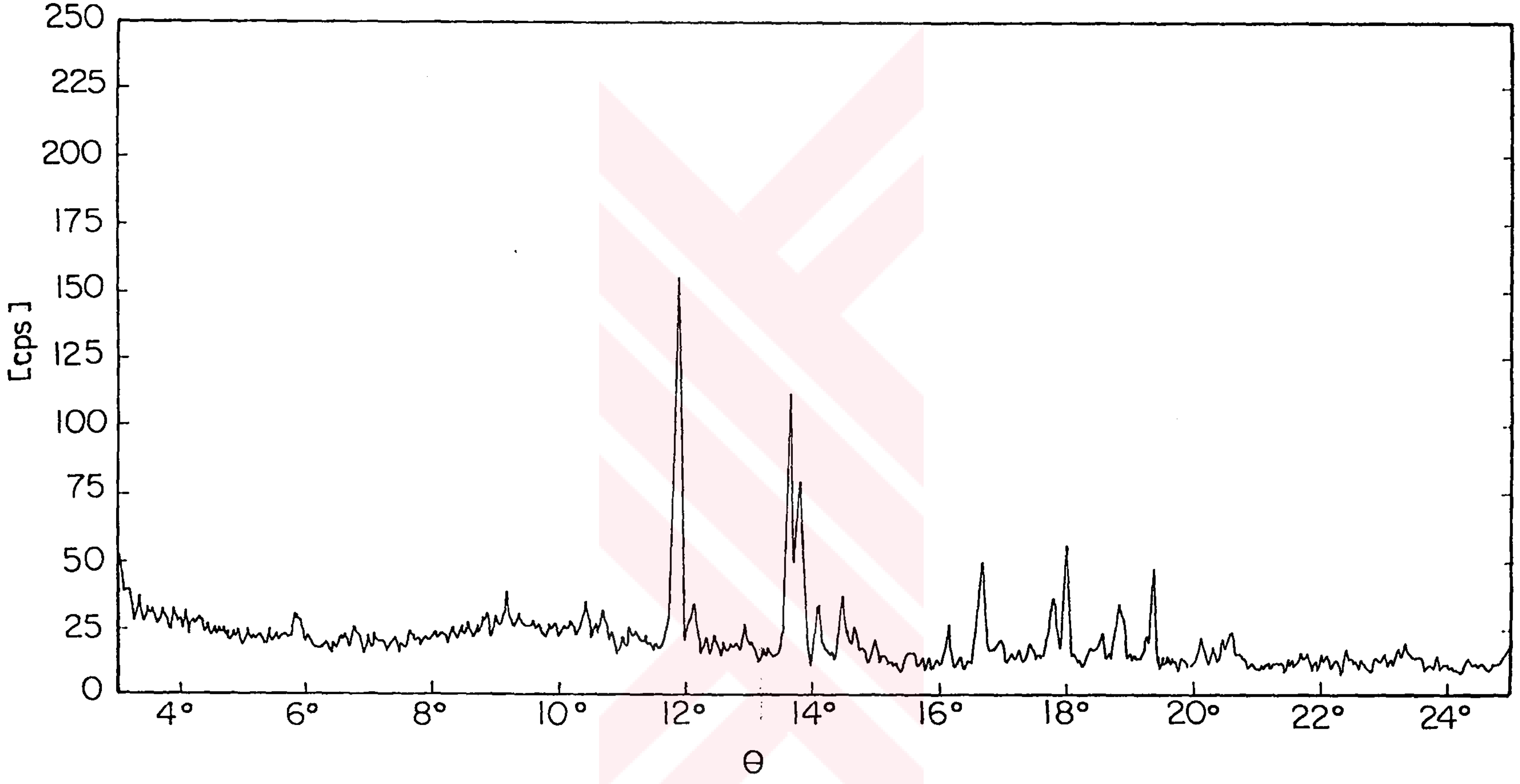


Figure3.13. X-Ray Powder Spectrum of monomer

Table 3.6. X-Ray Powder Analysis of Acetylenedicarboxylic acid

I/I_0	θ_{obs}	h k l	d_{obs}	d_{cal}
1	5.856	2 0 0	7.5575	7.559
2	6.790	0 1 0	6.5152	6.4550
9	9.180	0 0 1	4.8283	4.7619
6	10.71	2 0 -1	4.1450	4.029
100	11.89	1 1 1	3.7387	3.7003
5	12.47	3 0 -1	3.5673	3.4473
7	12.94	2 1 1	3.4399	3.2344
77	13.66	4 1 1	3.2617	2.6362
39	13.82	0 2 0	3.2247	3.2274
13	14.10	1 2 0	3.1619	3.1528
15	14.66	5 0 0	3.04296	2.9488
7	14.98	2 2 0	2.9800	2.9554
12	16.16	4 1 -1	2.7493	2.6699
23	16.69	4 1 1	2.6821	2.6363
3	17.57	3 1 -1	2.5513	2.8381
12	17.82	2 2 1	2.5170	2.4427
6	18.58	1 0 -2	2.4175	2.4110
10	18.86	1 0 2	2.3829	2.2941
39	19.27	2 2 1	2.5228	2.4427
31	19.40	2 0 -2	2.3341	2.2811
5	20.13	1 1 2	2.2382	2.1617
5	20.32	4 2 -1	2.2182	2.1703
5	20.59	2 1 -2	2.1903	2.1462

The cell parameters and space groups reported by Benghiant[64].

a= 14.894A°

b= 6.420A°

c= 4.862A°

β=90.90A°

z=4

Space group $P2_1/n$

The agreement between the results obtained in this work and that of reported are good. The noticable difference is in space group. Since there are limited data in this work, most probably, the correct space group is $P2_1/n$.

The X-Ray powder spectrum of polyacetylenedicarboxylic acid obtained by irradiation under vacuum condition for 3 weeks, 3.5months, 6 months are given in Figure 3.14, Figure 3.15, Figure 3.16. Most of the polymers are amorphous, with some crystallinity. These crystalline peaks have the same peak position as that of monomer, but intensities are smaller and they are superimposed on amourphous peaks of polymer.

The polymer spectrum obtained under vacuum condition for 3.5 months irradiation by Gamma source indicated that the polymer obtained is highly crystalline. The conditions can not be specified, but it can be due to recrytallization type or polymerization mechanism.

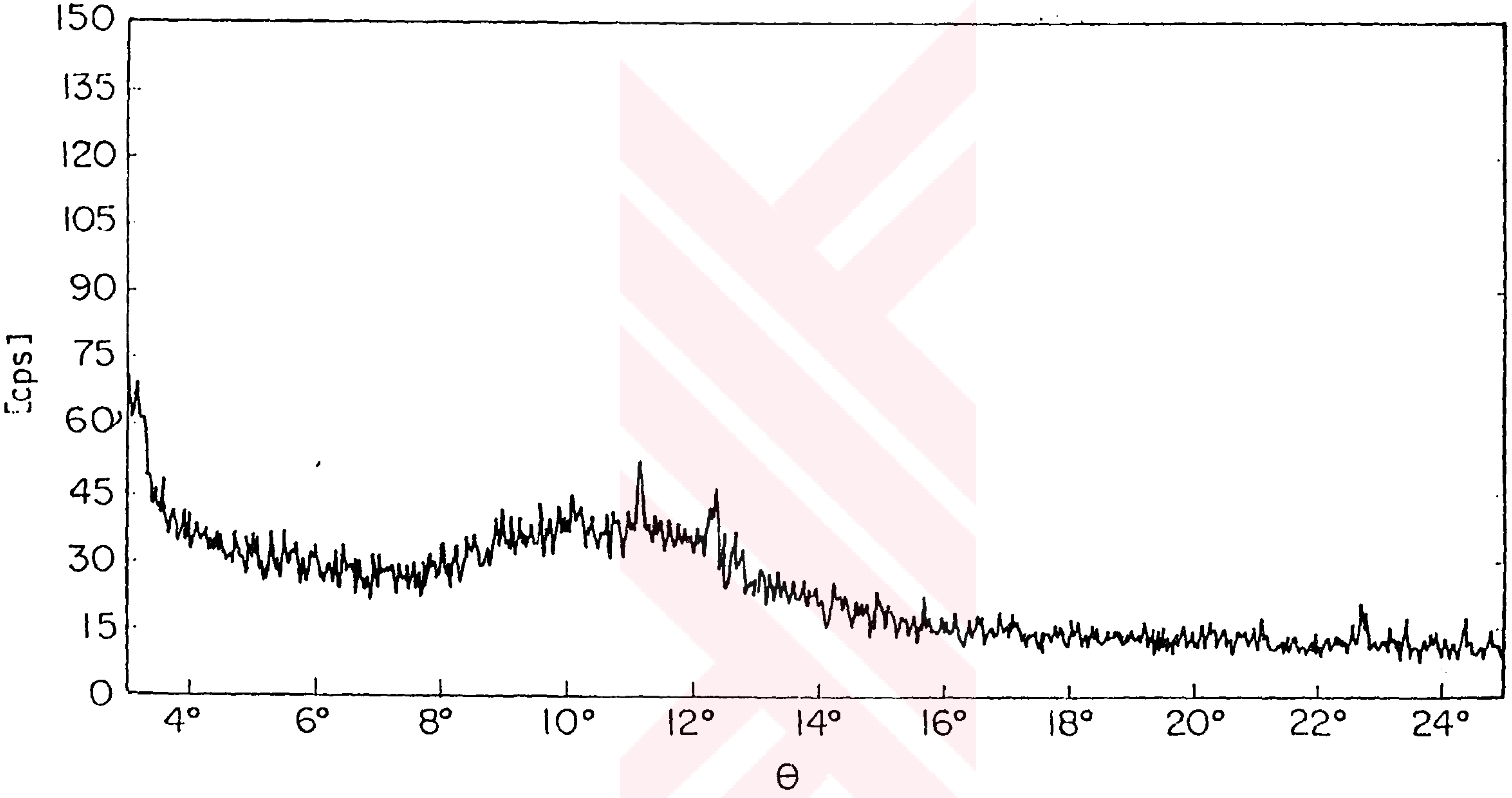


Figure 3.14. The X-Ray Spectrum of polymer obtained by irradiation for 3 weeks under vacuum condition

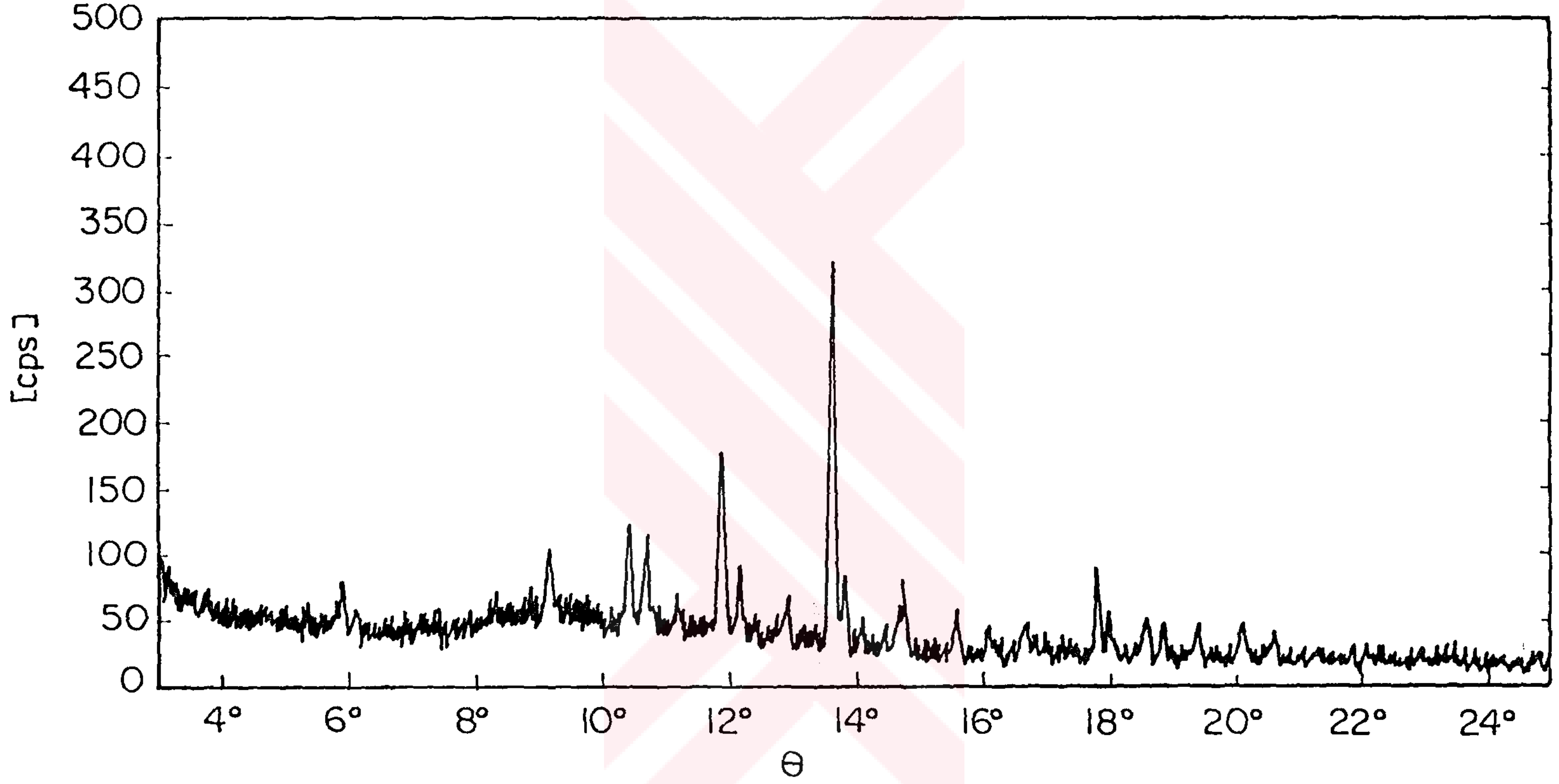


Figure 3.15. The X-Ray Spectrum of polymer obtained irradiation for 3.5 months under vacuum condition

Table3.7. The X-ray Powder Analysis of polyacetylenedicarboxylic acid

I/I_0	θ_{obs}	h k l	d_{obs}	d_{cal}
4	5.850	2 0 0	7.55755	7.559
7	7.870	0 0 0*	5.6256	-
19	10.71	2 0 -1	4.1450	4.029
8	11.190	3 1 0	3.9693	3.9103
43	11.890	1 1 1	3.7387	3.7003
15	12.160	0 0 0*	3.6569	-
6	12.890	3 0 1	3.4530	3.3932
100	13.630	4 1 0	3.2688	3.1943
18	13.820	0 2 0	3.2247	3.2274
14	14.74	5 0 0	3.0275	2.9412
7	15.58	0 0 0*	2.8680	-
7	16.67	4 1 1	2.6852	2.6405
17	17.78	2 2 1	2.5225	2.4427
5	18.60	1 0 -2	2.4150	2.4110
7	18.87	1 0 2	2.3817	2.2941
6	20.10	1 1 2	2.2414	2.1617

* this data could not be indexed

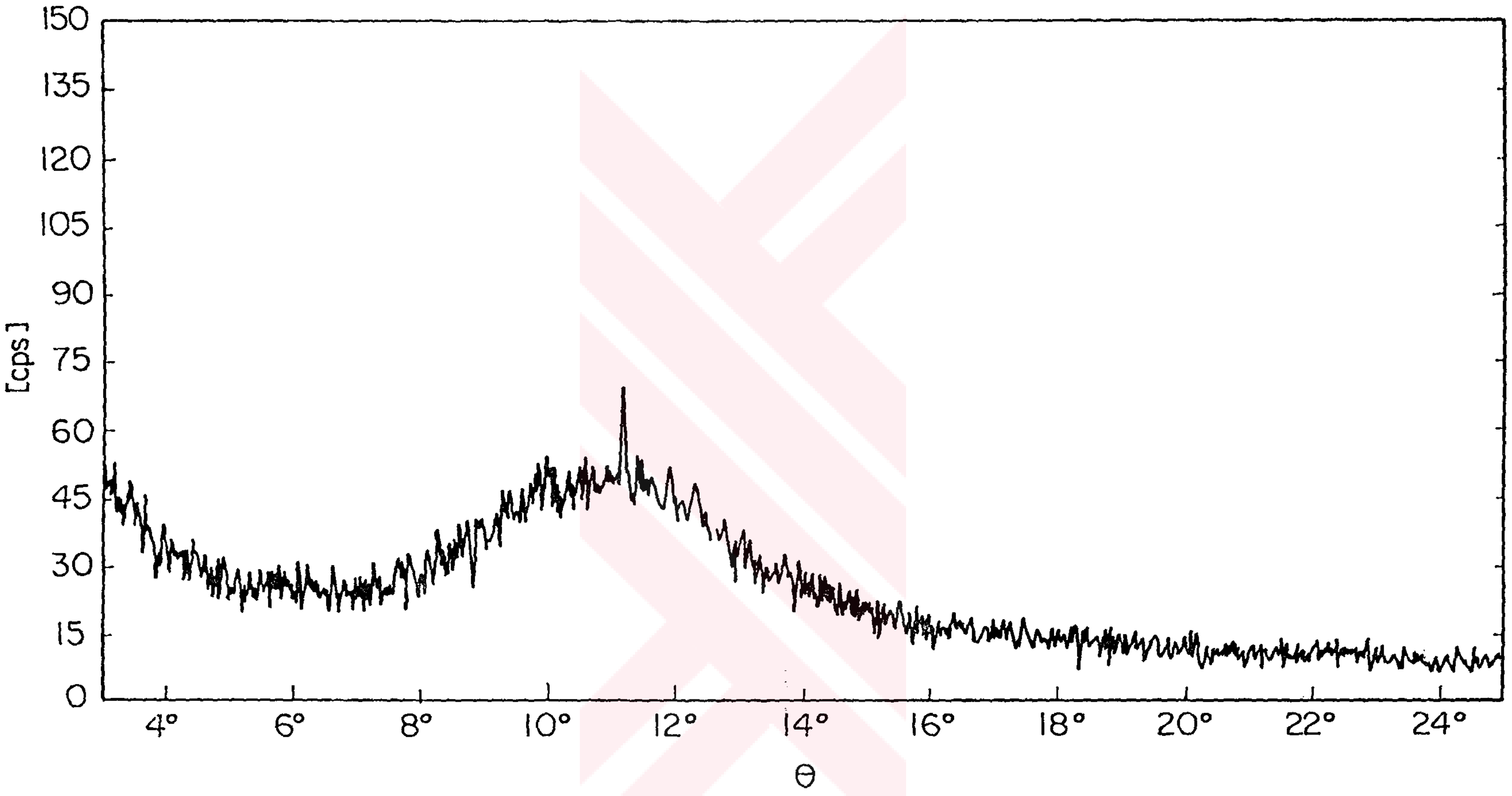


Figure 3.14 The X-Ray Spectrum of polymer obtained by irradiation for 6 months

The powder diffraction data for crystalline polymer is seen in Table 3.7. By using the computer programme, the crystal structure is indexed. But some of the peaks did not fit to the indexed structure. For example 16 peaks are observed and 13 peaks fitted to the indexing pattern, however, 3 peaks did not. This could be expected, since polymer, even though crystalline, is not a simple compound. There migth be another fraction with different chain and molecular structure. The cell parameters of the polymer are as follows:

a= 15.155A°
b= 6.455A°
c= 4.862A°
β=91.65°

The resultant values are very similar to the values obtained for monomer. Thus, the polymer is crystalline and polymerization follows a topotactic reaction mechanism.

The X-Ray powder spectrum of polymer obtained irradiation in open air for 3 months is shown in Figure 3.17. Polymer is partially crystalline, but the percentage of crystallinity is low. The peak positions are the same as that obtained for crystalline polymer.(Figure 3.15)

The X-ray powder spectrum of polymer - monomer mixture, the residual monomer are shown in Figure 3.18, Figure 3.19 respectively. The X-Ray Spectrum of polymer-monomer mixture before seperation indicated that the spectrum showed only monomer peaks. Since monomer peak intensity is much higher than that of polymer intensities. Polymer peaks if exist remained under the monomer peaks. The X-Ray spectrum of residual monomer showed that the monomer which is not polymerized, retained its structure during polymerization. Therefore, monomer molecules that does not give CO will not polymerize.

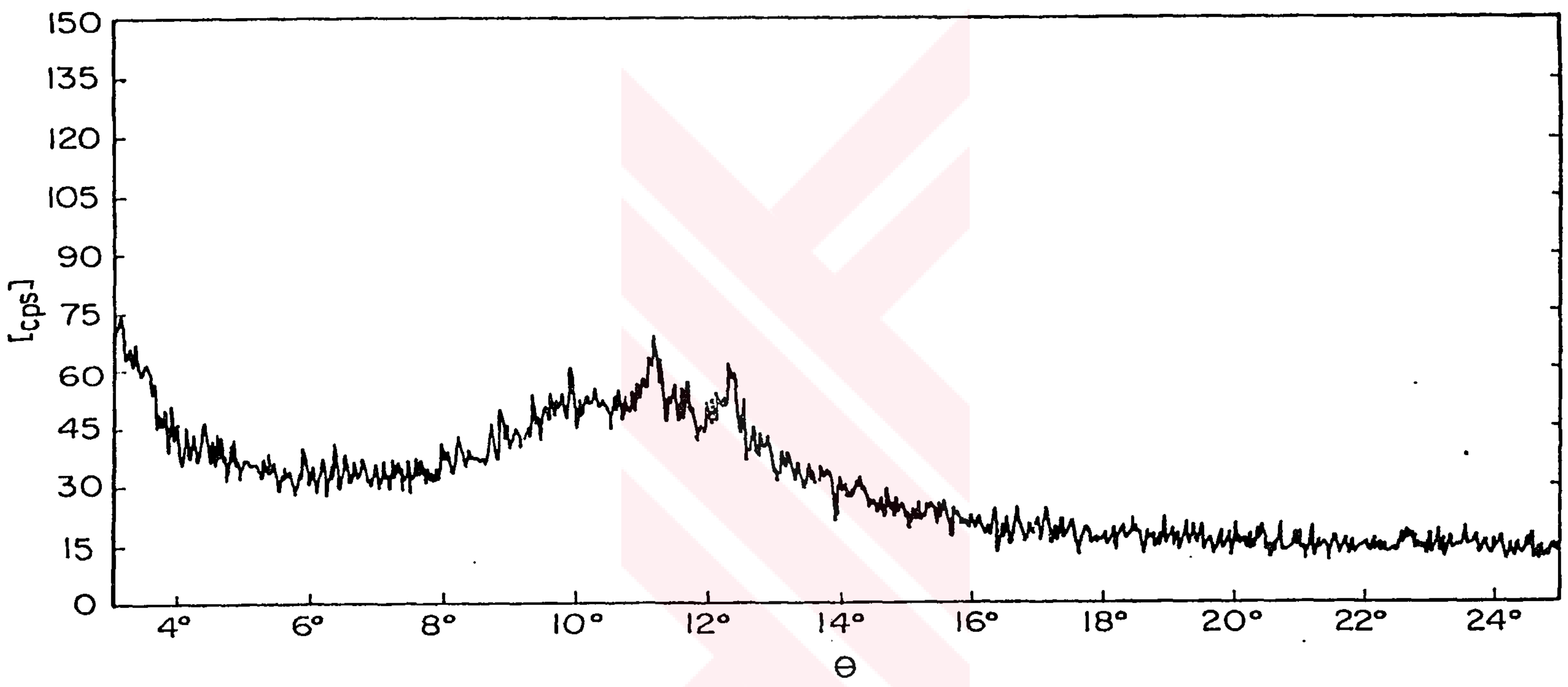


Figure 3.17. The X-Ray Spectrum of polymer obtained by irradiation in air condition for 3 months.

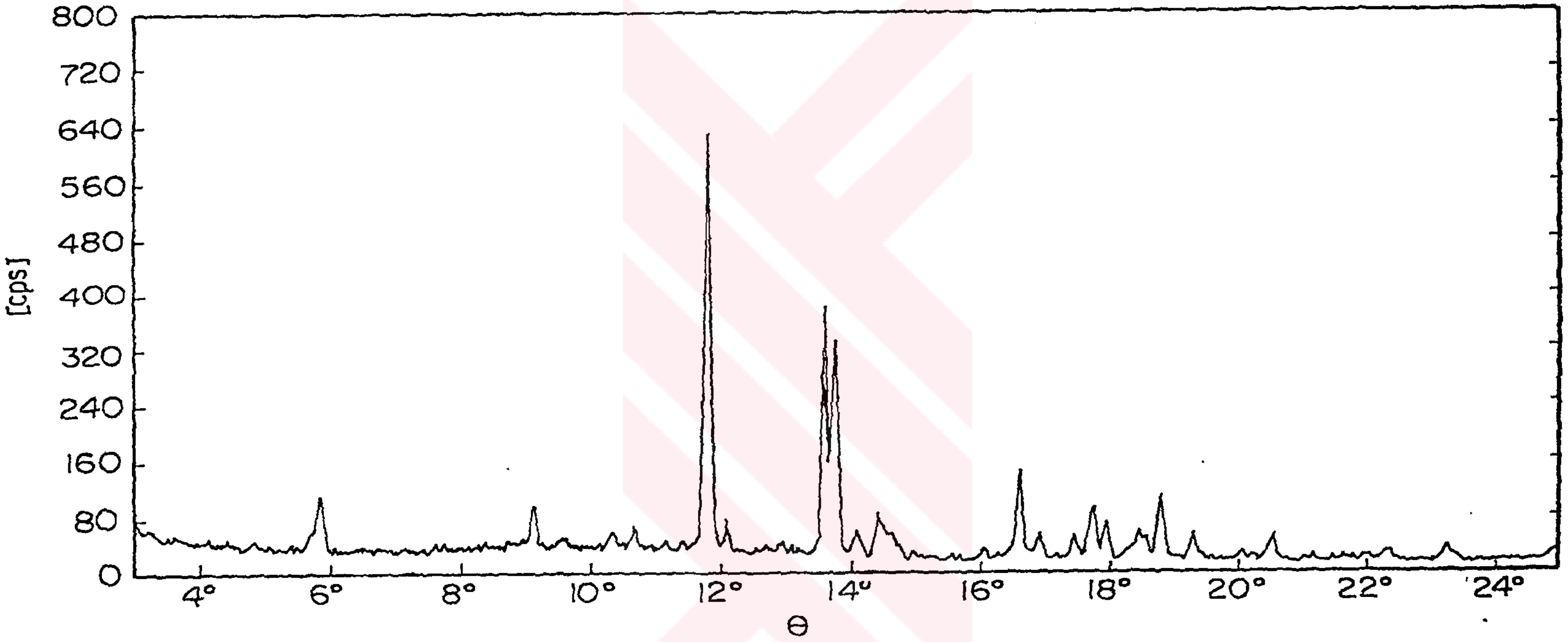


Figure 3.18.The X-Ray Powder Spectrum of polymer and monomer mixture

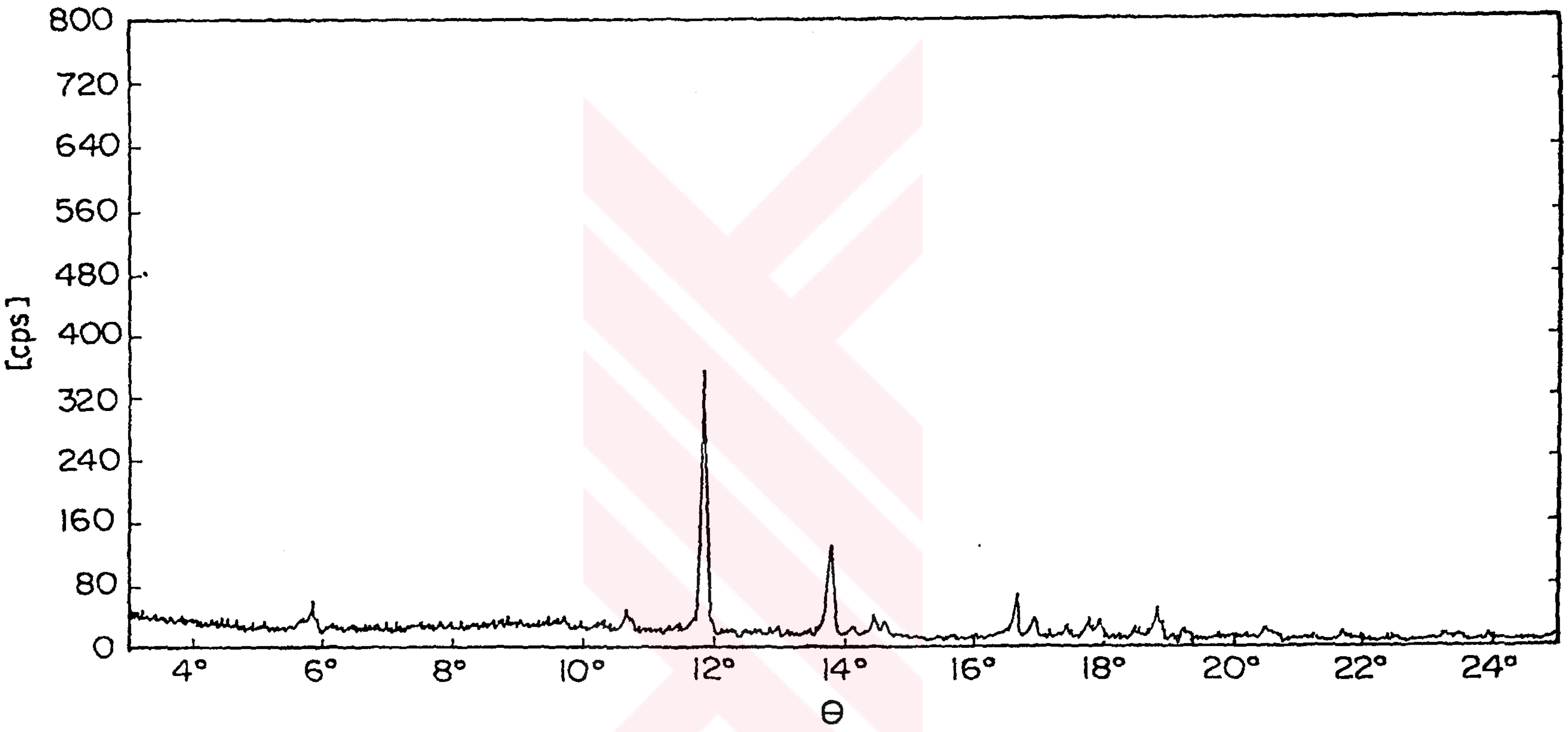


Figure 3.19. The X-Ray Powder spectrum of residual monomer

3.6. Nuclear Magnetic Investigation

The NMR spectra of monomer, polymer are shown in Figure 3.20, Figure 3.21. In the monomer spectrum, carboxylic group is observed at 155 ppm and C≡C bond peak is at 78 ppm . But in the polymer spectrum, all peaks are assigned to the solvent peaks. One point is that intensity of carboxylic peaks is higher than CF_3 peaks as if in solvent spectrum. This may indicate that the polymer carboxylic group is overlapped with solvent peaks. However, the polymer is slightly soluble in solvent and therefore it is not possible to make any reasonable comment on the polymer structure that can be deduced from ^{13}C-NMR spectrum. In order to get good result a solid-state ^{13}C-NMR spectrum of polymer will be taken in future.

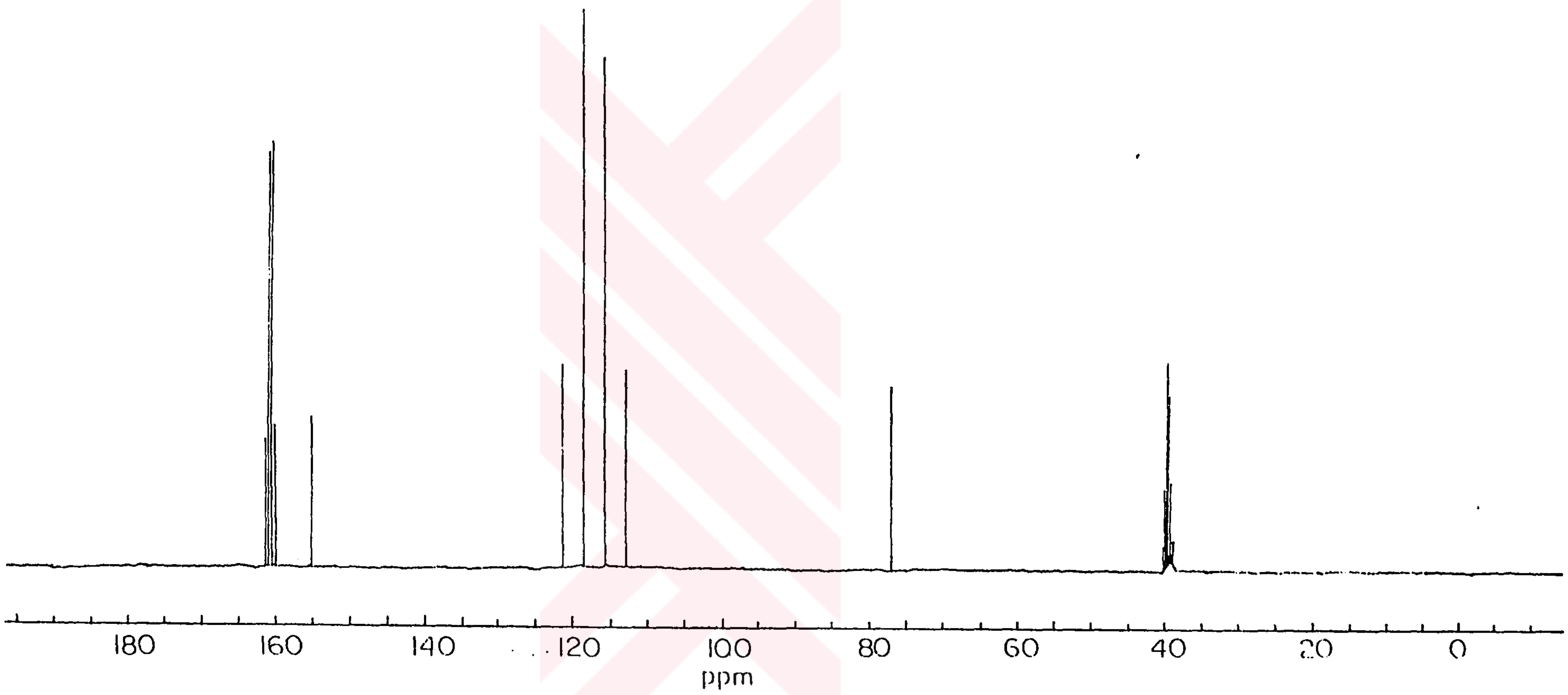


Figure3.20.The NMR spectrum of acetylenedicarboxylic acid

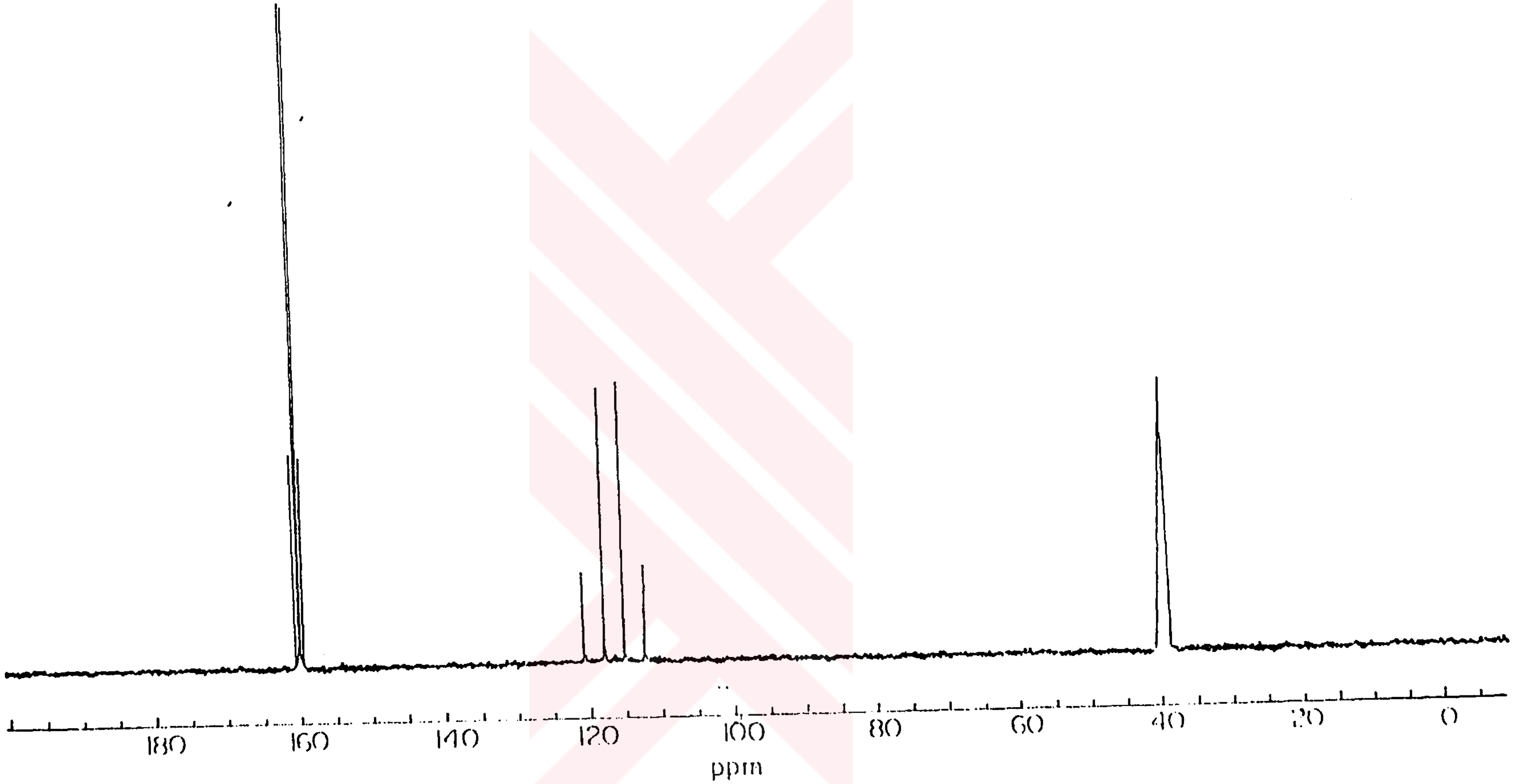


Figure 3.21. The NMR spectrum of polyacetylenedicarboxylic acid

CHAPTER IV
CONCLUSION

Radiation induced solid state polymerization was carried out in open atmosphere and under vacuum condition. The behavior of two conditions is a typical trend for polymerization following autocatalytic kinetics. The behavior of intrinsic viscosity with percent conversion does not change regularly.. According to GPC result, the polymer molecular weight distribution is narrow and it is a monomodel. Unfortunately, the standarts were not available to prepare calibration curve for calculation of polymer molecular weight. Since polymer is not soluble in any common solvent, we couldn't try other methods e.g, cryscopic methods, ligth scattering.

Infrared investigation indicated that intensity of C=O peak absorptions and also intensity of C≡C peak absorption decreased in the polymer spectrum. An intense cyclic etheric C-O-C bond stretching is appeared in the polymer spectrum. This is an indication of side group cyclization in the polymer chain.

UV analysis showed that there is a conjugation in the polymer chain since the peak position of monomer is retained but shifted slightly to higher wavelenght and showing a shoulder. This is in good aggrement with reported results[54].

Mass spectroscopic results also supported that there is a side group cyclization in the polymer chain.

Thermal behavior of polymer samples have been studied by DSC, TGA, MS and applying high temperature. DSC thermogram of monomer showed that monomer shows an exothermic peak at 204 °C, which can indicate that there is a phase change to a new crystal structure. DSC thermogram of polymer gives a T_g value of 157.08°C with no melting or decomposition up to 350°C. The high T_g value for polymer is due to the rigid structure of it.

TGA thermograms of monomer showed that the decomposition temperature of monomer is 226.05°C and weight lost 91%.. But, for the polymer thermogram, the decomposition maximize at 214°C and total weight loss is about 10%. High temperature studies indicated that polymer is thermally stable, it is not decomposed even if at 1200°C. IR investigations at high temperatures study showed that polymer goes to aromatization.

Conductivity measurements showed that the polymer conductivity is very low in the range of MΩ level. Even if it's doped with iodine vapor the conductivity changed slightly. Polymer chain contains aromatic side groups cyclization which can also decrease conductivity.

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