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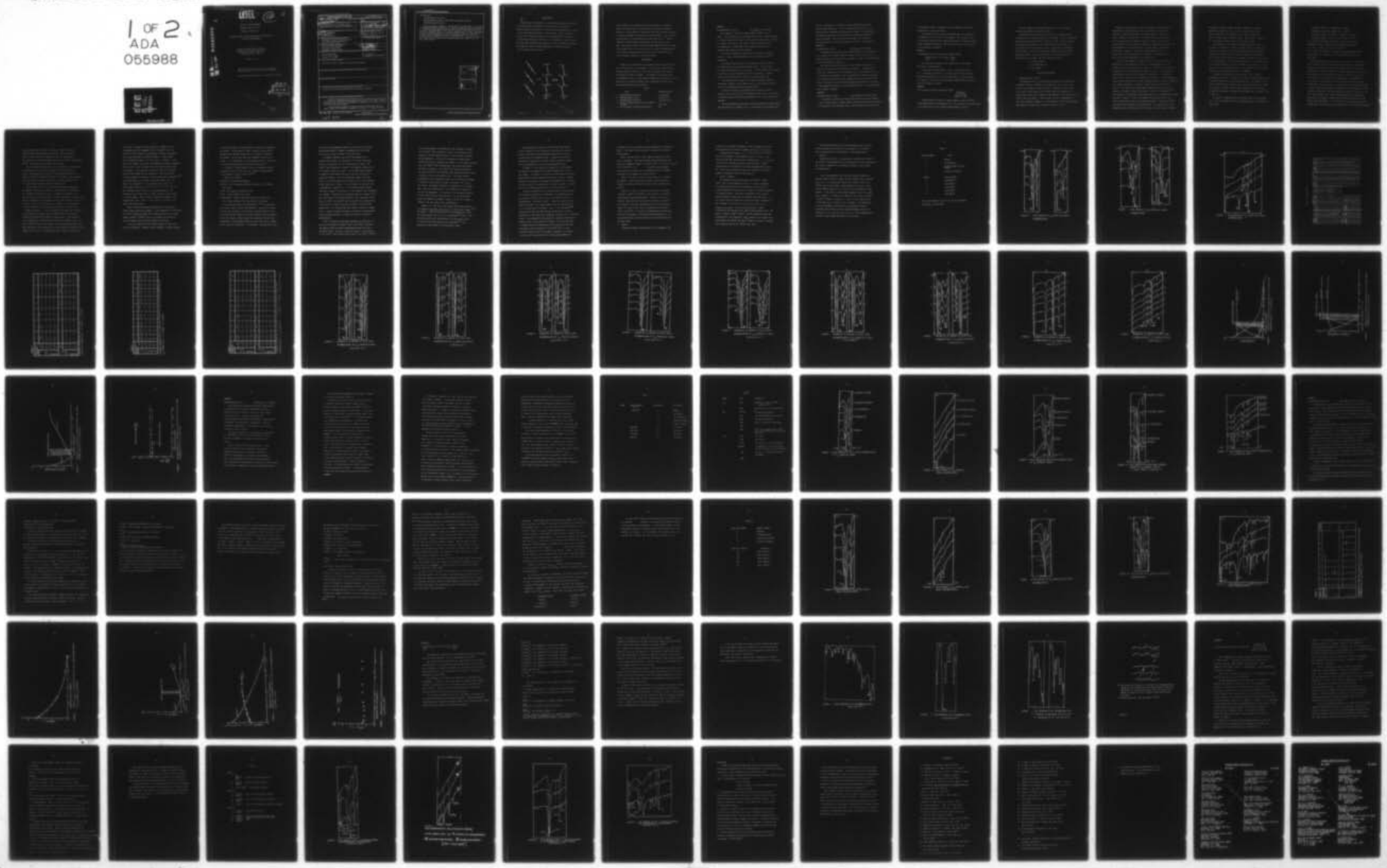

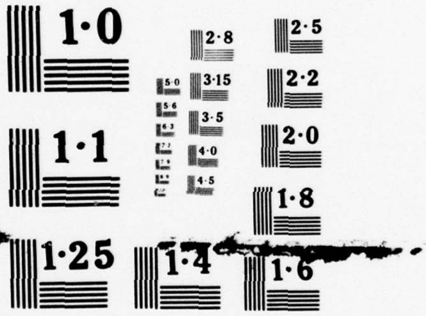
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INFRARED STUDIES OF THE SOLID STATE POLYMERIZATION OF DIACETYLENE MONOMERS

by

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Infrared spectroscopic investigation of the solid state polymerization of a number of conjugated diacetylenes has been done and a number of bands have been used to follow the polymerization mechanism, side chain packing, morphology and phase changes.

A solid solution through the entire range of polymerization and a phase change from a monomer rich phase to a polymer rich phase has been

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observed with

Heptadecadiyne-2,4-Acid-1

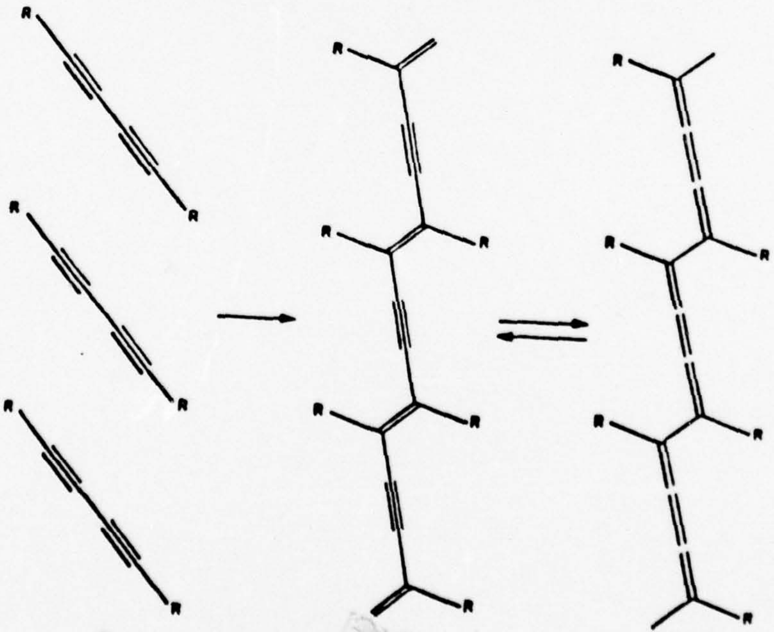
Heptadecadiyne-2,4-OL-1 (Only after prolonged treatment)

Heptadecadiyne-4,6-Acid-1

Using the bands at 2030cm^{-1}, 1590-1600cm^{-1} and 805-870cm^{-1} the presence of oligomers has been observed in all the as polymerized samples excepting o,o'-bis phenyl gluterate diacetylene (BPG) and 5,7-dedecadiyne-diol-1,12-bis phenyl urethane (TCDU). The soluble oligomers have a major contribution from the butatriene structure. Poly BPG and poly TCDU also have been seen to have a major contribution from the butatriene structure. The other polymers have an acetytenic backbone. Excepting BPG a complete reaction of all monomer after a given dose of radiation has been observed with all other diacetylenes.

INTRODUCTION

Spectroscopic investigation of substituted conjugated diacetylenes and polyacetylenes and polyacetylenes dates back to the 1920's. However detailed investigation of the solid state polymerization of many of these conjugated diacetylenes is more recent. Single crystals of many of these diacetylene monomers can be polymerized by the action of (i)[1] thermal annealing; (ii)[2] light (u.v. irradiation); (iii)[3] ionizing radiation and (iv)[4] mechanical sheer. Wegner[1] and his co-workers have shown that these diacetylenes undergo 1:4 addition reactions according to the following reaction scheme:



I III II

Thus according to this reaction scheme the polymer is a resonance hydrid of II(butatriene or cumulene) and III(acetylenic structure). However it is not possible to generalize the actual molecular structure of the final polymers from different starting monomers. X-ray structure determination of a few polydiacetylenes have been done.[2-5] However detailed I.R. spectroscopic analysis was not done prior to this work. The present research has convincingly demonstrated that a number of key bands in the I.R. can be used to (i) follow the polymerization, (ii) structural changes during the solid state polymerization, and (iii) electronic structure of the final polymer.

EXPERIMENTAL

Table 1 gives the names of the conjugated diacetylenes that were used in this research. The monomers 1,2,3, and 5 were obtained from Professor Wegner's group at the Institut fur Makromolecular Chemie, Universitat Freiburg, W. Germany. The monomer 4 was obtained from Dr. Baughman's group at Allied Chemical Corporation, New Jersey (U.S.A.). Hereafter all the above compounds will be described by using their abbreviated names as given in Table 1.

TABLE 1

	Name	Abbreviated Name
1.	Heptadecadiyne-2,4-Acid-1	C_{12}-Diyne-AC
2.	Heptadecadiyne-2,4-OL-1	C_{12}-Diyne-OL
3.	Heptadecadiyne-4,6-Acid-1	C_{10}-Diyne-C_2-AC
4.	Poly(5,7-dodecadiyne-diol-1,12-bis phenyl urethane	Poly TCDU
5.	0,0' bis phenyl gluterate diacetylene	BPG

MONOMER 1

Heptadecadiyne-2,4-acid-1 $CH_3-(CH_2)_{11}-C{\equiv}C-C{\equiv}C-COOH$

This monomer is soluble in common organic solvents such as hexane. In the solid state it is highly reactive and a slight exposure to ordinary light will initiate the solid state polymerization. However, it is stable in solution. The solid is stable in the dark and at low temperatures. Under normal crystal growth conditions from solution large crystals are not obtained.

This monomer undergoes polymerization very rapidly by ordinary light, u.v. light, thermal annealing, X-ray irradiation and $C^{60}-\gamma$ irradiation.

For infrared spectroscopic work the monomer solution in hexane was added dropwise onto potassium bromide powder. Care was taken to prevent polymerization of this material. The KBr pellets were prepared in the dark at constant temperature (15°C) and humidity. The KBr pellets were vacuum dried in a desicator overnight before use.

The infrared work was done with a Fourier Transform (Digilab) instrument. Exposure of the sample to the I.R. beam during scanning did not cause appreciable further polymerization.

Pellets for infrared investigation were irradiated by $Co^{60}-\gamma$ radiation with a dose rate of 0.135 megarad an hour and the I.R. spectra at different doses were recorded sequentially up to a total dose of 120 Megarads.

The γ-irradiation was carried out with two samples, one under vacuum and the other one in presence of air. No difference in the spectra were noticed. The monomer is colorless but with polymerization turned blue and then blue-violet. The "as polymerized" sample after a 120 megarad dose was powdered and extracted with hexane. By microfiltration and repeated extraction it was separated into insoluble polymer and soluble oligomers. Both the fractions were made into KBr pellets and vacuum dried in a desicator overnight for the I.R. investigation.

MONOMER 2

Heptadecadiyne 2,4-OL-1 $CH_3-(CH_2)_{11}-C\equiv C-C\equiv C-CH_2OH$

This monomer has the same general chanracteristics as the monomer 1. It is soluble in all common organic solvents, stable in solution, but highly reactive in the solid state on exposure to light. On polymerization the colorless monomer turns red.

For infrared studies KBr pellets of the monomer were made in the dark in the same way as was described for monomer 1. The monomer KBr pellet was γ-irradiated at room temperature and in the presence of air to a total dose of 120 megarads. The "as polymerized" sample was separated into insoluble polymer and soluble oligomer fractions by extraction with hexane. The spectra for the following samples were recorded, 1) monomer, 2) intermediate dose sample, 3) as polymerized sample, 4) insoluble polymer and 5) soluble oligomers.

MONOMER 3

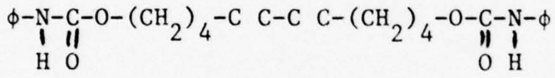
Heptadecadiyne-4,6-acid-1 $CH_3-(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_2-COOH$

This monomer, which has the same general characteristics of monomers 1 and 2 is also soluble in common organic solvents as hexane and chloroform. It crystallizes in the monomeric state from a solution in petroleum ether as rectangular flakes of macroscopic size and undergoes solid state polymerization to give red flakes.

This monomer has also been studied sequentially as a function of γ-irradiation to a total dose of 120 megarads. The spectrum of the as polymerized sample has been compared with those of insoluble polymer, soluble oligomers and monomer. KBr-pellets were made in the same way as was described for monomer 1.

MONOMER 4

5,7-dodecadiyne-diol-1,12-bis phenyl urethane (TCDU)



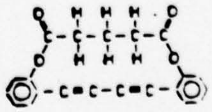
$$\phi-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{O}-(\mathrm{CH}_2)_4-\mathrm{C}\ \ \mathrm{C}-\mathrm{C}\ \ \mathrm{C}-(\mathrm{CH}_2)_4-\mathrm{O}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-\phi$$

This particular diacetylene was studied only in the polymer form after a 50 megarad dose.

A macroscopic red-gold single crystal of poly(TCDU) used by Drs. V. Enkelmann and Lando[2] in a previous study for X-ray crystal structure determination was used for unpolarized I.R. and polarized I.R. studies. The crystal was ground, made into a KBr pellet and vacuum dried for further I.R. study.

MONOMER 5

0,0'-bis phenyl gluterate diacetylene (BPG)



The BPG monomer is soluble in common organic solvents and forms needle shaped crystal of macroscopic size. The crystals can be polymerized in the solid state to give red-gold polymer-monomer crystals.

This is a highly reactive diacetylene and it was not possible to get a pure monomer for infrared studies.

A KBr pellet of an inactive crystal form of the monomer was used to observe the C≡C vibrational region of the monomer. The "as polymerized" sample was the one used by David R. Day[3] for crystal structure analysis. This sample was irradiated for 60 megarad and was then leached, but as found from the X-ray analysis, it has a composition of 65% monomer and 35% polymer. Another "as polymerized" sample was ground and then leached many times to obtain pure polymer. It was then made into a KBr pellet for I.R. study. The three samples used were

1) inactive monomer
2) as polymerized and
3) pure polymer

RESULTS AND DISCUSSION

1. Heptadecadiyne-2,4-Acid-1

Infrared spectra of C_{12}-Diyne-Ac were obtained in the region from 3100-450cm^{-1} and are presented in the Figures 1A, 1B, 1C, 1D, and 1E. The key to the figures is given in Table 2. Figures 2A, 2B(1), 2B(2), 2C(1), 2C(2), 2D(1), 2D(2), 2E(1) and 2E(2) give the sequential I.R. spectra from a dose of zero megarad to 120 megarads in the spectral regions A,B,C,D, and E of Figure 1. Table 3 gives the dose corresponding to a particular spectrum of Figure 2. In both Figures 1 and 2 the band symbols have identical values which are given in Tables 4,5, and 6.

Figures 3-5 give the plots of dose in megarad versus the intensity of absorption of some frequencies which are relevent to the study of conversion, solid solution formation and phase changes. Figure 6 is a plot relating to crystallinity. The data for the last four figures have been taken from the sequential spectra. Figure 1A contains well-defined bands at three frequencies 2955cm^{-1}(a), 2920cm^{-1}(b), and 2850cm^{-1}(c) representing the C-H stretching modes of the $CH_3-(CH_2)_{11}$ side chains. In spectrum 1 through 4 of the spectral series there is no major change except that the shoulder near b (2920cm^{-1}) corresponding to in phase C-H vibrations^6 decreases upon polymerization.

Figure 1B (2300-2000cm^{-1}) presents the C≡C vibrational zone for the monomer and for the polymerized samples. In spectrum number 1 for the monomer, there are two characteristic bands at d (2250cm^{-1}) and e (2160cm^{-1}). In spectrum 2 for the as polymerized sample, the band at e has completely disappeared and the band d has decreased in intensity to a considerable extent, while a strong band has appeared at f (2100cm^{-1}). In the sequential spectra series (Figures 2B(1), 2B(2)) a gradual decrease of band at 2250cm^{-1}(d) and a gradual increase of the band at 2100cm^{-1} with dose can be easily observed. The 2160cm^{-1}(e) band disappears completely after a dose of 35 megarad. The bands at 2250cm^{-1} and 2160cm^{-1} are due to the symmetric[56,63] ans asymmetric C≡C vibrational modes respectively in the monomeric diacetylene. The band at 2100cm^{-1} is due to the symmetrical vibrational mode of the central carbon-carbon bond in the polymeric backbone. Ideally the 2250cm^{-1} band should also disappear with polymerization. Its presence after a 120 megarad dose can be attributed to the presence of a small amount of monomer, but when the soluble oligomer fractionis studied in this region (spectrum 4, Figure 1B), there is only a slight indication of a band at 2250cm^{-1}(d) and no indication of a band at 2160cm^{-1}(e), which are characteristic monomeric bands. The spectrum 3 (Figure 1B) for the insoluble polymer shows a reduced 2250cm^{-1} band.

The appearance of the symmetric backbone vibrational mode in the polymer at a relatively low value of 2100cm^{-1} makes it evident that there is a very strong π-electron delocalization along the backbone. In going from monomer (two C≡C bonds) to polymer (an equivalence of one C≡C bond in every repeat unit) the number of bands has reduced from 2 to 1 and because of electron delocalization the force constant of this C≡C bond has decreased to a value of 2100cm^{-1} in the polymer. At this point, it can be concluded that there is no detectable trace of monomer present in this system after a dose of 120 megarad.

In Figure 3 the intensities of the bands at 2250 & 2160cm^{-1} representing the amount of monomer and at 2100cm^{-1} representing the amount of polymer formed have been plotted against dose. The intensity of the 2250cm^{-1} band decreases constantly until it almost reaches zero, whereas the intensity of 2100cm^{-1} band increases continuously and at about a 35 megarad dose reaches a constant value at which time the 2160cm^{-1} band is about 0.

In Figure 1C ($2000\text{-}1550\text{cm}^{-1}$) the following features are observed:

(i) In all of the spectra the C=O stretching frequency is a doublet as given below:

1-monomer, $1700cm^{-1}$(e), $1670cm^{-1}$(g), $\Delta\nu=30cm^{-1}$.

2-aspolymer $1715cm^{-1}$(d), $1690cm^{-1}$(f), $\Delta\nu=25cm^{-1}$.

3-insoluble polymer, $1725cm^{-1}$(c), $1690cm^{-1}$(f), $\Delta\nu=35cm^{-1}$.

4-soluble oligomer, $1735cm^{-1}$(b), $1715cm^{-1}$(d), $\Delta\nu=20cm^{-1}$.

(ii) Excepting the monomer (spectrum 1) all the rest exhibit a considerably greater intensity for the higher frequency band.

(iii) The $\Delta\nu$ in each case is within $20-40cm^{-1}$.

(iv) In going from monomer to oligomers or higher molecular weight polymers there is an increase in the C=0 stretching frequency by about $30cm^{-1}$.

The C=0 doublets are not unusual in the solid state of carboxylic acids[7-11] where there are strong interactions between the -COOH groups. The greater intensity for the higher frequency bands in spectra 2,3,4 as compared to 1 implies disruption of hydrogen bonding with polymerization. The increase of the C=0 stretching frequency as mentioned in point iv can be related to a decrease in the concentration of H-bonding[7,12-14] or an increase in delocalization along the backbone and thus extensive conjugation of the C=0 electrons. In the spectra of such materials changes of crystal form, which influence the degree or type of H-bonding can result in marked differences in the C=0 frequency (as observed in this case) and, since these materials have a paraffin like packing of the $CH_3-(CH_2)_{11}$ side groups, the change in packing also will greatly influence the $-CH_2-$ bending and rocking modes. It is evident from the sequential spectra in Figures 2C(1), 2C(2) that the band at $1700cm^{-1}$(e) for the monomer disappears slowly after a dose of 37 mrad. The band at $1670cm^{-1}$(g) starts shifting slowly towards higher wave numbers. This observation makes it clear that after a substantial dose the composition of the system will be oligomer+polymers with a trace amount of undetectable monomer. The reasons can be summed up as follows:

The C=0 stretching frequency is very succeptible to the molecular environment and also is easily detectable in a minute amount of sample. The characteristic monomeric C=0 stretching frequency is a doublet at $1670cm^{-1}$(g,strong) and $1700cm^{-1}$(e,shoulder), which disappears and shifts slowly with dose and appears in a region representative of a high molecular weight, highly conjugated system.

One can argue that the C≡C stretching frequencies representing the monomeric form are still present at the doses where the monomeric C=0 stretching frequencies are gone. Following the sequential I.R. spectra one can see that the $2160cm^{-1}$ band for the monomer slowly decreases and then disappears at approximately the same dose (37 mrad, spectrum 17, Figure 9B 2) as for the C=0 stretching frequency. But the symmetric C≡C band at $2250cm^{-1}$ is still quite strong and may be present in the oligomeric material. On the other hand as the chain length increases the characteristic polymeric band at $2100cm^{-1}$ goes on increasing in intensity and becomes the strongest at higher doses. This phenomenon is also supported by a characteristic band for the polymeric form. The band at $1770cm^{-1}$, which at this moment is not definitely assigned to any particular motion, can be assumed to be a characteristic frequency for the $-(CH_2)_n$ group with n>4, in juxtaposition with a highly delocalized C≡C π-electron. This band has been observed in a number of polydiacetylenes and this assignment will be discussed later. The $1770 cm^{-1}$ (a) band appears as the monomeric $C=O$ band e disappears and g starts shifting its position towards d. These changes can be followed in Figure 2 C(1) and 2 C(2). In Figure 1 C this band is not present in spectrum 4 representing the soluble oligomers, which also do not show a significant triple bond character along the backbone. On the contrary it shows a strong $C=C$ stretching doublet[15-19] at $1650 cm^{-1}$(h) and $1630 cm^{-1}$(i). Thus the backbone of these oligomers are similar to the butatriene model compounds.[20-24] These bands appear as a shoulder in spectrum number 2 and 3 of Figure 8 C at $1630 cm^{-1}$(i). The intensity of this band at an early stage is different and lower than that at a later stage and the band might also be shifted to a different position. The appearance of $C=C$ bands and the $1770 cm^{-1}$ band may also be related to a phase change. These two sets of bands do not appear in the "monomer rich" phase. After a phase change to a "polymer rich" phase, these bands appear.

These $C=C$ bands are highly characteristic of low molecular weight polymer and soluble oligomers. In the oligomers the intensities of such $C=C$ vibrations exceed that of $C\equiv C$ and thus we see a strong doublet ($1650 cm^{-1}$, $1630 cm^{-1}$) but in the polymer the situation is just the opposite and the doublet appears as a shoulder.

It is to be noted that in the entire conversion range there are three components: monomer, soluble oligomers, insoluble polymer.

In the initial stages of polymerization all these three components are present. In and around the phase transition region soluble oligomers and insoluble polymer with a trace amount of monomer are present. In the final stage only oligomers and polymer are present. It is likely that the data presented above is indicative of the phase change observed by electron diffraction.[25]

In Figure 1 D (1550-1200cm^{-1}) and in the sequential spectra in Figure 2 D(1) and 2 D(2) there are a number of bands related to the packing of $-(CH_2)_n-$ with $n>4$.[26-32]

These are as follows:

a→1470cm^{-1}, CH_2 bending deformation.

b→1420cm^{-1}, Sh, CH_3 bending deformation related to the "monomer rich" phase.

c→1380, CH_3 bending deformation related

d→1350 to the "polymer rich" phase

p→1350-1180cm^{-1} region, progression bands due to coupled out out of plane rocking or twisting motions of CH_2 groups.

The progression bands are characteristic [32-40] of long chain fatty acids, esters, alcohols and paraffins. Excepting in the case of acids, the intensity of the bands are very much redcued. They are associated with coupled out of plane rocking or twisting motions of the $-CH_2-$ groups. These motions are associated with the trans arrangement of the methylene groups and a particular type of packing such as occurs in n-paraffins. In consequence, anything which interferes with this arrangement modifies the spectrum in this region. During polymerization a dramatic disappearance of these bands occurs as can be seen in Figure 2 D(1) and 2 D(2).

As normally observed, the $1470cm^{-1}$ band appears with a shoulder and in Figure 1 D (spectrum 1) it is quite strong and sharp but in spectrum 2,3,4 it is weak and not as sharp. The $1420cm^{-1}$ band in spectrum 1 (Figure 1 D) disappears completely as can be seen in spectra 2,3, and 4. On the other hand the bands at $1380cm^{-1}$(c) and $1350cm^{-1}$(d) can be seen only in spectra of polymerized samples. In the as polymerized sample (spectrum 2 Figure 1 D) the broad band d has c within it, but in the insoluble polymer (spectrum 3, Figure 1 D) the two bands are separated with c appearing as a shoulder of d. In the hexane soluble oligomer (spectrum 4, Figure 1 D) the band c is the strongest with d appearing as a shoulder. Considering the sequential spectra in Figures 2 D(1) and 2 D(2) there is a continual decrease of the intensities of the bands at $1470cm^{-1}$ and $1420cm^{-1}$ with the progress of polymerization. After a dose of 18 Mirad (spectrum 13, Figure 2 D(2)) the band appears with c as a shoulder and after further conversion c merges into d. During the gradual increase of the band d, the progression bands p gradually decrease to almost zero with the progress of polymerization.

A plot of intensity versus dose following the sequential I.R. spectra of the bands at $1420cm^{-1}$, $1470cm^{-1}$ and $1350cm^{-1}$ indicates the region at which the phase transformation between the solid solutions occurs. This plot is given in Figure 4. The intensity of the $1470cm^{-1}$ band decreases with respect to the band at $1350cm^{-1}$, but with the progress of polymerization the integrated intensity of the $1470cm^{-1}$ band increases to a point in the transition zone (Figure 4) and then remains constant in the new phase throughout the polymerization. Thus with the progress of polymerization, starting from the zero megarad dose (Figure 4) to the phase transition zone, the $1470cm^{-1}$ band corresponding to CH_2 bending deformation increases in intensity. The $1420cm^{-1}$ band rapidly decreases to zero and the $1350cm^{-1}$ band increases with polymerization and reaches a constant value in the transition zone. The almost complete disappearance of the progression bands can be explained by assuming a reduction of order and/or a change in packing of the $-(CH_2)_n$ side chain. The change in packing is considered to be the reason here. That the crystallinity is not reduced will be evident in the next few paragraphs. The increase in the integrated intensity of the $1470cm^{-1}$ band and the splitting of the CH_3 deformation modes into $1350cm^{-1}$ and $1380cm^{-1}$ supports the idea of a change in packing of the side chains after polymerization.

Figure 1 E, 2 E(1) and 2 E(2) contain other bands related to the packing of CH_3-$(CH_2)_n$ side chain in the 1200-$450cm^{-1}$ region.[33-35] The doublet $750cm^{-1}$(d) and $720cm^{-1}$(e) are characteristic bands for $(CH_2)_n$ groups, with $n>4$, in the crystalline[36-39] state. This vibration arises from a rocking mode of the CH_2 groups (and is not strictly a skeleton mode) and the vibrations[36,38] are generally at right angles to the hydrocarbon chains.

One important point about the 750 and 720cm^{-1} vibrations is that a material in the crystalline state will show a doublet because of interaction with neighboring molecules, but will be a single peak in the amorphous phase. Studies of the relative intensities of these bands therefore afford a convenient method for the determination of the crystalline/amorphous ratio.

In Figure 1 E, this doublet is present in all four spectra, in spectrum 4 the doublet is very small (because there is much less sample). In Figures 2 E(1) and 2 E(2) the sequential effect of polymerization on these bands has been shown. There is a gradual decrease in intensity of the doublet with polymerization. However, the initial ratio of the intensities of these two bands is the same as that in the final spectrum (120 M. rad dose) (Figure 6).

The band at 905cm^{-1}(a) in the initial stage of polymerization and the band at 835cm^{-1}(b) at high degrees of polymerization can be correlated very well with a phase transformation during the polymerization. As shown in Figure 5 when the intensity of the 905cm^{-1} and 835cm^{-1} are plotted against dose the transition zone is at the same place as in Figure 3 and 4 . The literature[40,41] indicates that these two bands are due to the CH_2 out of plane deformation of CH_2 groups in the immediate vicinity of the π-electron system. In the monomer the CH_2 group has a sp-carbon atom and the packing is that of the monomer rich phase. In the initial stage of polymerization the concentration of such CH_2 groups decreases and causes a drop in intensity of the 905cm^{-1} band. In the transition region because of a change in packing in the polymer rich phase the vibrational mode for the CH_2 group adjacent to sp^2-carbon atoms of the backbone becomes predominant and appears at 835cm^{-1}. This 835cm^{-1} band increases in intensity with further polymerization.

There is one more band in this region at 600cm^{-1}(g), which must be considered. This band decreases with polymerization and completely disappears (Figure 2 E(1) and 2 E(2)) at the point where the phase transition occurs. No specific band assignment can be made for this band but it is probably related to skeleton vibrations in the monomer rich solid solution.

Figure 3 is a plot of intensity versus dose for ν=2250cm^{-1} and 2100cm^{-1}. These bands relate directly to the monomer and oligomer concentration (2250cm^{-1}) and the polymer concentration (2100cm^{-1}).

Figure 4 is a plot of intensity versus dose for the bands ν=1470cm^{-1}, 1420cm^{-1} and 1350cm^{-1}, and is related to the phase transformation during polymerization. Figure 5 is a plot of intensity versus dose for the bands with ν=905cm^{-1} and 835cm^{-1}, also related to the phase transformation in the solid solution. Figure 6 is a plot of the ratio of intensities of the doublet 750cm^{-1} and 720cm^{-1} as a function of polymerization and gives an idea about the change in crystallinity with polymerization. The conclusions derived from these figures and the presented spectra are given below:

1. Figure 3

The band as 2160cm^{-1} representative of the assymmetric $C\equiv C$

vibration of the monomer disappears at about 37 Megarad dose, thus giving evidence that almost all monomer has reacted at this point.

Considering the intensity of the 2160cm^{-1} band at zero Megarad dose to be equivalent to 100% monomer spectrum 17 (Figure 9 B_2) indicates about 98% conversion after 37 Megarad dose. It is important to note that in the phase transition zone the band at 2100cm^{-1} representative of the polymeric π-electron backbone motion levels off. This can be considered to mean that conversion of monomer to polymer is negligible after this leveling off.

2. Figure 4, Figure 5

By considering the spectral region from 2300cm^{-1} through 450cm^{-1} over all the sequential spectra, it is quite reasonable to conclude that there are three components in solid solution during polymerization and they are a) monomer, b) soluble oligomers, c) insoluble polymer. These three components form two distinct solid solutions on either side of the phase transition region. In the initial stage of polymerization before the phase transition, we have a 'monomer rich' phase in a solid solution which contains oligomers and polymer. The phase change involves a change in packing of the paraffinic side chains during polymerization. The bands at 1420cm^{-1}, 905cm^{-1}, 600cm^{-1}, and the progression bands are representative of the packing of $(CH_2)_n$ groups in the 'monomer rich' phase whereas the 1350cm^{-1} and 835cm^{-1} bands are related to the packing of $(CH_2)_n$ groups in the 'polymer rich' phase.

This phase transformation occurs when polymer content is about 63-70% (calculated on the basis of the intensity of the 2250cm^{-1} band as representative of 100% monomer at zero mergarad dose).

3. Figure 6

Considering the ratio of intensities of the bands with ν=750cm^{-1} and 720cm^{-1} at zero megarad dose as representative of 100% crystallinity, one can see a constancy of crystallinity through the entire range of polymerization.

4.

In the "as polymerized" and "insoluble polymer" samples the backbone 2100cm^{-1} band is stronger than the 1630cm^{-1} band corresponding to C=C. In the sequential spectra this 1630cm^{-1} band is not observed in the early stages of polymerization but only at a dose of about ≃31Mrads (Figure 9 C(2), spectrum 16) corresponding to ≃60% polymer. On the other hand the soluble oligomers show a very small peak at 2250cm^{-1}, a strong band at 1630cm^{-1}, and no peak at 2150cm^{-1} or 2100cm^{-1} (Figure 1 C bands h,i). This is a clear indication of a butatriene type of structure in the oligomers. The implication is that the oligomers contain more of a contribution from the butatriene type structure and the insoluble polymer has more contribution from the acetylenic type structure. These assignments are verified in other studies described in this section.

Table 2

Spectrum Number	Form
1	Monomer
2	As Polymerized
3	Leached Polymer (Solvent Hexane)
4	Leached Out Solution

Figures	Spectral Region
A	3100-2800cm^{-1}
B	2300-1000cm^{-1}
C	2500-1550cm^{-1}
D	1550-1200cm^{-1}
E	1200-450cm^{-1}

Key to the Figures 2A, 2B, 2C, 2D, 2E of the monomer

$CH_3-(CH_2)_{11}-C\equiv C-C\equiv C-COOH$.

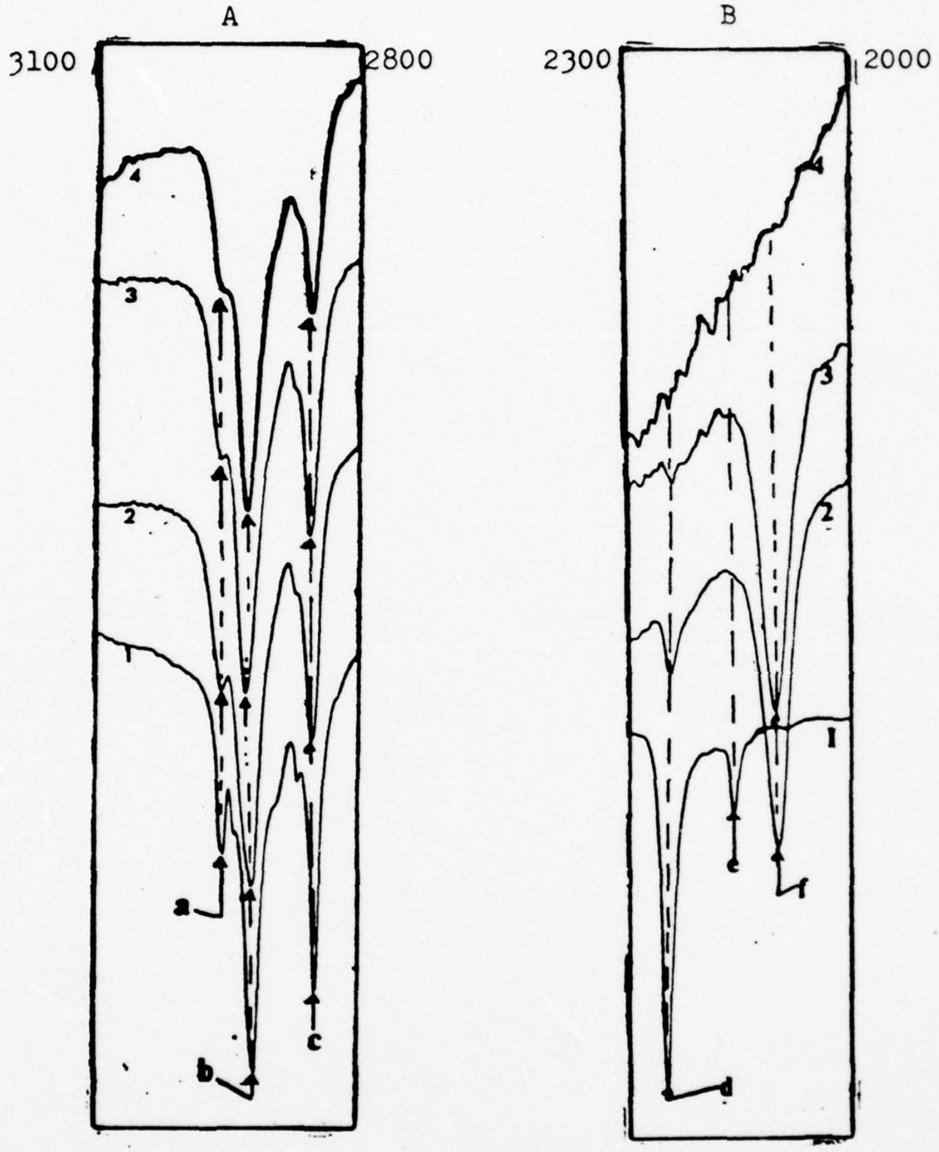


FIGURE: 1 FTIR SPECTRA OF C_{12}-DIYNE-ACID(BULK) POLYMERIZATION.

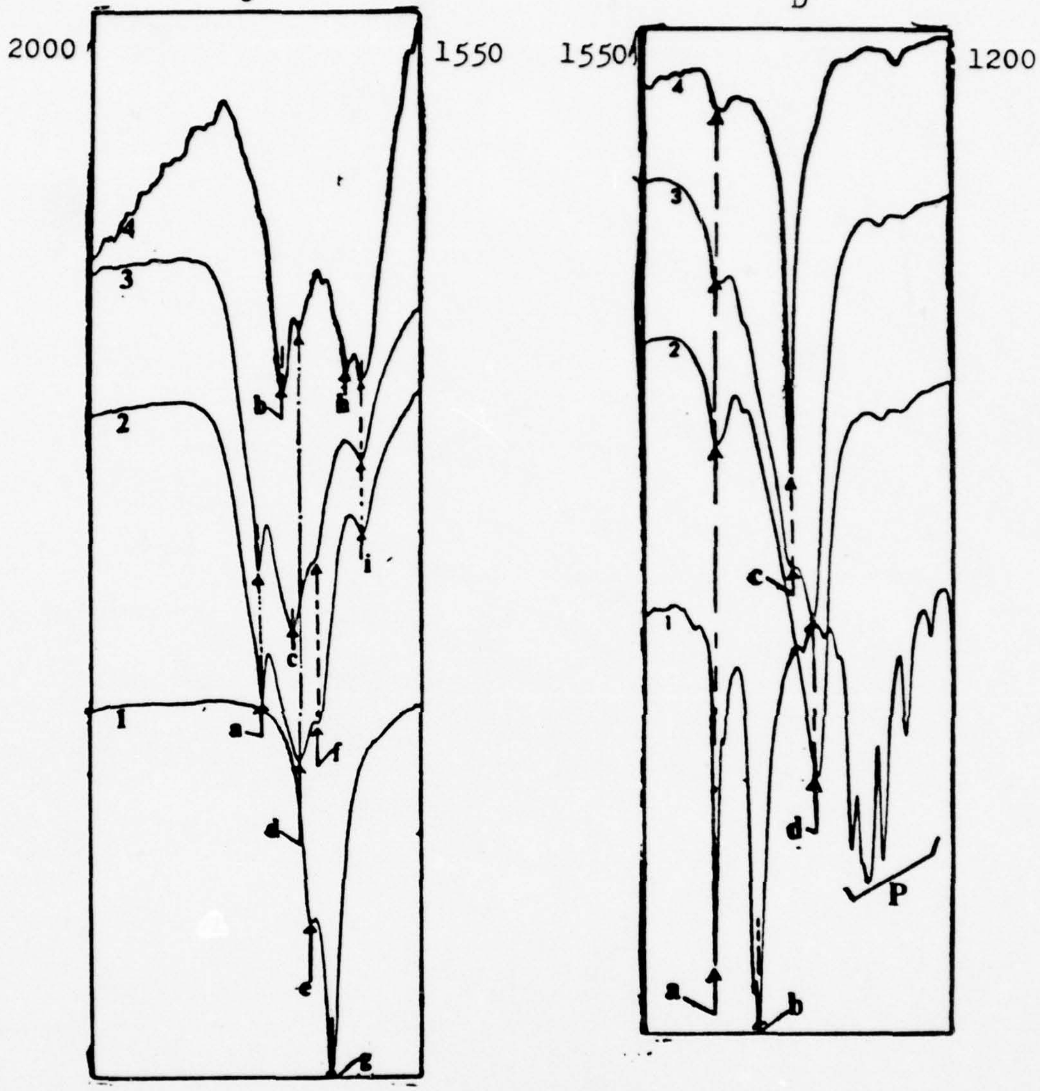


FIGURE: 1. FTIR SPECTRA OF C_{12}-DIYNE-ACID (BULK) POLYMERIZATION.

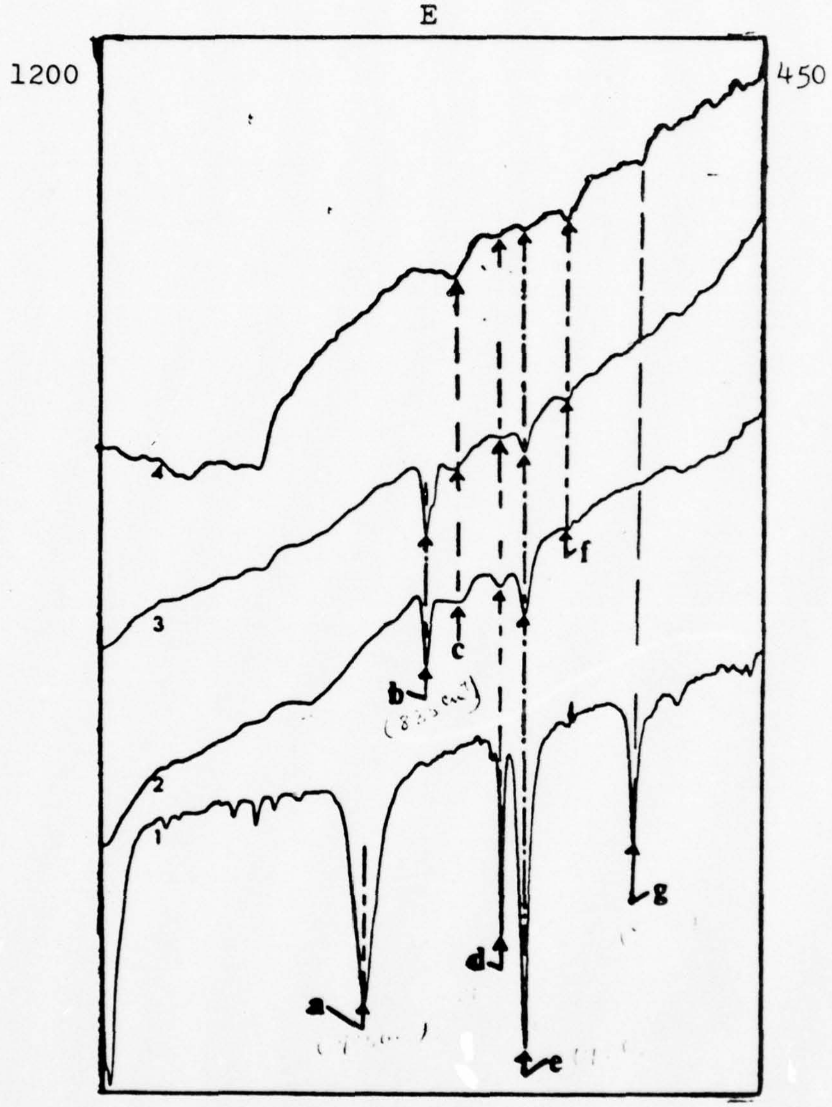


FIGURE: 1. FTIR SPECTRA OF C_{12}-DIYNE-ACID (BULK) POLYMERIZATION.

Table 3 Key to Figure 2

TABLE. 3

FIGURE. A.	
Spectrum Number	Dose (M.Rad)
1	0.00
2	0.40
3	1.50
4	4.80
5	8.90
6	37.80
7	56.23
8	68.6
9	86.60
10	100.50
11	120.00

(CONTINUED)-------

FIGURES. B_1 & B_2.			
Spectrum Number	Dose (M.Rad)	Spectrum Number	Dose (M.Rad)
1	0.00	13	14.76
2	0.40	14	17.72
3	1.06	15	23.98
4	1.45	16	31.90
5	3.03	17	37.80
6	4.75	18	56.23
7	6.34	19	68.60
8	7.13	20	86.60
9	8.12	21	100.50
10	8.90	22	120.00
11	9.75		
12	11.90		

TABLE. (CONTINUED)----

FIGURES. C_1 & C_2.		FIGURES. D_1 & D_2.	
SPECTRUM NUMBER	DOSE (M.RAD)	SPECTRUM NUMBER	DOSE (M.RAD)
1	0.00	1	0.00
2	0.40	2	0.40
3	1.06	3	1.45
4	1.45	4	4.80
5	3.03	5	6.34
6	4.75	6	7.13
7	6.34	7	8.12
8	7.13	8	8.91
9	8.12	9	9.75
10	8.90	10	11.90
11	9.75	11	14.76
12	11.90	12	17.73
13	14.76	13	23.98
14	17.72	14	31.90
15	23.98	15	37.80
16	31.90	16	56.23
17	37.80	17	68.60
18	56.23	18	86.60
19	68.6	19	100.50
20	86.6	20	120.00
21	100.50		
22	120.00		

TABLE.

FIGURES. E_1 & E_2.			
SPECTRUM NUMBER	DOSE (M.RAD)	SPECTRUM NUMBER	DOSE (M.RAD)
1	0.00	8	23.98
2	0.40	9	37.80
3	1.50	10	56.23
4	4.80	11	68.60
5	8.12	12	100.50
6	8.90	13	120.00
7	11.90		

TABLE: 4

	Spectrum Number	a	b	c	d	e	f
FIGURES: 1 A, 2 A.	cm^{-1}	2955	2920	2850			
	1	P	P	P			
	2	P	P	P			
	3	P	P	P			
	4	P	P	P			
FIGURES: 1 B, 2 B_1, B_2.	cm^{-1}				2250	2160	2100
	1				P	P	A
	2				P	A	P
	3				P	A	P
	4				A	A	A

OBSERVED FREQUENCIES FOR THE BANDS IN INFRA-RED SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID. P= PRESENT, A= ABSENT;

TABLE: 5

Spectrum Number		a	b	c	d	e	f	g	h	i
FIGURES: ${}^{1}_{2}C$ C_1, C_2;	cm^{-1}	1770	1735	1725	1715	1700	1690	1670	1650	1630
	1	A	A	A	A	P	A	P	A	A
	2	P	A	A	P	A	P	A	A	P
	3	P	A	P	A	A	P	A	A	P
	4	A	P	A	P	A	A	A	P	P

OBSERVED FREQUENCIES IN INFRA-RED SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID; A =ABSENT, P = PRESENT.

TABLE: 6

SPECTRUM NUMBER		a	b	c	d	e	f	g
FIGURES 1 D, 2 D_1, D_2:	cm^{-1}	1470	1420	1380	1350	Pr		
	1	p	P	A	A	P		
	2	P	A	A	P	A		
	3	P	A	P	P	A		
	4	P	A	P	A	A		
FIGURES: 1 E, 2 E_1, E_2:	cm^{-1}	905	835	800	750	720	670	600
	1	p	A	A	P	P	A	P
	2	A	P	P	P	P	A	A
	3	A	P	P	P	P	P	A
	4	A	A	P	A	A	P	A

OBSERVED FREQUENCIES FOR THE BANDS IN INFRA-RED SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID . P =PRESENT, A =ABSENT, Pr=Progression Bands.

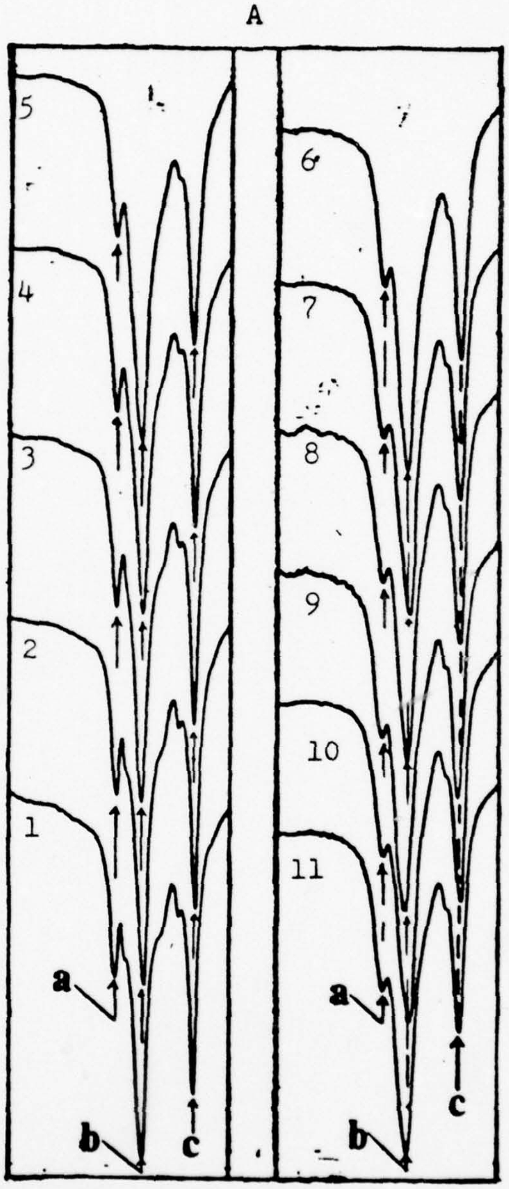


FIGURE: 3 SEQUENTIAL IR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID(BULK). (3100-2800 cm^{-1}).

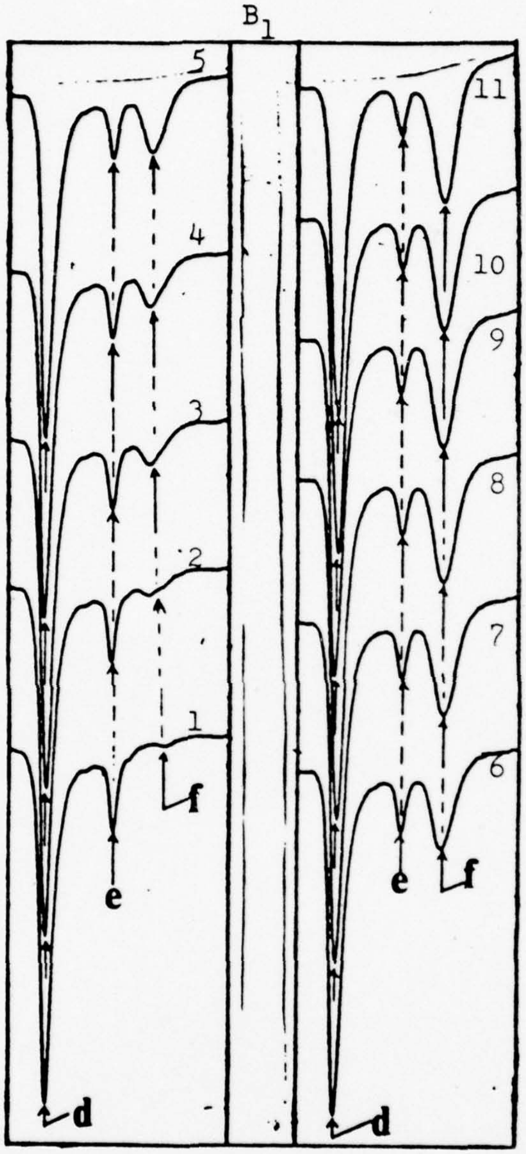


FIGURE: 2 SEQUENTIAL IR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID (BULK). (2300-2000 cm^{-1}).

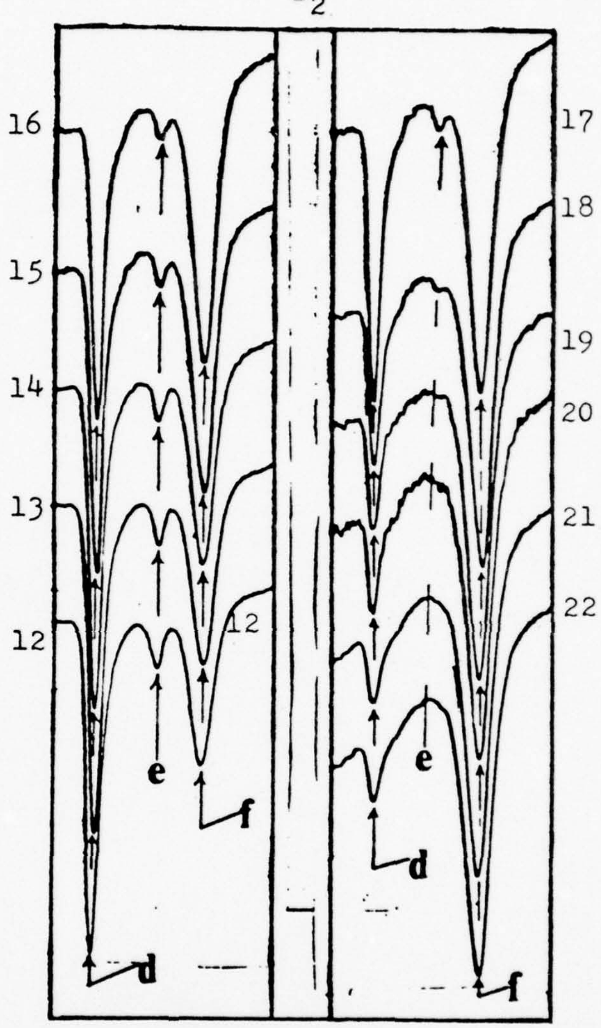


FIGURE: 2 SEQUENTIAL IR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID(BULK). (2300-2000 cm^{-1})

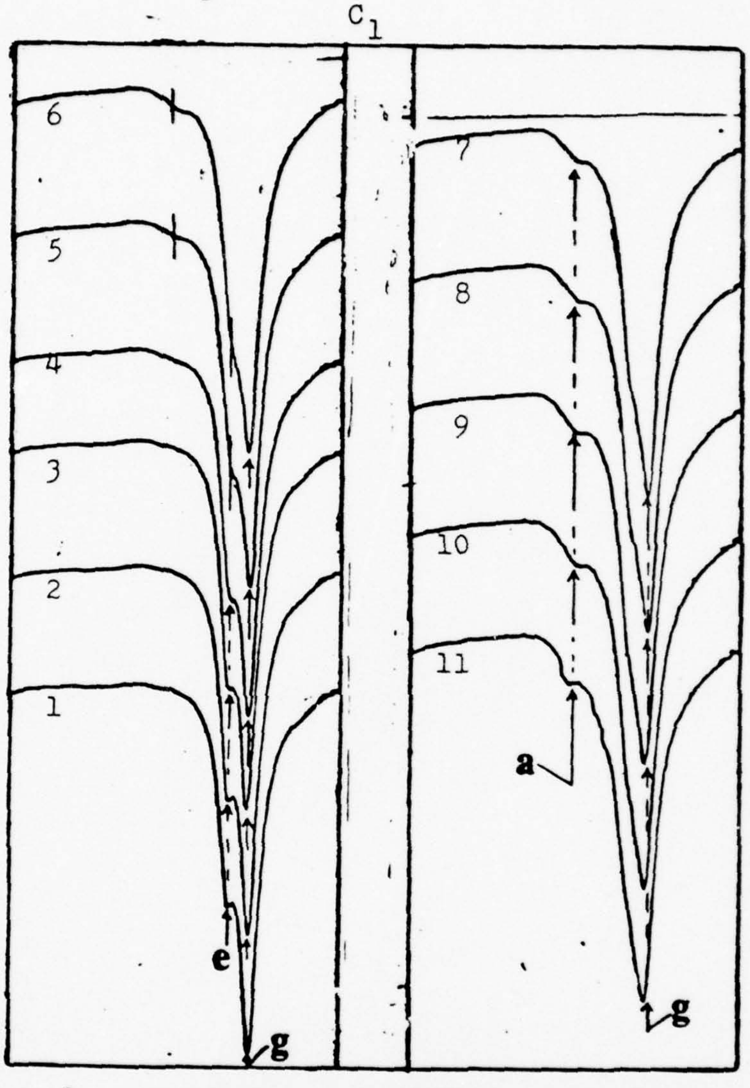


FIGURE: 2 SEQUENTIAL IR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID (BULK). (2000-1550 cm^{-1}).

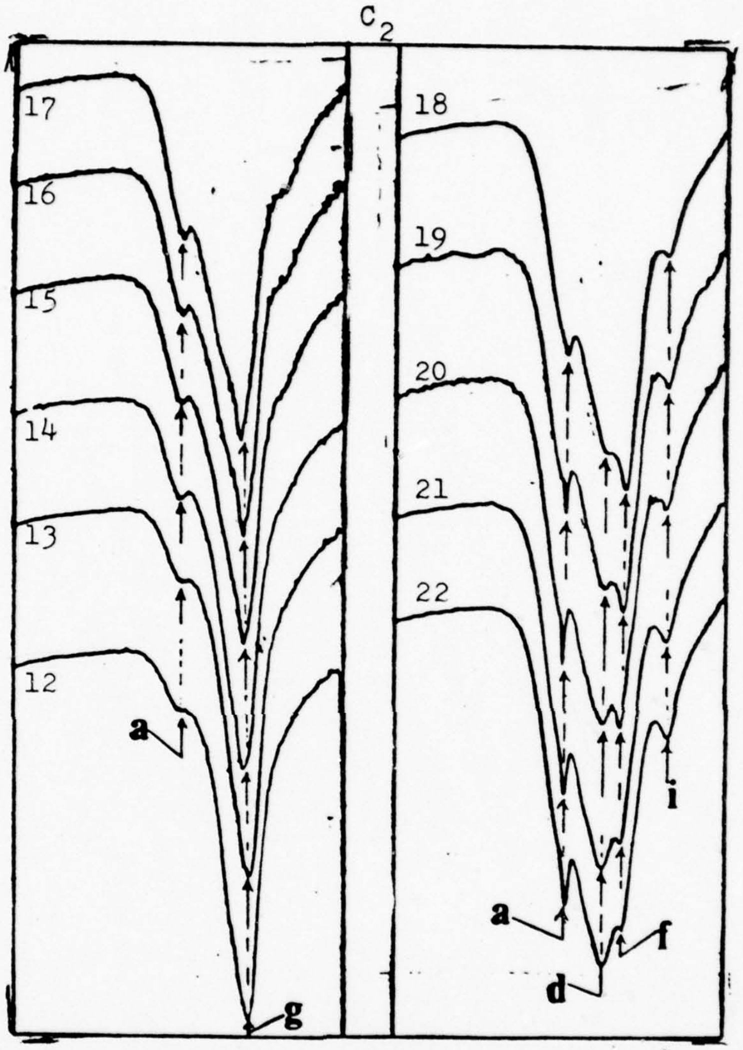


FIGURE: 2. SEQUENTIAL IR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID (BULK). (2000-1550 cm^{-1}).

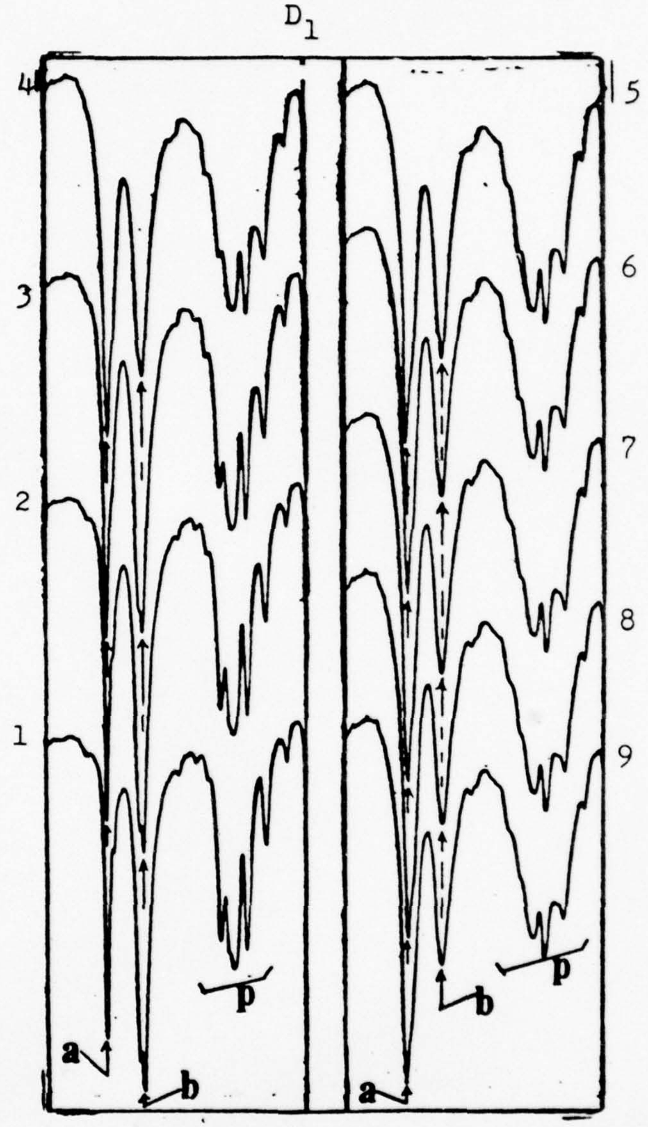


FIGURE: 2 SEQUENTIAL IR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID (BULK). (1550-$1200cm^{-1}$).

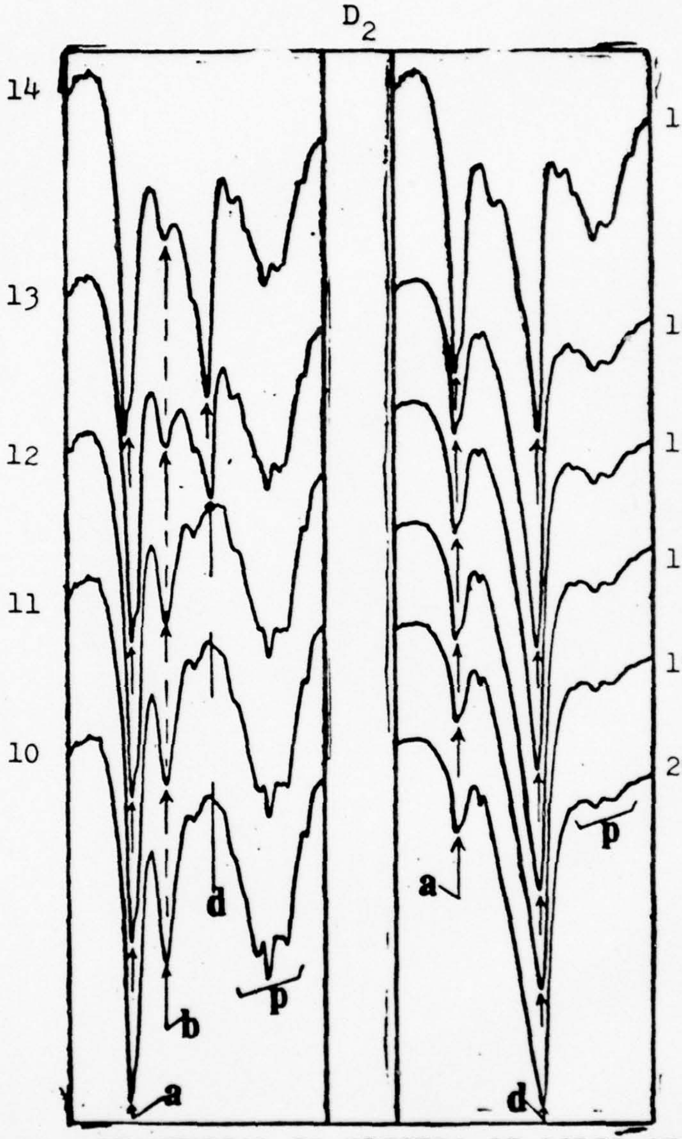


FIGURE: 2 SEQUENTIAL IR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID(BULK). ($1550-1200\,cm^{-1}$).

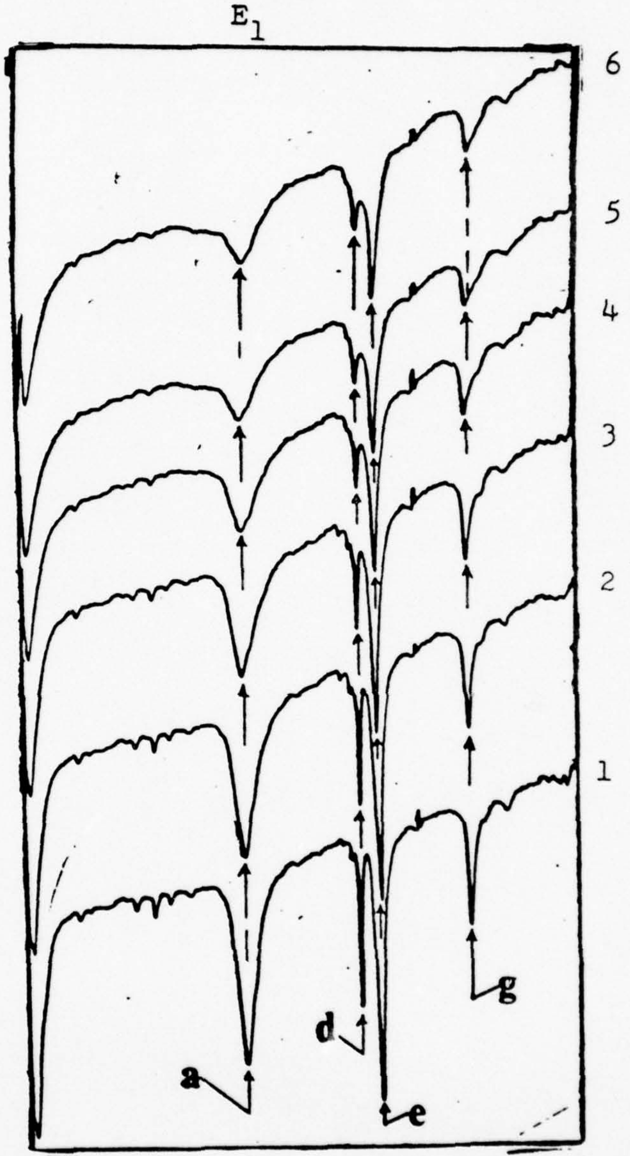


FIGURE: 2 SEQUENTIAL IR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID(BULK). (1200-450 cm^{-1}).

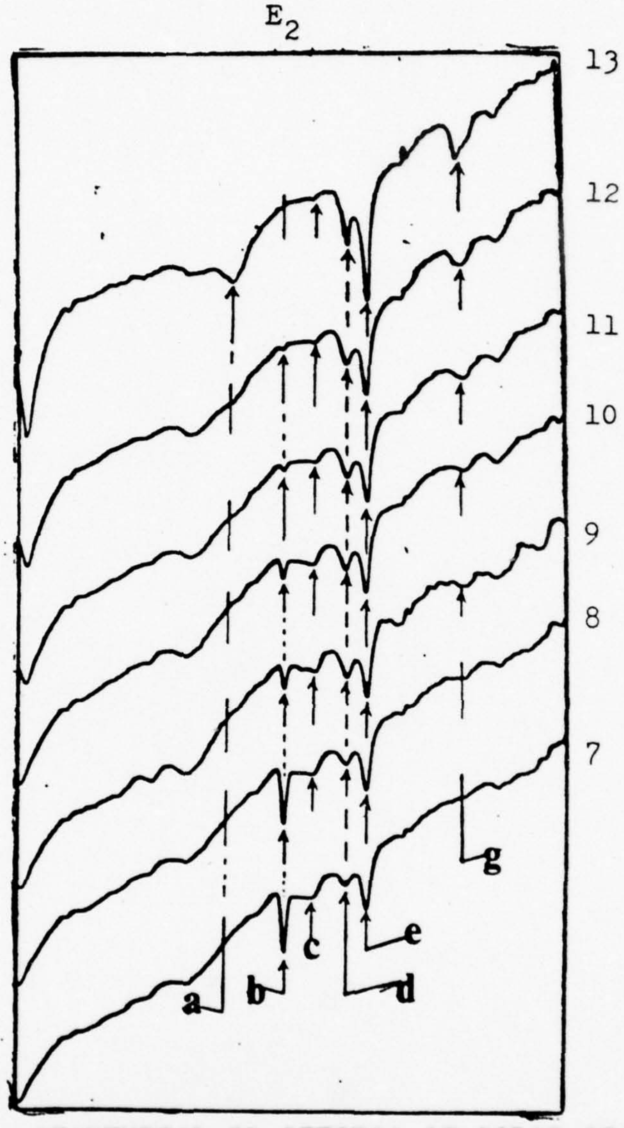
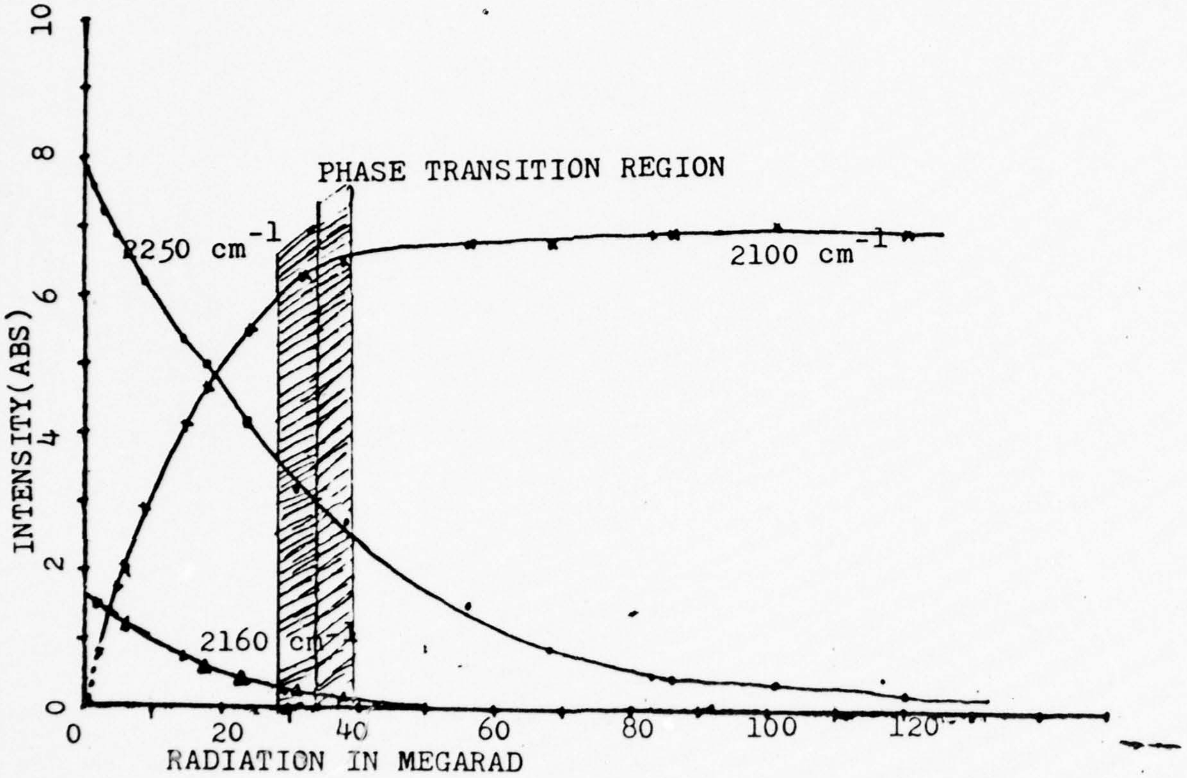


FIGURE: 2 SEQUENTIAL IR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID(BULK). ($1200\text{-}450 cm^{-1}$).



FIGURE; 3 INTENSITY VS RADIATION IN MEGARAD FOR THE SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID.

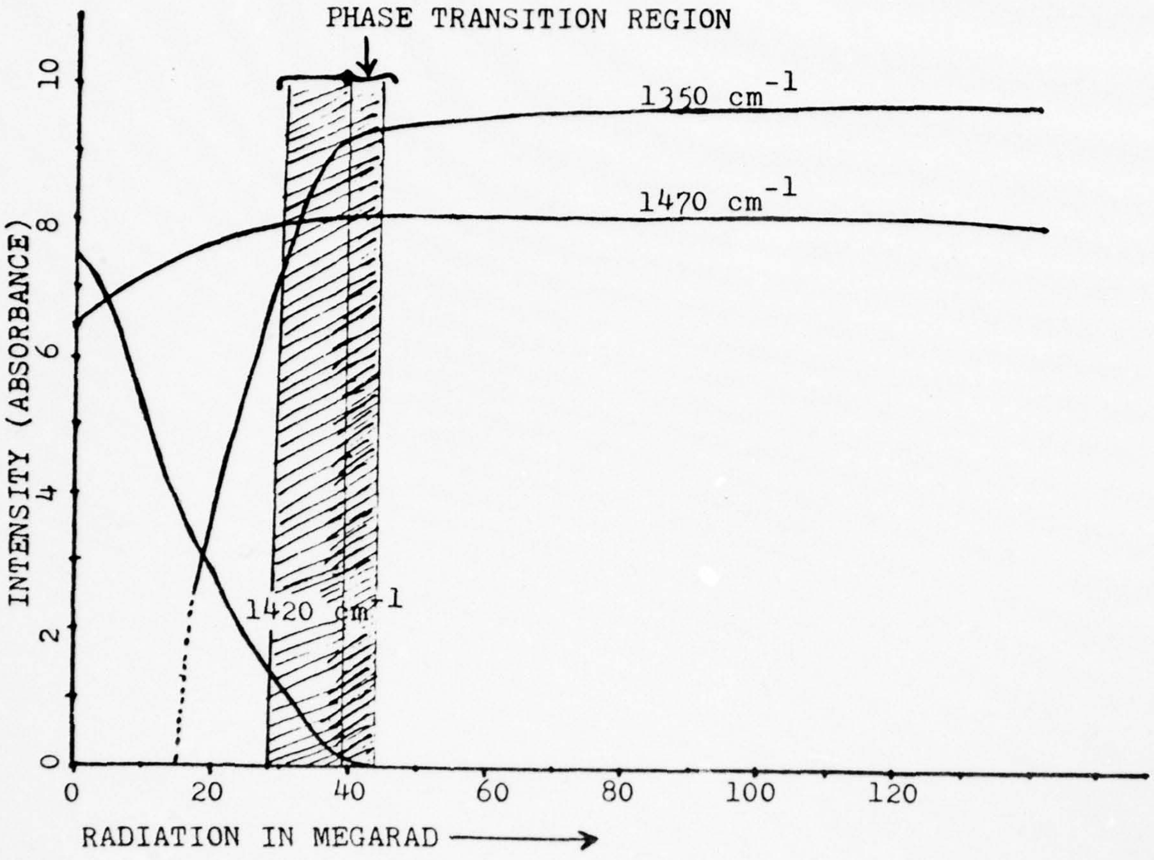


FIGURE: 4 INTENSITY VS RADIATION IN MEGARAD FOR THE SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID.

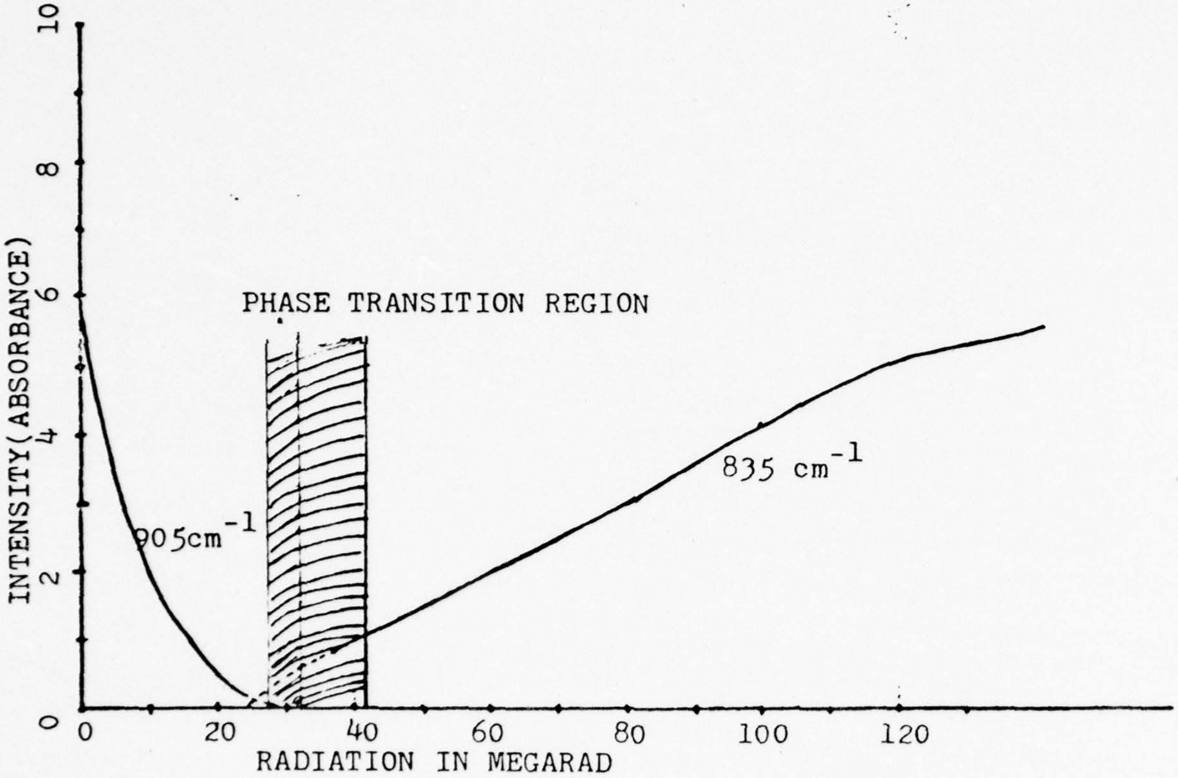


FIGURE: 5 INTENSITY VS RADIATION IN MEGARAD FOR THE SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID.

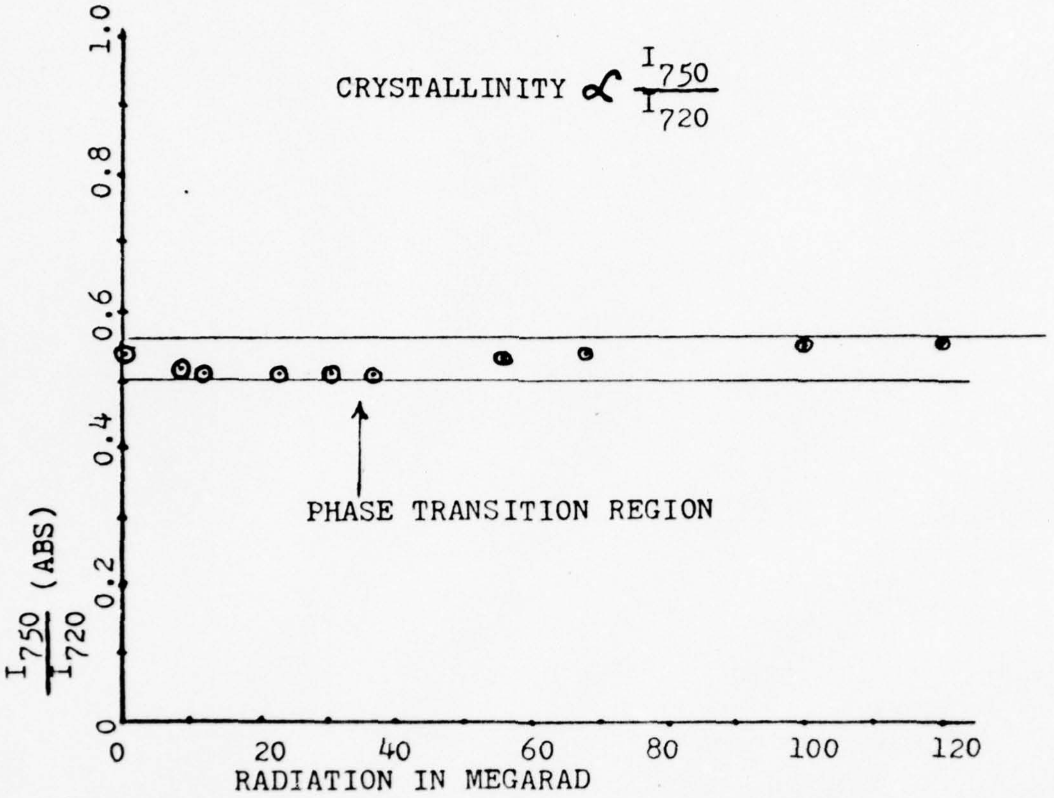


FIGURE: 6 CRYSTALLINITY AS A FUNCTION OF RADIATION IN THE SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-ACID.

MONOMER-2

Heptadecadiyne-2,4-OL-1 $CH_3-(CH_2)_{11}-C\equiv C-C\equiv C-CH_2OH$

The infrared spectra during solid state polymerization of C_{12}-Diyne-OL in the region 3100-450cm^{-1} are shown in Figures 7A, 7B, 7C, 7D and 7E. The key to these figures is given in Table7. A,B,C,D, and E denote the spectral regions 3100-2800cm^{-1}, 2000-1550cm^{-1}, 2000-1550cm^{-1}, 1550-1200cm^{-1} and 1200-450cm^{-1} respectively. The band assignments representative of the modes in these spectral regions are given in Table 8.

The bands at 2955cm^{-1} (a), 2920cm^{-1}(b) and 2850cm$^{-1(c)}$ are present in all the five spectra in Figure 7. As in the case of MONOMER 1, no change is observed in this region.

Figure 7 shows the C≡C vibrational zone. In this region few changes could be observed. The apparent monomeric form (spectrum 1) shows only one band at 2250cm^{-1} corresponding to the symetric C≡C vibrational mode. With polymerization no distinct new mode appears. This situation can be rationalized in terms of the lower polarity of the alcohol as compared to the acid, discussed previously.

The detailed band assignments for the bands in Figures 7C, 7D, and 7E are given in Table 8.

In Figures 7C, 7D, and 7E one can see that the bands at $1740cm^{-1}$, $1355cm^{-1}$ and $1030cm^{-1}$ might be used to follow conversion and the doublet at $720cm^{-1}$, $680cm^{-1}$ can be used to observe changes in crystallinity. A CH_2 group adjacent to a delocalized π-electronic system shows a band 37-40 in the region $1710\text{-}1790cm^{-1}$. It has been assigned to be a combination CH_2 rocking mode. In a system with a strong polar group (like $-NO_2$ or -COOH) at the other end of the π-electron center this CH_2 combination mode tends towards $1790cm^{-1}$ and this was the observation with MONOMER 1. On the other hand this CH_2 rocking combination band appears at a lower frequency when there is a weak polar group at the other end of the π-electron center. The $1740cm^{-1}$ band is assigned to the combination mode. In the monomer it is weaker than the band at $1630cm^{-1}$ but as polymerization proceeds it increases in intensity and becomes stronger than the $1640cm^{-1}$ mode. As the combination band at $1740cm^{-1}$ increases in intensity the component bands ($1030cm^{-1}$, $710cm^{-1}$) decrease in intensity. With polymerization the $1740cm^{-1}$ band broadens and its center moves to $1720cm^{-1}$. A similar behavior of this CH_2 rocking combination mode has been observed in MONOMER 1.

In Figure 7C, in spectra 1, 2, and 3 one can see a decrease of the band at $1630cm^{-1}$. In spectrum 4 (insoluble polymer) both the bands at $1720cm^{-1}$ and $1630cm^{-1}$ are well resolved. In spectrum 5 (soluble oligomers) the bands are similar to monomer spectrum 1. In Figure 7E, spectrum 1 the $800cm^{-1}$ band is broad and becomes sharper with polymerization (spectrum 3). For the insoluble polymer (spectrum 4) and soluble oligomers (spectrum 5) the bands $810cm^{-1}$ and $830cm^{-1}$ are well resolved. It is apparent that the band at $800cm^{-1}$ ranges from $800\text{-}830cm^{-1}$ and with polymerization it appears as a doublet. The band assignment has already been shown in Table 8.

The CH_2 adjacent to asp^2-C atom in the polymeric backbone has an out of plane deformation mode in this region and so it difficult to make a specific assignment. It is logical to assign the bands at $1630cm^{-1}$ and at $830\text{-}800cm^{-1}$ to C=C stretchings (ν_2 andν_3 of butatriene) in a butatriene type of molecule. Three backbone modes in butatriene and its derivitives have been reported (ν_1, ν_2 and ν_3). They occur at $\sim 2079cm^{-1}$ (ν_1), $\sim 1620cm^{-1}$(ν_2) and $\sim 805cm^{-1}$(ν_3) 20-24. There are numberous examples where only ν_2 and ν_3 can be observed with variable ($\pm$ $10cm^{-1}$) positions and intensities. This is observed in spectrum 1 of Figure 7. In this context it is to be noted that spectrum 1 does not represent an actual monomer but has considerable oligomer in it. C_{12}-Diyne_OL is a more reactive monomer that its acid anaglog (MONOMER 1). In solution and at a low temperature (during storage) it will begin to polymerize and can be seen as red colored particles. In the solid state when kept in the infrared beam for a few minutes (at room temperature) it undergoes considerable polymerization which can be seen from its red color and spectroscopically (spectrum 1 of Figure 7A,B,C,D, and E) as well. But this polymerized fraction is soluble in the common solvent (used to dissolve monomer). Hence it has been considered to be monomer with considerable

soluble oligomer in it. That the low molecular weight soluble oligomers,as in the case of MONOMER1, has a butatriene type of structure is indicated by the bands at 1630cm^{-1} and 830-810cm^{-1}.

The detailed band assignments for Figure 7D can been seen in Table 8. As has been observed for the MONOMER 1 the 1355cm^{-1} band increases in intensity with polymerization as compared to the 1470cm^{-1} band. The band at 1430cm^{-1} disappears with polymerization. The -OH deformation modes (1400cm^{-1}, 1260cm^{-1}) are well resolved in the oligomers (spectrum 5). With polymerization 1400cm^{-1} band merges into the broad, intense 1355-1380cm^{-1} band.

As has been mentioned earlier the bands at 1030cm^{-1} and 720-680cm^{-1} have been assigned to $(CH_2)_n$ rocking modes and they decrease continously with polymerization, whereas their combination mode (1740cm^{-1} region) increased in intensity.

Table 7

Figure	Spectral Region (cm^{-1})	Spectrum No.	Description
	3100-2800	1	Monomer
		2	Intermediate
		3	As Polymerized
		4	Insoluble Polymer
		5	Soluble oligomer
	2300-2000	1-5	(as above)
	2000-1550	1-5	(as above)
	1550-1200	1-5	(as above)
	1200-450	1-5	(as above)

Table 8

Figure	νcm^{-1}	Assignments
17C	1740	Combination, $(CH_2)_n$ rocking ($1030+710 cm^{-1}$)
	1630	Butatriene ν_2, C=C stretching mode
17D	1470,sh	CH_2-bending deformation
	1430	sym. and asymmetrical CH_3 bending
	1400	Inplane OH deformation
	1380	Asym. & symmetrical $-CH_3$ bending
	1355	
	1260	-OH in plane bending, when coupled with a torsional mode of an adjacent CH_2 group.
17E	1100	C-O stretch
	1030	CH_2 rocking
	930	sp-C CH_2-out of plane deformation
	830-800	i) butatriene ν_3, C=C (one bound) ii) sp^2-C CH_2-out of plane deformation
	720	$(CH_2)_n$, n> 4 rocking mode related to packing
	680	

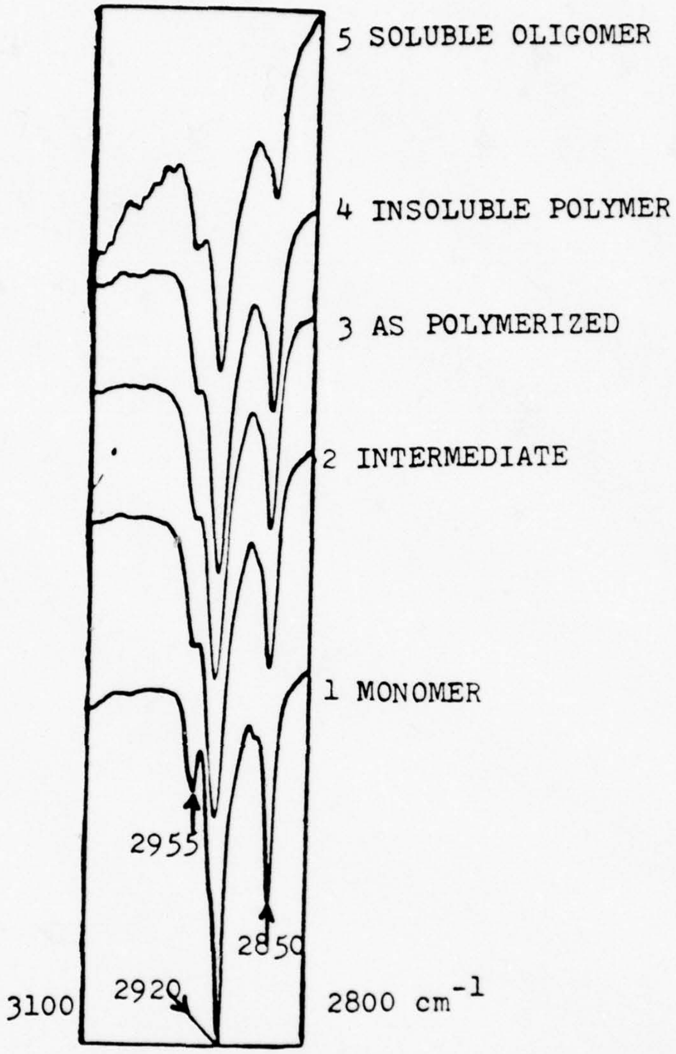


FIGURE: 7 A FTIR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-OL (BULK).

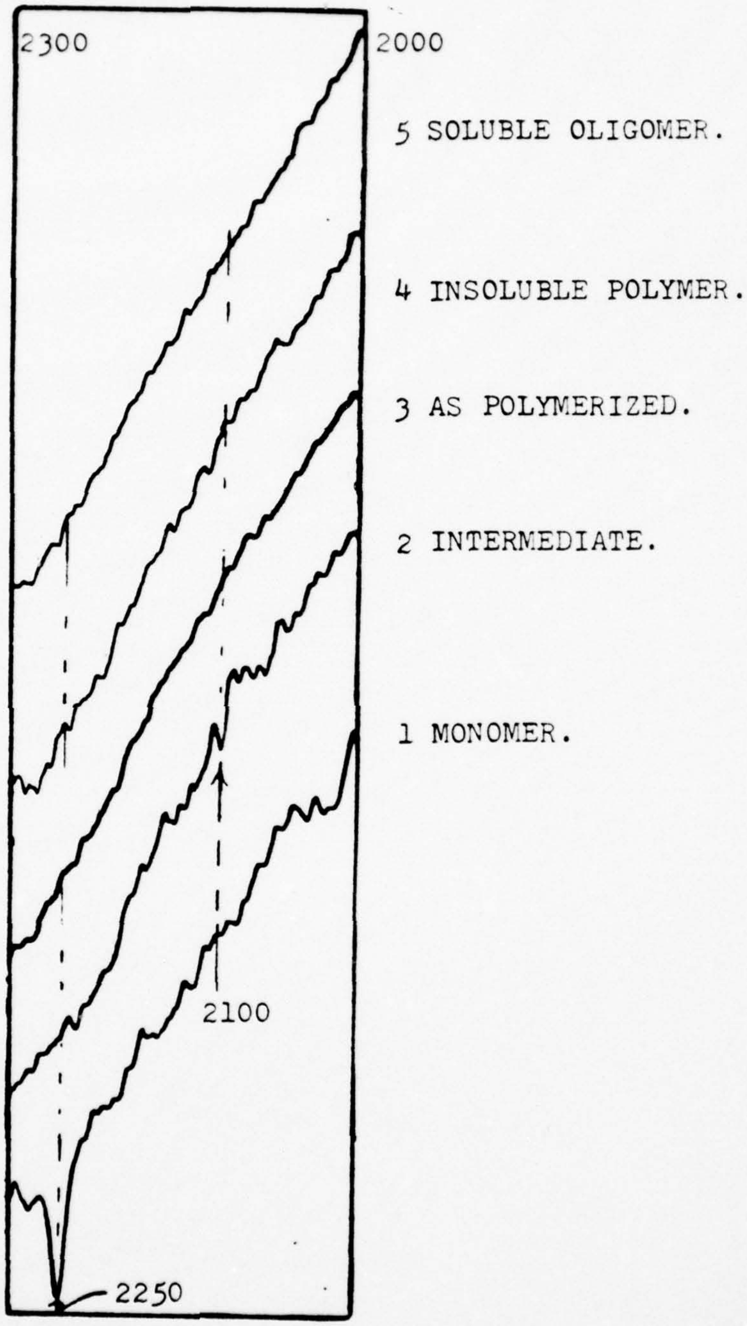


FIGURE: 7B FTIR SPECTRA OF C_{12}-DIYNE-OL (BULK) POLYMERIZATION.

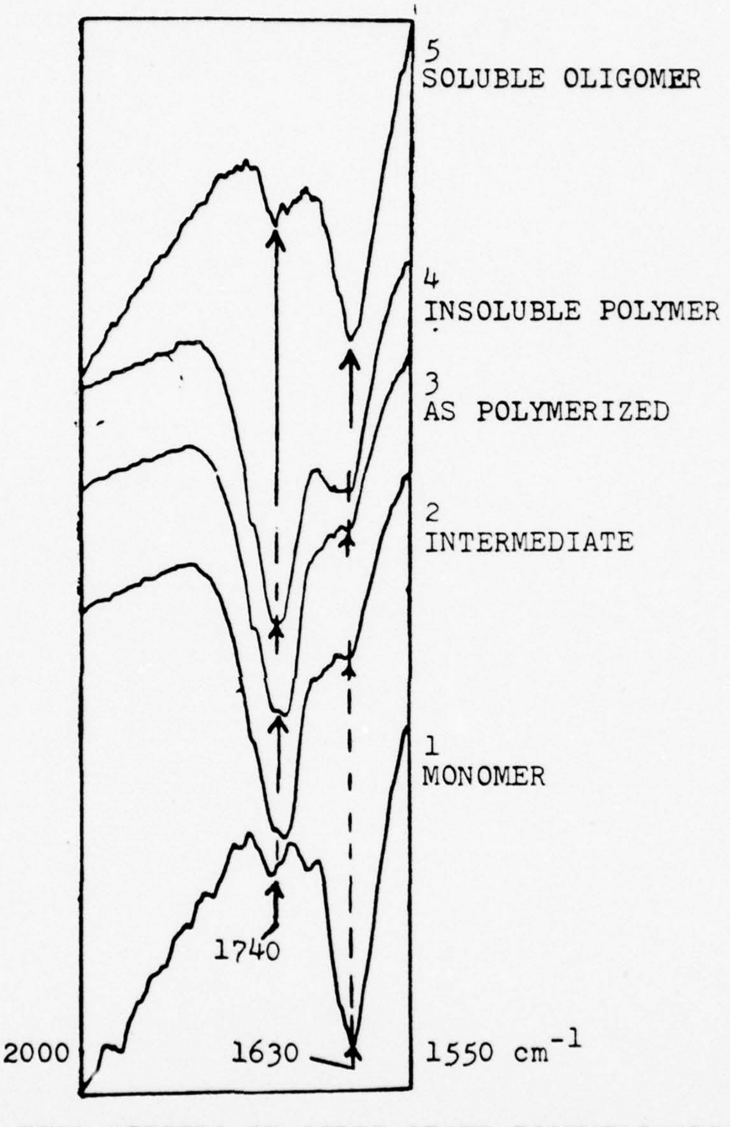


FIGURE: 7C FTIR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-OL (BULK).

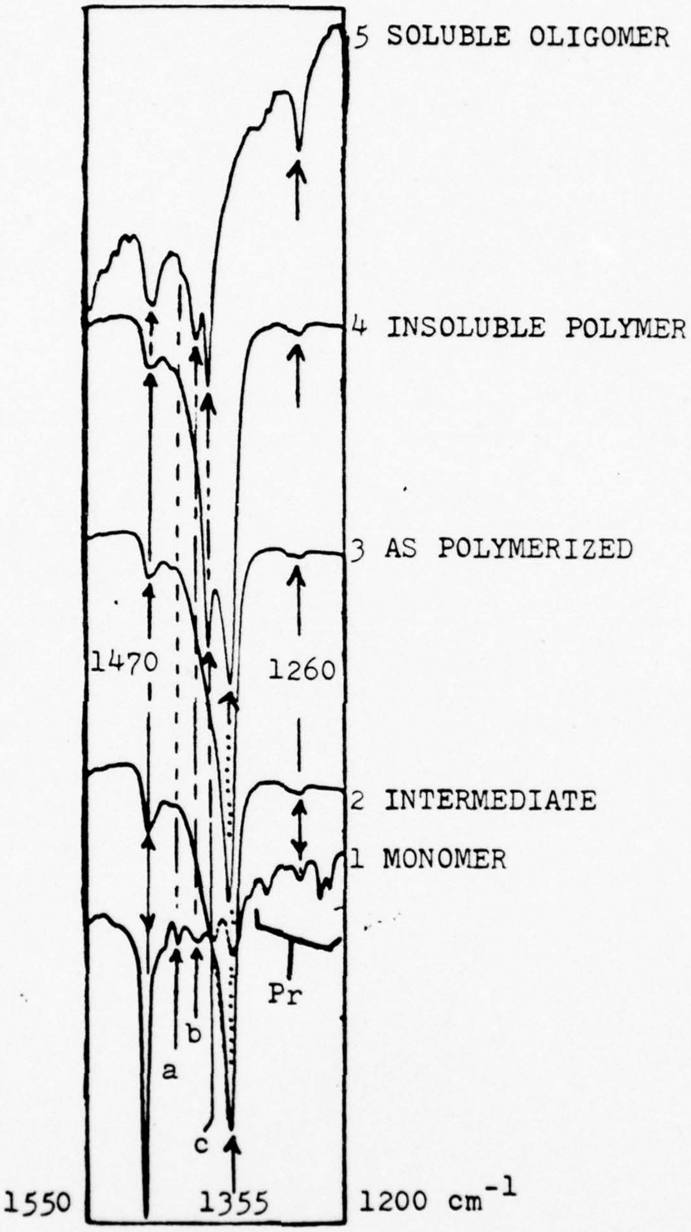


FIGURE: 7D FTIR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-OL (BULK). (a =1430, b=1400, c=1380 cm^{-1}).

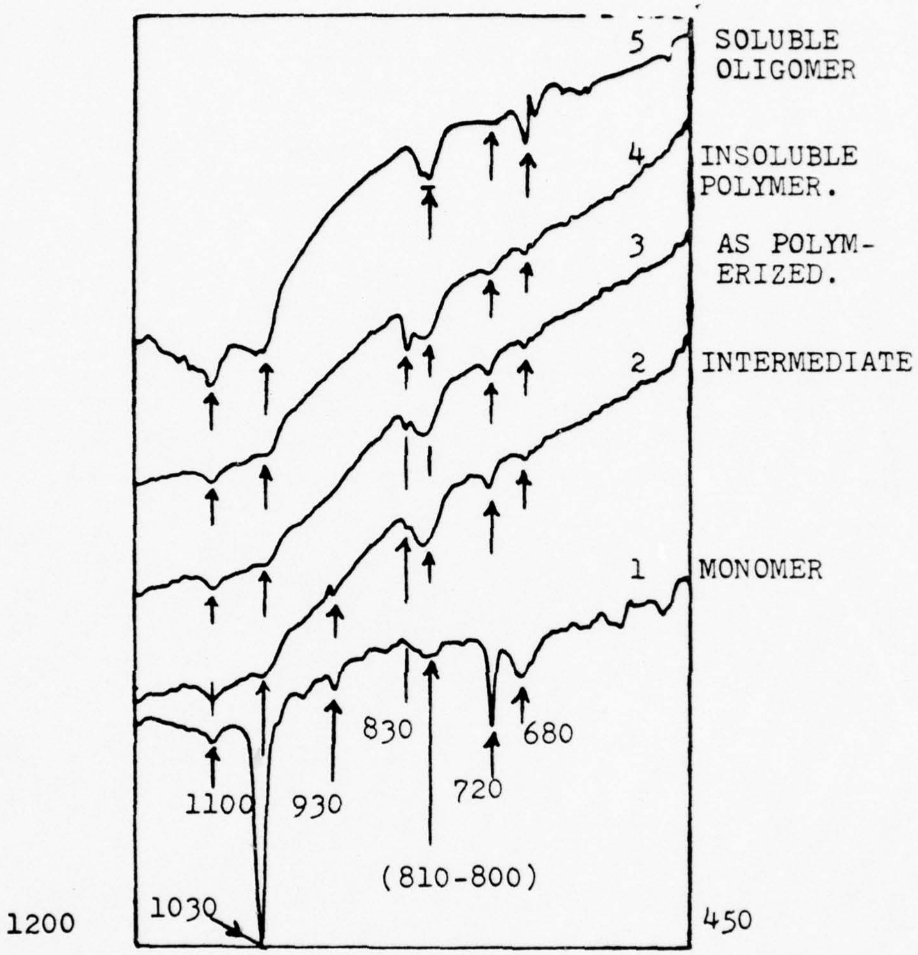


FIGURE: 7E FTIR SPECTRA OF SOLID STATE POLYMERIZATION OF C_{12}-DIYNE-OL (BULK)

MONOMER 3

Heptadecadiyne-4,6-Acid-1 $CH_3-(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_2-COOH$

In this material the polar-COOH group is two carbon atoms away from the diacetylene rod in the monomer and theπ-delocalized carbon atoms of the polymeric backbone. Thus the polar effect of the -COOH group in the delocalized π-electron system should be negligible. This is observed in the $C\equiv C$ stretching frequency as well as in the C=O stretching frequency. The key to Figures 8A,B,C,D and E is given in Table 9.

Thus Figure 8A (3100-2800cm^{-1}) represents the C-H stretching modes in the $CH_3-(CH_2)_n$ hydrocarbon chain. As we proceed from spectrum 1 through 4 no major change can be observed. In the 2300-2000cm^{-1} region in Figure 8B there are two bands at 2195cm^{-1} and 2150cm^{-1} corresponding to the symmetric and asymmetric vibrational modes of $C\equiv C$ bonds in the monomer. In most of the diacetylenes the detectable bands are at 2250cm^{-1} and at 2150cm^{-1}. The reason for the shift of the 2250cm^{-1} band to 2195cm^{-1} is not clear at this moment. During polymerization the 2195cm^{-1} band disappears prior to the 2150cm^{-1}, which is contrary to the observation for MONOMER 1 (where 2150cm^{-1} disappears first). The differences may relate to the fact that the polar group is farther removed from the diacetylene unit.

Complete disappearance of the 2150cm^{-1} band after a dose of Megarad 22-25 is indicative of the fact that practically all the monomer has reacted to yield oligomers and/or polymer.

In Figure 8C the spectral region 2000-1550cm^{-1} has been plotted, Table 10 gives the band frequencies for Figures 8 C and 8D The following are the band assignments: 40-42.

a→$1770cm^{-1}$, combination band (~1040+720)cm^{-1}, $-CH_2$ rocking mode.

b→$1690-1720cm^{-1}$, C=O stretching mode.

c→$1630-1615cm^{-1}$, C=C stretching mode.

As with the previously discussed systems, the $1770cm^{-1}$ band is assigned to $(CH_2)_n$ rocking adjacent to a delocalized π-electron and appears only after some conversion to polymer. The appearance of this band is also accompanied the decrease in intensity for the component modes (Figure 8E), decrease in intensity of the $920cm^{-1}$ band and the appearance of an $835cm^{-1}$ band (Figure 8E).

These bands are related to the different (CH_2) vibrational modes and are succeptible to its enviroment (packing and electronic). It has also been observed that the $1630cm^{-1}$ band appears simultaneously with the $1770cm^{-1}$ band. The C=O stretching frequency at $1690cm^{-1}$ broadens with the progress of polymerization, but in contrast to MONOMER 1, the band does not shift its position. This observation gives an additional support to the explanation for the shift in the C=O stretching frequency to $1720cm^{-1}$ in MONOMER 1, where with the progress of polymerization the C=O bonding electrons are conjugated with the delocalized π-electrons of the backbone.

As has been observed with the other compounds, this compound also shows a strong doublet at $1630-1615cm^{-1}$ (Figure 8E spectrum 4) for the oligomers. This suggests a butatriene type of structure for the soluble oligomers as in compounds 1 and 2.

In the spectral region $1550-1200cm^{-1}$ (Figures 8D, there is a significant difference among the spectra of monomer, polymer and oligomer. The band frequencies are given in Table 17 and the assignments 26-41 are as follows:

a→1460cm^{-1}, CH$_2$-bending deformation in -CH$_3$ groups.

b→1430cm^{-1}, sym. and asym. C-H bending deformation in -CH$_3$ groups.

c→1415
cm^{-1} -CH$_2$-deformation adjacent to C=O group
d→1400

e→1370cm^{-1} sym. and asym. C-H bending deformation

f→1355cm^{-1} in -CH$_3$ groups

g→1350
1170cm^{-1} progression bands (?)
h→ 1260cm^{-1}, CO and -OH coupled inplane deformation.

In this case with the progress of polymerization, the bands at 1460cm^{-1} and 1430cm^{-1} decrease in intensity as compared to the new band at 1355cm^{-1}. In the as polymerized and in the insoluble polymer spectra (spectra 2 and 3 of Figure 8D) these two bands are present as shoulders of the broad and strong 1355cm^{-1} band. The oligomers (spectrum 4, Figure 8D) have well resolved bands at 1460cm^{-1} and 1370cm^{-1}. A comparison of the spectra 4,2 and 1 identifies the oligomers as distinct from the monomer and polymer.

The progression bands, in this case, seem to be somewhat different from those in MONOMER 1. With polymerization all the bands between 1350-1170cm^{-1} disappear completely with the exception of a weak band at 1215cm^{-1} (Figure 8D). The oligomer has sharp bands both at 1260cm^{-1} and 1215cm^{-1} and is quite similar to the monomer in this region (spectra 4, Figure 8D). The appearance of the bands at 1215cm^{-1}, 1260cm^{-1}, 1300cm^{-1}, 1430cm^{-1}, and 1460cm^{-1} in the oligomer (spectrum 4, Figure 8D) suggest a monomer-like crystal packing for the oligomers. This is also supported by the bands at 1690cm^{-1} and 1720cm^{-1} (Figure 8C, spectra 1 and 4) which are present in both the oligomer and monomer spectra.

The spectral region 1200-450cm^{-1} has beeen plotted in Figures 20E.

The band assignments are: 28-32,56,58, 6-10, 40, 42

p→1170cm^{-1}, progression band?
a→1100cm^{-1}, C-O stretch
b→1040cm^{-1}, CH_2 rocking (asym)
c→920cm^{-1}, sp-c, CH_2 out of plane deformation
d→835cm^{-1}, sp^2-c, CH_2 out of plane deformation
e→ 800cm^{-1}, ν_3 of butatriene
f→770cm^{-1}, (??) probably related to the packing of
$(CH_2)_2$ groups
g→$\genfrac{}{}{0pt}{}{720}{700}$cm^{-1} ,$(CH_2)$ rocking perpendicular to the paraffinic chain. (crystalline)

Lower bands, complex skeletal modes

In Figure 8E, spectrum 1, there is a sharp band at 770cm^{-1} which decreases in intensity with the progress of polymerization and does not appear at all in the as polymerized or polymer samples. Sequential spectra show a gradual decrease of this 770cm^{-1} band with polymerization, and after a dose of 23 Megarad it disappears completely. The bands at 835 cm^{-1} and 800cm^{-1} appear with the disappearance of the 770cm^{-1} band. The 920cm^{-1} band of the monomer decreases in intensity and broadens with polymerization but does not disappear completely in the as polymerized spectrum (spectrum 2 of Figure 8E). The exact nature of the 770cm^{-1} band is not known.

Since it does not appear in monomers 1 and 2 it may be related to the packing of the $(CH_2)_2$ group between the diacetylene rod and the -COOH group. These $(CH_2)_2$ groups are subjected to rearrangement and electronic delocalized interaction when polymerization occurs. The details concerning the other bands have already been discussed with respect to MONOMER 1. A plot of the intensity of the $920cm^{-1}$ band (Figure 9) against dose follows the same trend as that for the $2250cm^{-1}$ band in MONOMER 1. On the basis of this band the as polymerized sample (spectrum 2, Figure 8E) represents about 98% polymer. This conclusion does not mean that the sample contains 2% monomer. From the bands at $770cm^{-1}$, $2195cm^{-1}$, and $2150cm^{-1}$ it is quite clear that after a dose of about 23 Megarad virtually all the monomer has reacted. Thus after a 23 Megarad dose the sample contains oligomers and polymer. The intensity of several bands against dose have been plotted in Figures 9, 10, 11 and 12.

Figure 10 is a plot of intensities of the 770^{-1} and the $835cm^{-1}$ bands against dose. The shadowed area in these figures (24-27 Megarads) represent a phase transition zone as in MONOMER 1. Similar behavior of the $1430cm^{-1}$ and $1355cm^{-1}$ bands also indicates a phase change.

The band at $1215cm^{-1}$ may arise for two reasons, as i) a combination C-O mode, ii) a CH_2 mode adjacent to the C=O group. Thus this band is sensitive to the enviroment which effects the C=O stretching frequency ($1690cm^{-1}$) as well. Because of considerable interaction probably originating with the increased concentration of oligomers and polymer with polymerization, the C=O stretching band broadens and the the $1215cm^{-1}$ band decreases in intensity. These data have been plotted in Figure 11 as the half width of the $1290cm^{-1}$ band and the intensity of the $1215cm^{-1}$ band versus dose. It can be seen that the intensity of the $1215cm^{-1}$ band is a smooth function (decreasing) of polymerization. The half width of the $1690cm^{-1}$ band is also a smooth function (increasing) of polymerization. It has been pointed out earlier that the $(CH_2)_n$ side group is involved in the packing of the molecules in the monomer or polymer phase and there is a phase change at about 24-27 Megarad. The phase change is not reflected in the $1215cm^{-1}$ and $1690cm^{-1}$ bands. This observation leads to the conclusion the the -COOH functional group is not affected by the phase change but only by the electronic interaction with the polymeric backbone.

Figure 12 shous a I_{720}/I_{700} versus dose plot and again the crystallinity seems to be almost constant through the entire polymerization.

As has been observed in MONOMER1, the above mentioned bands have been observed as sensitive to the side chain packing and are important in determining the crystalline packing of these molecules. In going from monomer to the polymer the side chain packing undergoes a change and this change is reflected by the bands related to the $(CH_2)_n$ groups. The bands are given as follows:

MONOMER PACKING	POLYMER PACKING
$770cm^{-1}$	$835cm^{-1}$
$1430cm^{-1}$	$1355cm^{-1}$
$1040+720cm^{-1}$	$1770cm^{-1}$

In the early stage of polymerization (below $\sim$24 Megarads) the monomer controls the packing and polymer forms a solid solution in this phase. In the final stages of polymerization (beyond 27 Megarad dose) the packing is of the polymer rich phase. In the polymer rich phase, there is no monomer but oligomer may form a solid solution in it.

TABLE 9

Spectrum Number	Sample Nature
1	Monomer
2	As polymerized
3	Insoluble polymer
4	Soluble oligomer

Spectral Region	Frequency
6A	3100-2800cm^{-1}
6B	2300-2000cm^{-1}
6C	2000-1550cm^{-1}
6D	1550-1200cm^{-1}
6E	1200- 450cm^{-1}

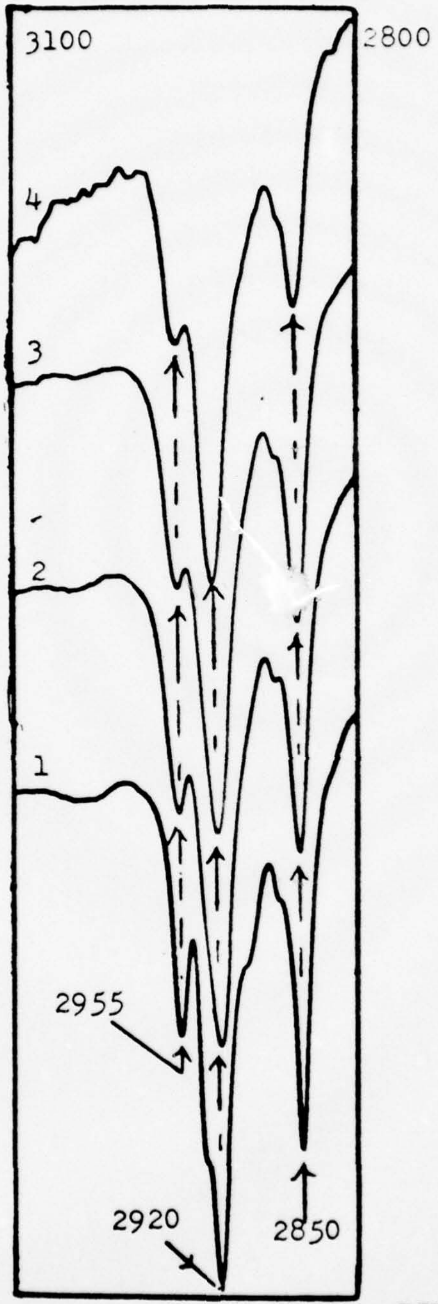


FIGURE: 8 A.FTIR SPECTRA OF C_{10}-DIYNE-C_2-ACID (BULK) POLYMERIZATION.

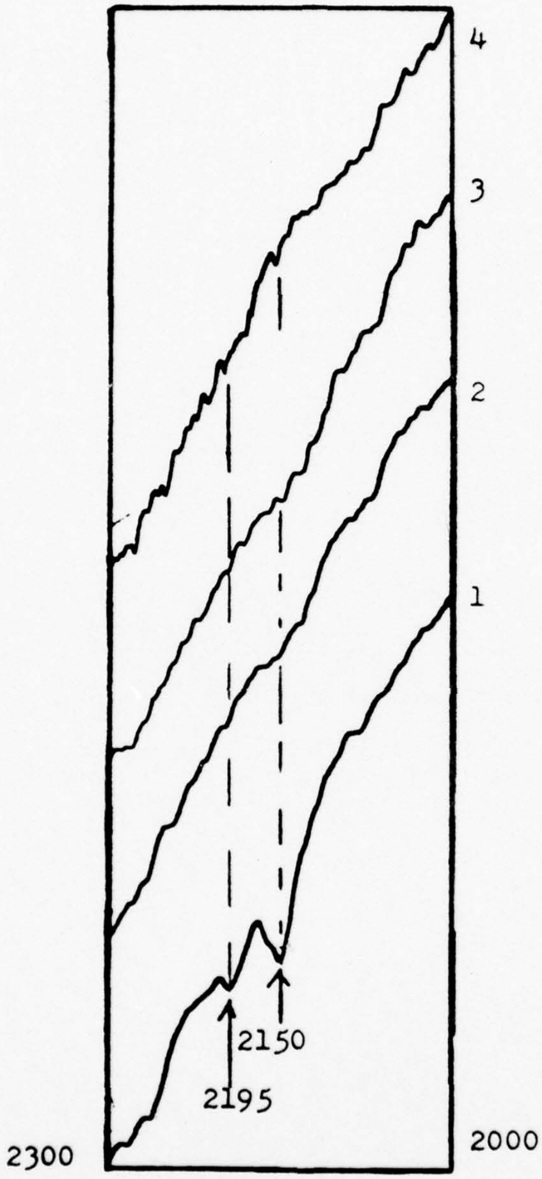


FIGURE:8 B FTIR SPECTRA OF C_{10}-DIYNE-C_2-ACID (BULK) POLYMERIZATION.

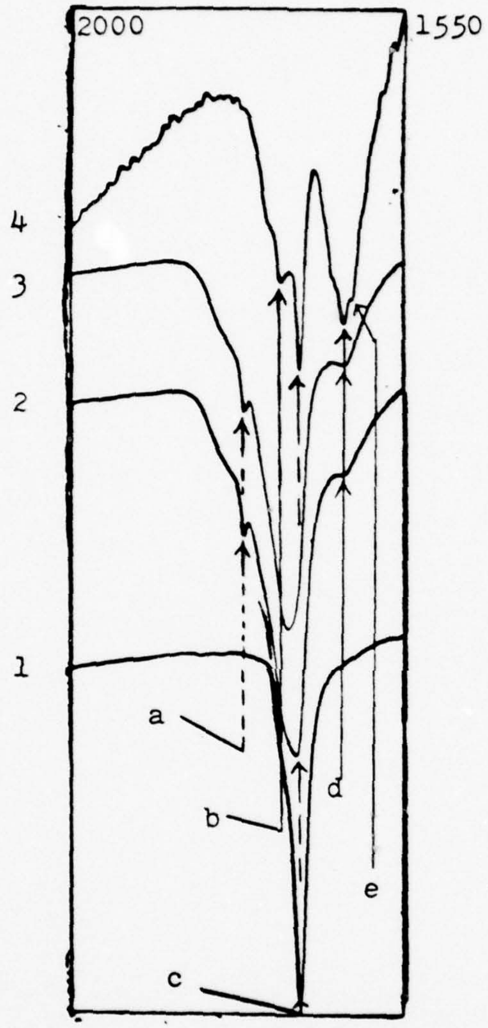


FIGURE 8c FTIR SPECTRA OF C_{10}-DIYNE-C_2-ACID (BULK)
POLYMERIZATION;

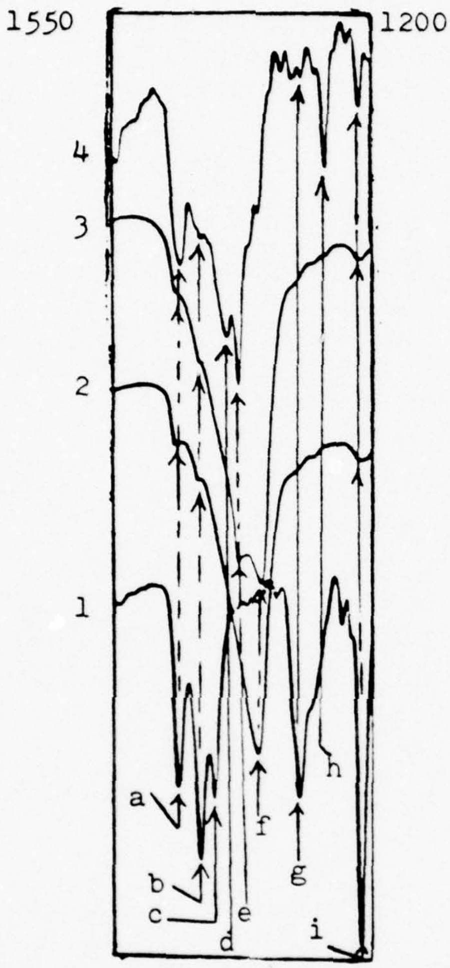


FIGURE: 8D FTIR SPECTRA OF C_{10}-DIYNE-C_2-ACID(BULK) POLYMERIZATION.

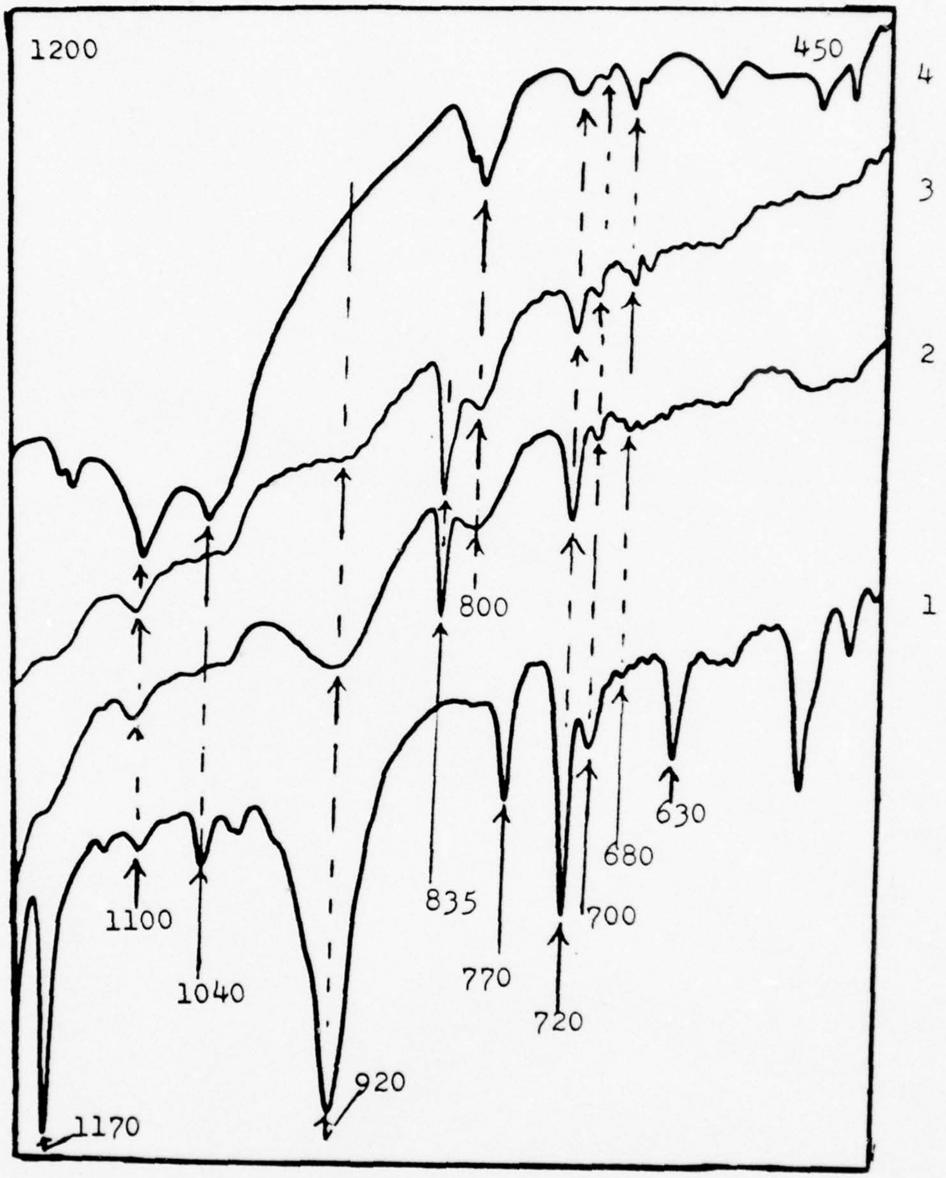


FIGURE: 8 E FTIR SPECTRA OF C_{10}-DIYNE-C_2-ACID (BULK) POLYMERIZATION.

TABLE: 10

BANDS--→	a	b	c	d	e	f	g	h	i	FIGURES
SPECTRUM #	1770	1720	1690	1630	1615 cm^{-1}					8C
1	A	Sh	P	A	A					
2	P	A	P	P	A					
3	P	A	1710	P	A					
4	A	P	P	P	P					
	1460	1430	1415	1400	1370	1355	1300	1260	1215 cm^{-1}	8D
1	P	P	P	A	A	vw	P	1280	P	
2	P	P	A	A	A	P	A	A	W	
3	P	P	A	A	P	P	A	A	W	
4	P	W	A	P	P	Sh	W	P	P	

FREQUENCIES OF THE BANDS OBSERVED IN INFRA-RED SPECTRA OF SOLID STATE POLYMERIZATION OF C_{10}-DIYNE-C_2-ACID IN BULK.

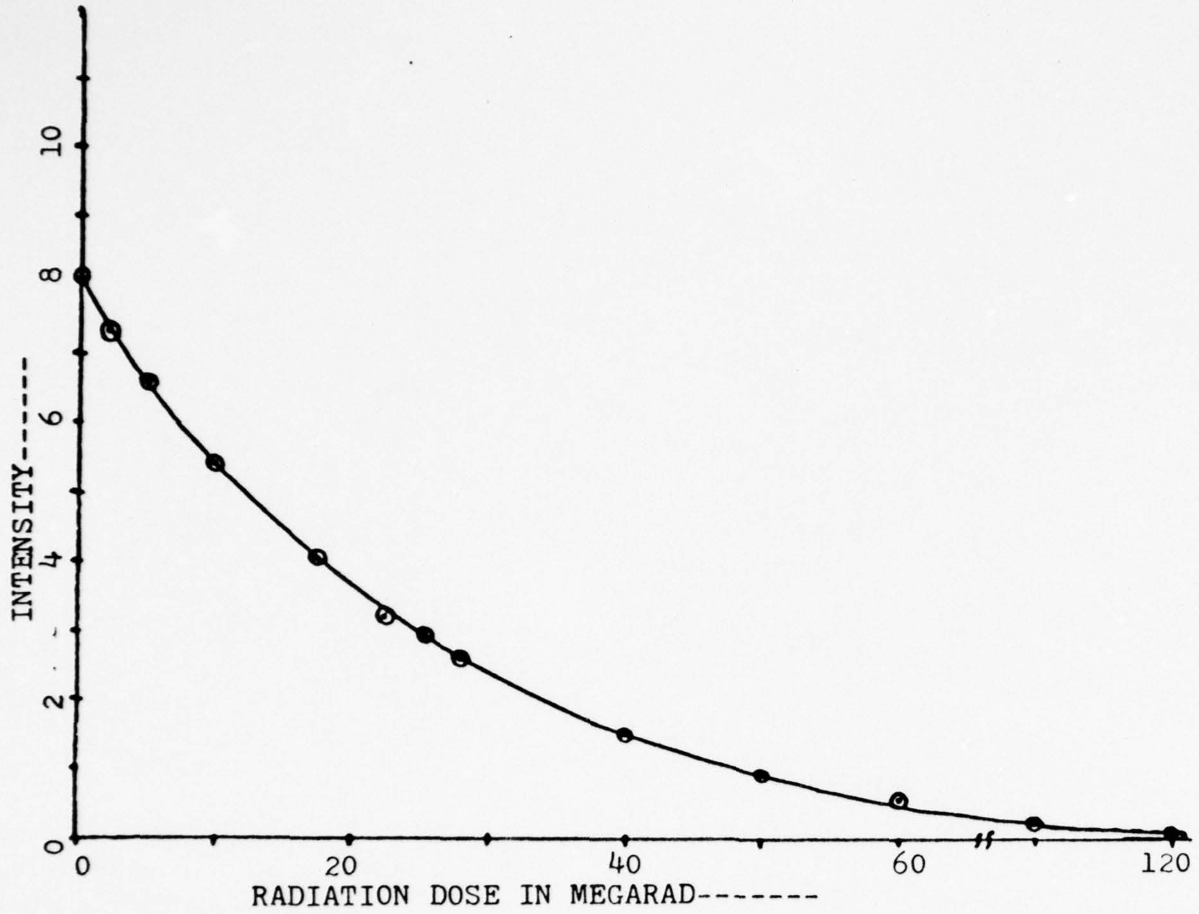


FIGURE: 9 PLOT OF I_{920cm}-1 VS RADIATION DOSE IN SOLID STATE POLYMERIZATION OF C_{10}-DIYNE-C_2-ACID(BULK).

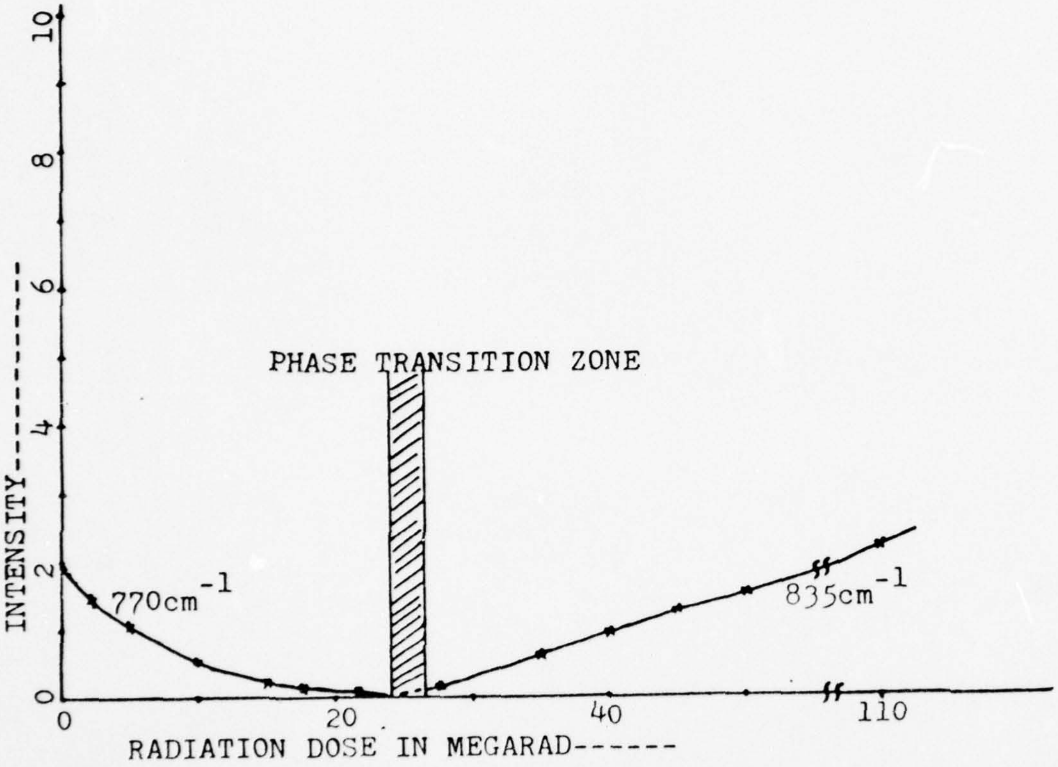


FIGURE: 10 INTENSITY VS RADIATION DOSE IN SOLID STATE POLYMERIZATION OF C_{10}-DIYNE-C_2-ACID.

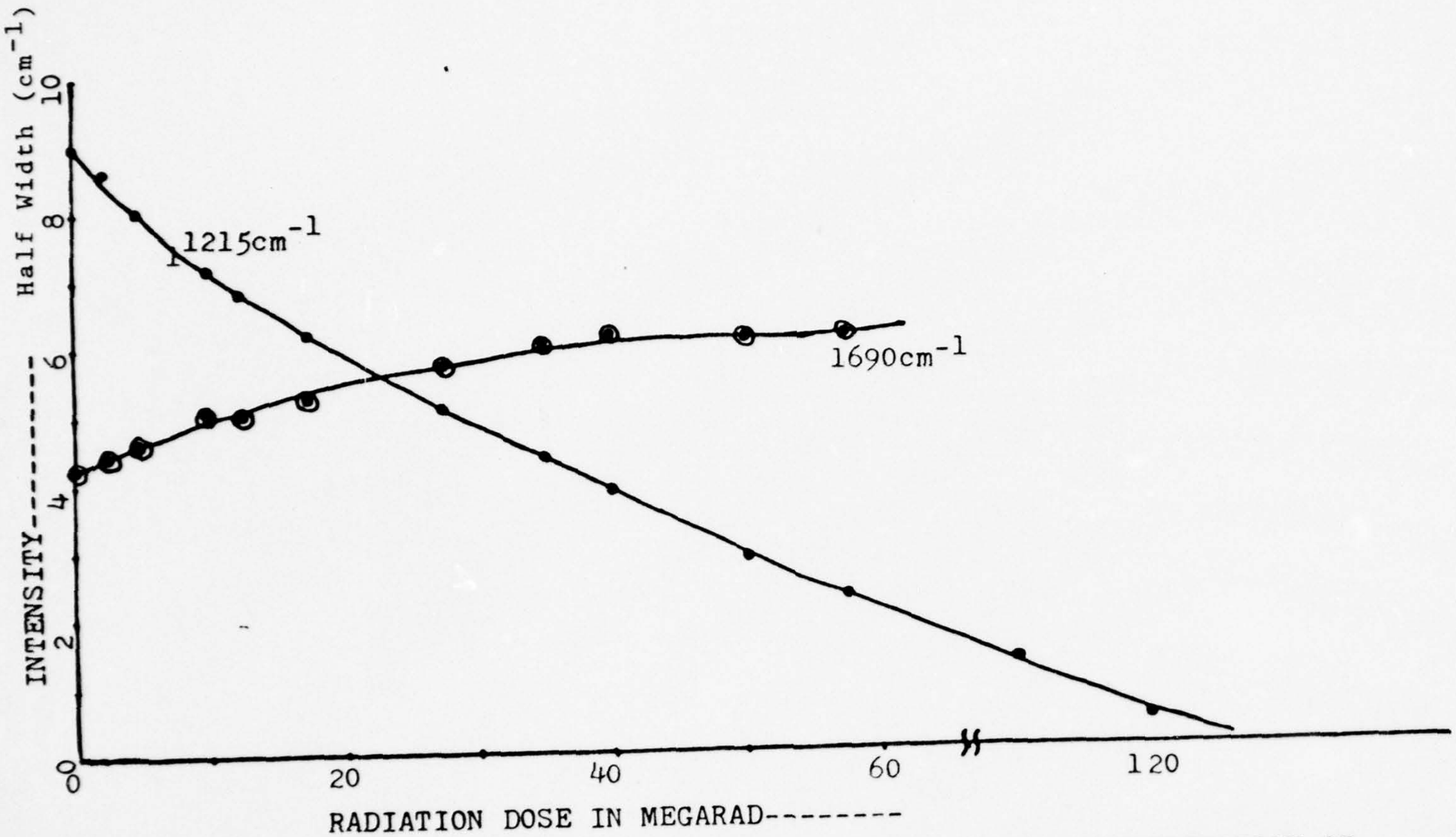


FIGURE: 11. INTENSITY VS RADIATION DOSE IN SOLID STATE POLYMERIZATION OF C_{10}-DIYNE-C_2-ACID.

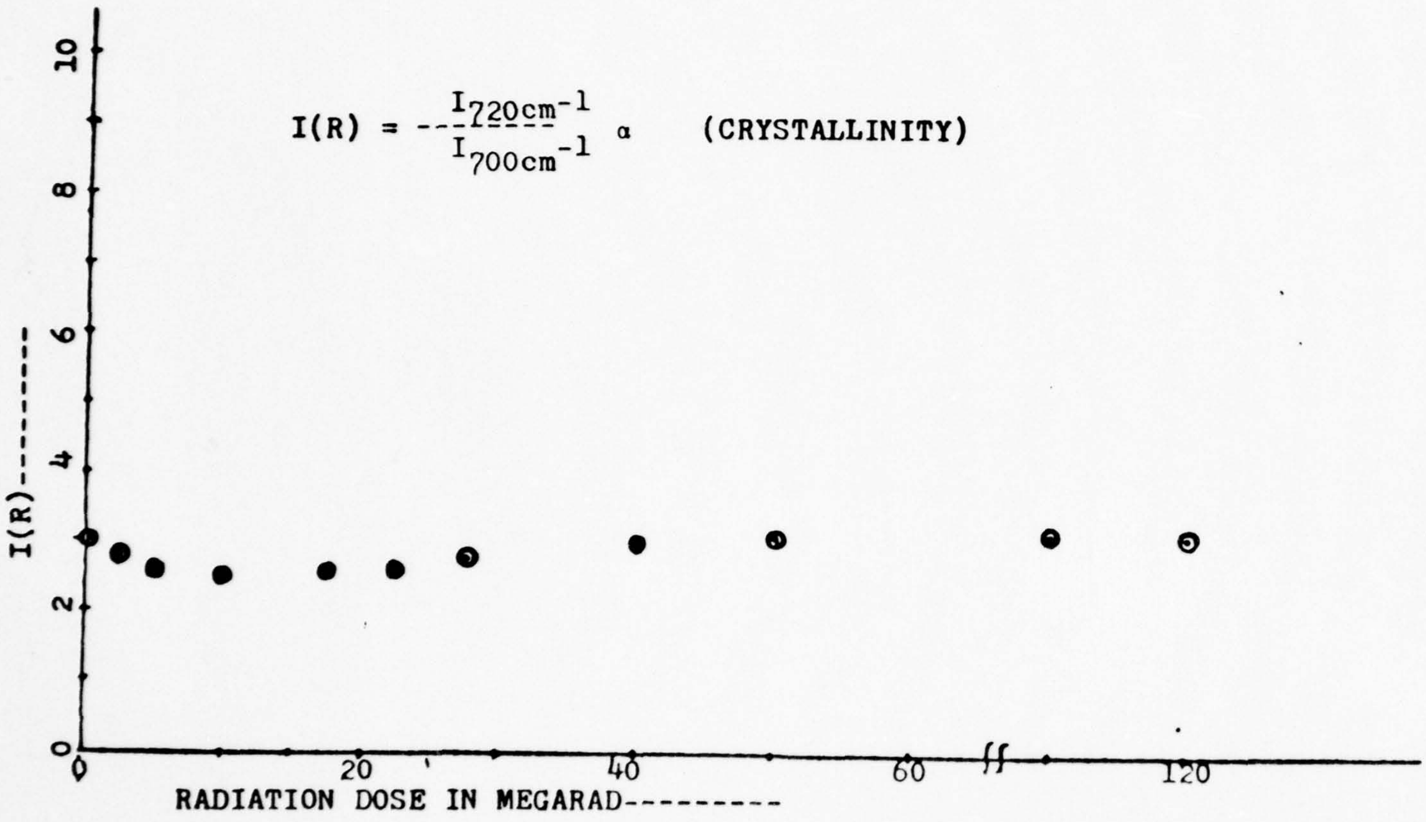
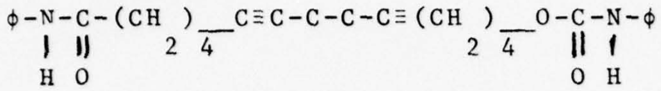


FIGURE: 12 CRYSTALLINITY VS RADIATION DOSE IN SOLID STATE POLYMERIZATION OF C_{10}-DIYNE-C_2-ACID.

MONOMER 4



$$\phi-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-(CH_2)_4-C\equiv C-C-C-C\equiv(CH_2)_4-O-\underset{O}{\underset{\|}{C}}-\underset{H}{\underset{|}{N}}-\phi$$

The molecular structure of the polymer has been established from the x-ray analysis of Drs. Enkelmann and Lando.[2]

The reported bond distances are consistant with a strong contribution of the butatriene resonating form for this polymeric backbone. Recently Baughman, on the basis of his optical spectroscopy data, has supported this idea of a butatriene backbone for Poly TCDU.

The present I.R. study was undertaken to confirm this assignment. Figure 13 shows the spectral region 2300-1550cm^{-1}. Figure 14 presents the C≡C vibrational region 2300-2000 cm^{-1} more clearly. Figure 15A and 15B presents the 900-750cm^{-1} region unpolarized and 90° polarized respectively.

It is quite interesting to note the bands representative of acetylenic/butatriene backbone motions. From experimental experience and literature studies 40-42 the following band assignments have been made for backbone vibrations:

Figure 13

a→2290cm^{-1} , C≡C symmetric stretching, monomer
b→2200cm^{-1} , C≡C asymmetric stretching, polymer
c→2150cm^{-1} , C≡C asymmetric stretching, monomer
d→2100cm^{-1} , C≡C symmetric stretching, polymer
e→2030cm^{-1} , C=C symmetric stretching, polymer, ν_1-butatriene
m→1615cm^{-1} , C=C symmetric stretching, polymer
n→1595cm^{-1} , C=C asymmetric stretching, polymer, ν_2-butatriene

Figure 15A and 15B

c→800cm^{-1} , C=C stretching, ν_3-butatriene, orthogonal to ν_1 and ν_2

The observations in this study can be summarized as follows:

1) Using aunpolarized I.R. beam the following bands could be seen from the as polymerized needle single crystal:

2290
2150 cm^{-1} for monomer or oligomer (Figure 13 and 14)

2200
2100cm^{-1} for polymer (Figure 13 and 14)

2030
1595cm^{-1} for polymer (Figure 13)

800cm^{-1} band as a shoulder, for polymer (Figure 15A).

ii) Using a 90° polarized beam: the C≡C vibrational modes did not appear as distinct bands, ν_1-butatriene

(2030cm^{-1} is reduced, the ν_2 (1595cm^{-1}) did not appear to change, ν_3(800cm^{-1}) band appeared as stronger than before. Figure 15B shows the 900-750cm^{-1} region with special reference to the band at 800cm^{-1}.

iii) Because of the presence of $(CH_2)_4$ groups adjacent to the π-delocalized backbone, one can see the presence of a characteristic 1790cm^{-1} band (combination CH_2 rocking modes) in Figure 13, (band j) as observed with the other compounds in this study. The relatively weak monomeric peaks could be accounted for as arising from the oligomers. Because of their short chain lengths they possess monomeric behavior at the chain ends.

Also from x-ray structure analysis 2 or from optical spectroscopy 43 no evidence for the existence of unreacted monomer was obtained. This can be correlated with the early observation with other compounds (monomers 1,2,3) that after a given radiation dose virtually all the monomer has reacted to give a wide range of oligomers and polymer.

In Figure 16 the butatriene backbone rod is inclined at an angle of about 20° with the c axis 2. This means that in our experiment the beam is not perpendicular to the butatriene backbone. (IR beam ⊥ to c axis). Thus we have a strong ν_3 (800cm^{-1}, Figure 15A) when unpolarized light was used and the presence of a strong ν_3(800cm^{-1}, Figure 15B), a moderately strong ν_2 (1595cm^{-1}) and absent ν_1 (2030cm^{-1}) when a 90° polarized beam was used. These data fit the reported requirements for a butatriene structure.

It is to be noted that some of these butatriene modes are in the same region as benzene C=C π stretching modes. This confusion is resolved by the experiment using the 90° polarized I.R. beam as discussed.

Thus this study supported Drs. Enkelman and Lando's early observation 2 of a butatriene backbone for the polymer.

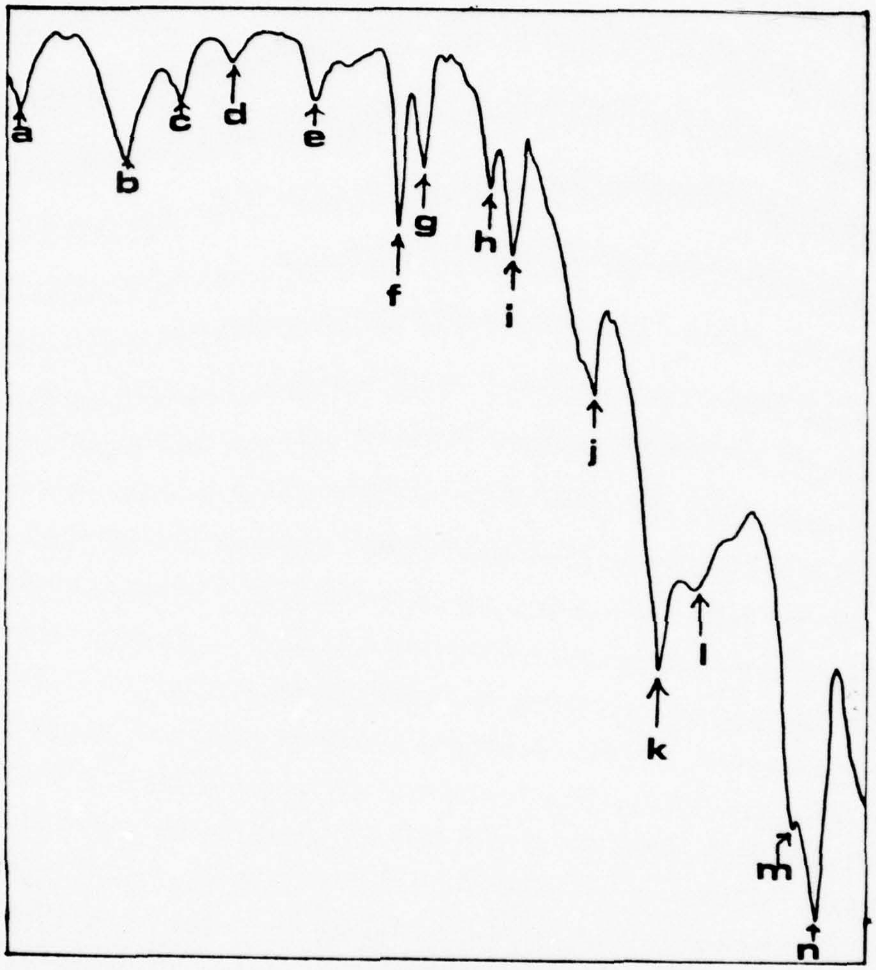


FIGURE: 13 FTIR SPECTRUM OF AS POLYMERIZED TCDU. (2300-1550 cm^{-1}).

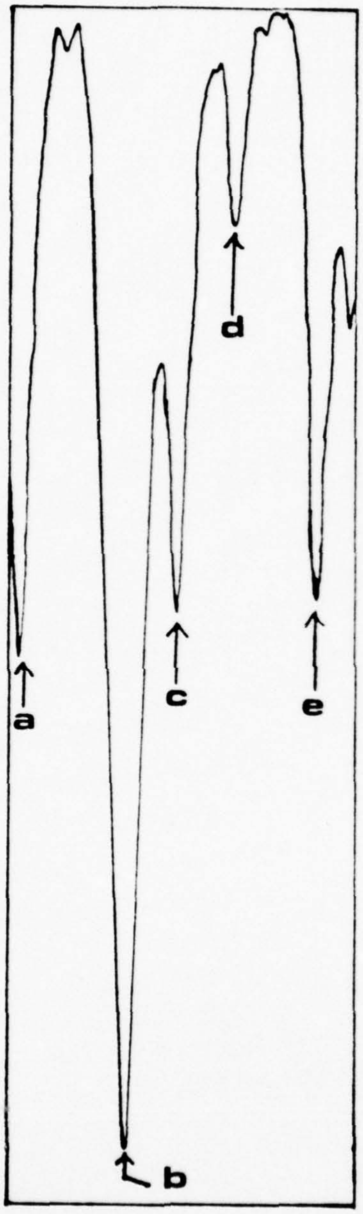


FIGURE: 14 FTIR SPECTRUM OF AS POLYMERIZED TCDU.
(2300-2000 cm^{-1}).

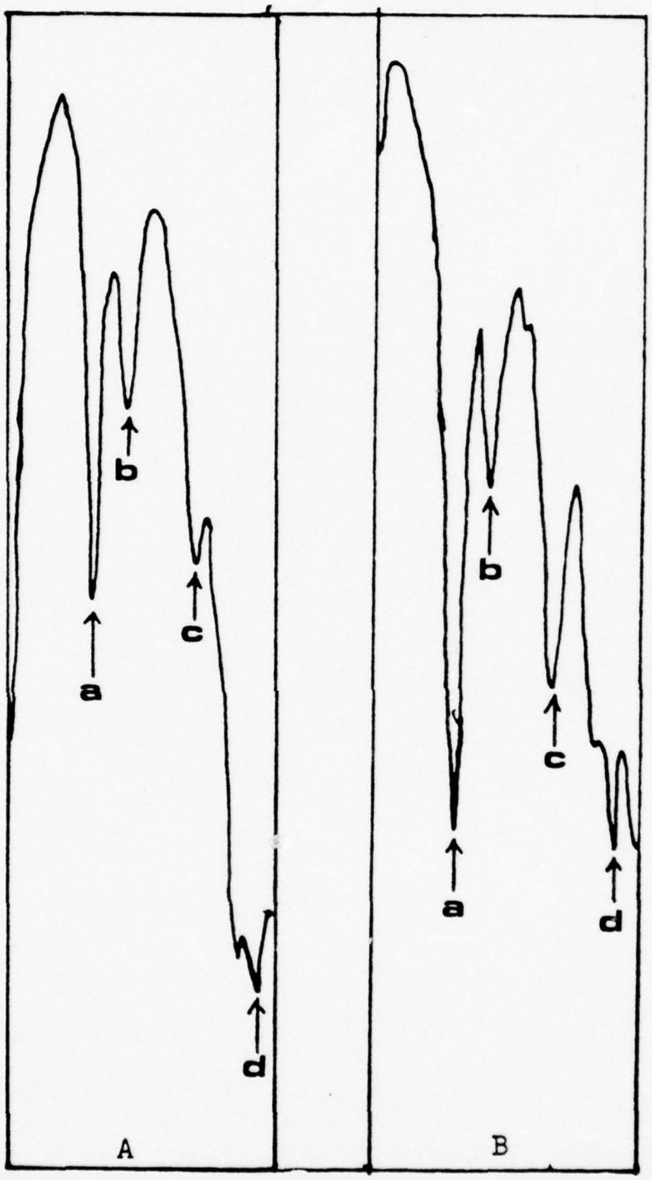
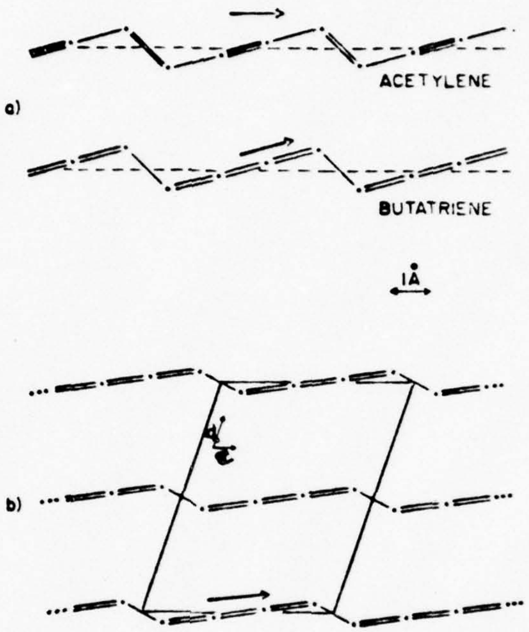


FIGURE: 15 FTIR SPECTRUM OF AS POLYMERIZED TCDU.
1 A =WITHOUT A POLARIZER (900-750 cm^{-1}).
B = POLARIZER AT 90° (900-750 cm^{-1}).



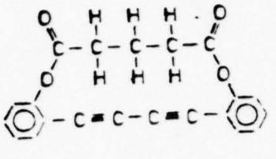
a) Two possible resonance structures for polydiacetylene backbone. The arrows show the polarization directions predicted by the exciton model. The two chains are drawn to scale with bond lengths taken from X-ray of TCDU.

b) Chain projection onto $\underline{\underline{ac}}$ plane of TCDU.

FIGURE 16.

MONOMER 5

o,o'bis phenyl gluterate diacetylene



This compound was studied through the spectral region of 3800-450cm^{-1}. Figures 17,18,19 and 20, present the spectral regions 3100-2700cm^{-1}, 2300-2000cm^{-1}, 2000-1500cm^{-1} and 1500cm^{-1}-450cm^{-1} respectively. Band assignments are given in Table 11.

The x-ray structure analysis of an "as polymerized" single crystals was dose in our laboratory.

Crystallographically active BPG has a C2/c symmetry whereas the inactive form has a Pc or P2/c symmetry. In both structures there are four molecules per unit cell. The $(CH_2)_3$ groups are in an all-trans arrangement for the active form but not necessarily in the inactive form. In Figure 17 the aromatic C-H stretching modes are well resolved for the inactive monomer (spectrum 1, bands a) in Table 11. In spectrum 2 these bands are either superimposed upon a broad band of the polymer and/or shifted because of different packing in the active and inactive forms. In spectrum 3 these bands are poorly resolved in part because of the small amount of sample.

Because of a strong interaction between the electron pair from the C=O oxygen and the adjacent C-H bond, the symmetric- C-H stretching frequency is shifted down to

$2760cm^{-1}$. The asymmetric stretching mode appears in its normal position as a doublet ($2855cm^{-1}$ and $2820cm^{-1}$). This interaction between the electron pair (C=O, oxygen) and the C-H bond electrons in the polymer and the polymerized samples becomes more intense and give two kinds of C-H modes. Their interaction gives a doublet for both the asymmetric and symmetric C-H stretching modes ($2855cm^{-1}$, $2820cm^{-1}$ and $2775cm^{-1}$, $2760cm^{-1}$).

The C≡C vibrational region is shown in Figure 18. There are a large number of bands in the unreactive form. The band assignments are given in Table 11. The reason for the appearance of the $2100cm^{-1}$ band in the unreactive form (spectrum 1) is not clear, but is suggestive of the fact that within the unreactive crystal there was some reactive form. These reactive molecules have reacted to give oligomers within the unreactive molecular matrix. (This possibility can not be ruled out because active and inactive crystals are grown from the same solution but at different rates).

In the as polymerized sample the characteristic monomer bands ($2220cm^{-1}$ and $2150cm^{-1}$) are reduced. In the pure polymer (spectrum 3) no C≡C stretching mode could be seen, the most probable reasons being the apparent symmetry of the long polymer chains and/or the small amount of sample.

Thus from the 2300-2000cm^{-1} region the following conclusions can be drawn:

i) The unreactive crystalline form of BPG contains active form within it. This reactive form polymerizes to give short chain oligomers.

ii) The "as polymerized" sample contains residual monomer and polymer but no oligomer. This is in accordance with previous x-ray crystal structure analysis 3 of the as polymerized sample where it was shown to have 65% residual monomer and 35% polymer in a solid solution.

iii) The absence of the 2100cm^{-1} band in the as polymerized sample and the pure polymer supports the above two conclusions.

The 2000-1500cm^{-1} region is shown in Figure 19. That the unreactive form has a different structure from the reactive form is clear from spectra 1 and 2 of Figure 19. In spectrum 1 the C=O stretching mode is a doublet at 1750cm^{-1} and 1770cm^{-1}($I_{1770} > I_{1750}$) but in spectra 2 and 3 the C=O stretching mode is comparatively broad and is centered around 1750cm^{-1}.

Because of the strong C=O stretching mode the group of four bands between 1660cm^{-1} and 1450cm^{-1} seem weak, because their intensities are relative to the C=O mode. They are actually stronger than all bands in the C≡C stretching region. These bands are characteristic of aromatic rings and the butatriene backbone 3 of the polymer chain. In Figure 20 the polymer as well as the monomer have a band at 805cm^{-1}. On the basis of these data no definite conclusion can be drawn, but the possibility of a butatriene backbone structure can not be ruled out. It can be seen that spectra 1,2 and 3 all have strong 750cm^{-1} bands in Figure 20. This is the characteristic aromatic C-H out of plane deformation. 40, 41.

This 750cm^{-1} band for an ortho substituted benzene ring is independent of substituent nature. The complex conbination of bands from 1235cm^{-1} to 950cm^{-1} are assigned to aromatic C-H in plane deformation. These bands are not analyzed individually but qualitatively some changes can be noticed between spectra 1, 2, and 3 of Figure 20.

Thus unlike monomer 1, as polymerzed BPG after a dose of 50 Megarad has residual monomer and polymer as a solid solution. No phase change can be observed. The unreactive form has characteristic infrared bands different from the active for m in the1500-450cm^{-1} region and in the C=O stretching region.

Table 11

Figure 17

a	3050 3070cm^{-1} 3090	Aromatic =C-H stretching modes
b→	2855cm^{-1}	CH$_2$ out of phase vibrations
c→	2820cm^{-1}	
d→	2775, 2760cm^{-1}	CH$_2$ inphase vibrations

Figure 18

a→	2250cm^{-1}	sym. C≡C stretching mode, monomer
b→	2220cm^{-1}	
c→	2180cm^{-1}	asym. C≡C stretching mode, monomer
d→	2150cm^{-1}	
e→	2100cm^{-1}	sym.C≡C stretching mode, (probably oligomer)

Figure 19

a→	1770cm^{-1}	C=O stretching, ester
b→	1750cm^{-1}	
c→	1660cm^{-1}	Benzene ring breathing modes, superimposed on backbone C=C stretching modes
d→	1600cm^{-1}	
e→	1580cm^{-1}	
f→	1490cm^{-1}	

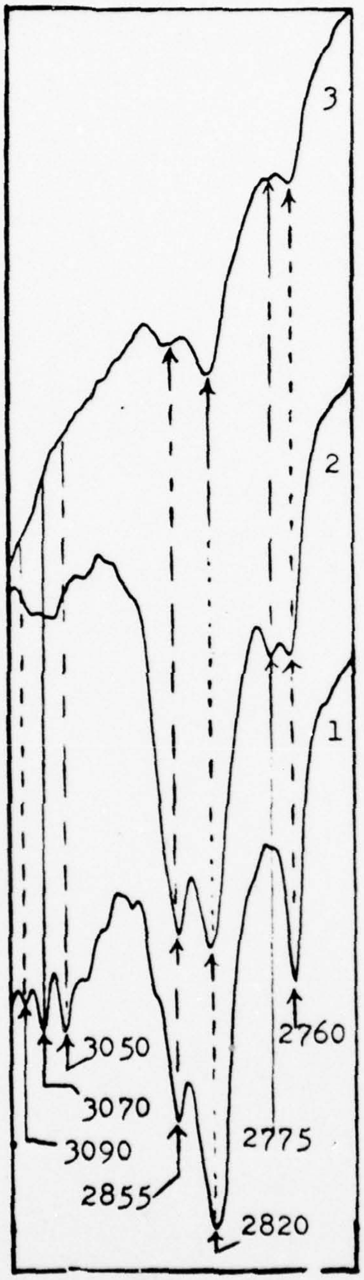


FIGURE: 17 FTIR SPECTRA OF BPG, 1.INACTIVE MONOMER, 2.AS POLYMERIZED, 3.PURE POLYMER. (3100-2700 cm^{-1}).

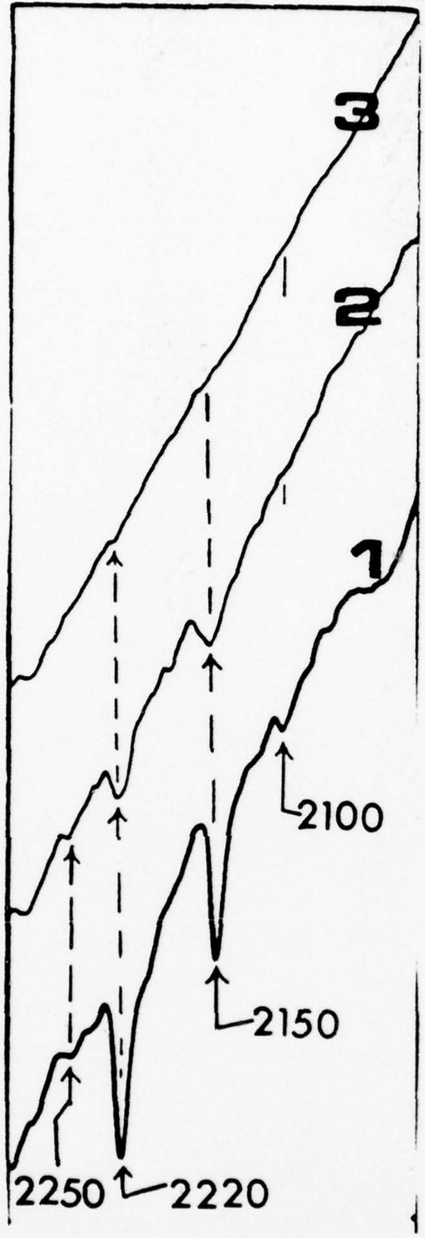


FIGURE: 18

O,O BISPHENYL GLUTERATE [BPG].

FTIR SPECTRA OF 1 INACTIVE MONOMER, 2 AS POLYMERIZED, 3 PURE POLYMER.

[2300—2000 cm^{-1}]

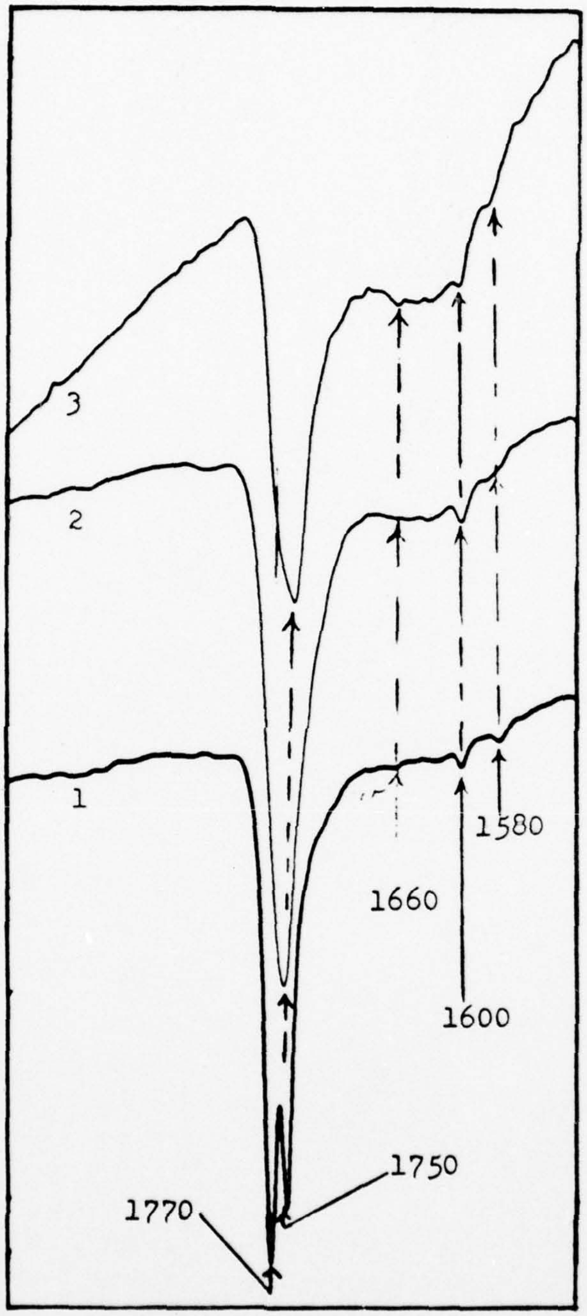


FIGURE: 19 FTIR SPECTRA OF BPG, 1. INACTIVE MONOMER 2. AS POLYMERIZED, 3. PURE POLYMER. (2000-1550 cm-1).

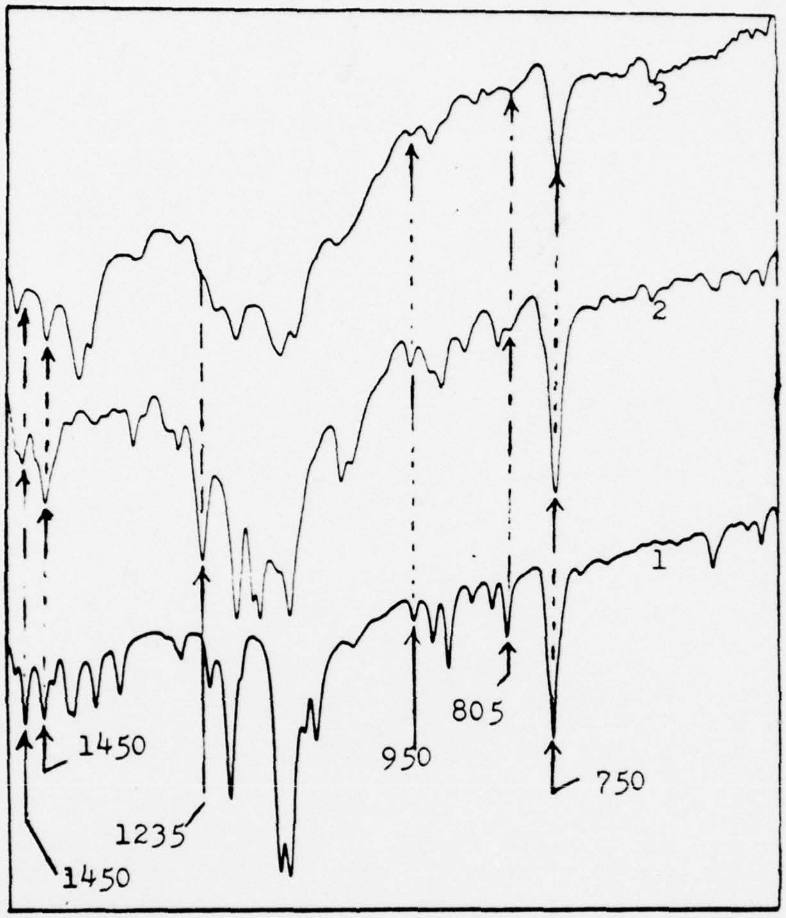


FIGURE:20 FTIR SPECTRA OF BPG, 1.INACTIVE MONOMER, 2.AS POLYMERIZED, 3.PURE POLYMER. (1500-450 cm^{-1}).

Conclusions

A number of interesting observations have been noted during infrared spectroscopic investigation of the polymerization of five different conjugated diacetylenes. These observations are summerized as follows:

1. A solid solution of monomer and polymer have been observed through the entire range of polymerization in the systems

$C_{12}-C\equiv C-C\equiv C-COOH$

$C_{12}-C\equiv C-C\equiv C-CH_2OH$ only after prolonged treatment

$C_{10}-C\equiv C-C\equiv -C_c-COOH$

2. A phase change from a monomer rich phase in the early stages of polymerization to a polymer rich phase in the later stages of polymerization has been observed in all the above diacetylene systems. In the polymer rich phase the oligomers and/or monomer form a solid solution in the polymer structure.

3. Eventually a complete reaction of all monomer molecules excepting BPG after a give irradiation (e.g. about 35 Megarad for C_{12}-Diyne-Acid) has been observed. Thus at a very low dose the samples contain unreacted monomer, soluble oligomers and polymer. At high dose primarily polymer with some oligomer are present. The presence of oligomers has been observed in all of the as polymerized samples except BPG and TCDU, where no definite conclusion can be drawn.

4. Soluble oligomers have a major contribution from the butatriene structure as indicated by strong and well resolved bands at 2030cm^{-1}, 1590-1600cm^{-1}, and 805-870cm^{-1}.

5. With the exception of poly TCDU and poly BPG all other polymers have an acetylenic backbone. Poly BPG does not show any indication of C≡C stretching modes in the I.R. and x-ray structure investigation indicates a strong contribution from the butratriene structure 3.

6. Some of the bands in poly TCDU which we claim to be positive evidence for a butatriene backbone are superimposed on bands originating in the benzene ring (compared with polystyrene).

This confusion has been resolved by polarized I.R. on a needle single crystal of poly TCDU. The I.R. beam is perpendicular to the needle axis (c-axis of the polymer backbone). The band at 805cm^{-1} appears strong only with the 90° polarized beam whereas the 2030cm^{-1} (ν_1 of butatriene) is considerably reduced (does not disappear because of benzene C=Cπ-stretching mode). This observation fits in with the butatriene stretching mode requirements as the 805cm^{-1} band should be perpindicular to the other two.

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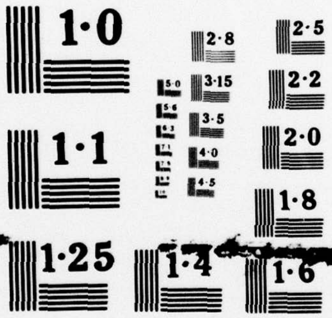

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