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RADIATION INDUCED SOLID-STATE POLYMERIZATION OF ACETYLENEDICARBOXYLIC ACID

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ABSTRACT

Radiation induced solid-state polymerization of acetylenedicarboxylic acid was carried out at room temperature in open atmosphere and under vacuum conditions. The gray colored powder polymer obtained was insoluble in most common solvents but only partially soluble in DMSO and THF. The limiting conversion to polymer was about 5%. The polymer was characterized by IR, UV, DP-MS, DSC, TGA, and XRD. The mechanism of polymerization was elucidated from the available data. Polymerization followed a free radical mechanism. However, before the addition of monomer molecules to the growing chain, at least one of the carboxylic groups of the monomer breaks away as CO or CO_2. The formation of side group cyclization takes place. At least one of the bonds in the side cyclic group is an etheric bond. The DSC, TGA, and XRD results showed that the polymer was partially crystalline and showed no melting up to 1200°C. The mechanism of polymerization and assigned chain structure was studied by the direct pyrolysis mass spectrometric method.

The crystal structure of monomer and polymer was investigated by the XRD method. Both monomer and crystalline polymer were monoclinic with similar cell parameters. Thus, the polymerization follows a topotactic mechanism. The unpolymerized monomer retains its crystal

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structure and, therefore, CO or CO_2 in the monomer molecule has to be eliminated before polymerization could take place.

Key Words: Solid-state polymerization; Acetylene; Disubstituted acetylene; Direct pyrolysis; Radiation polymerization

INTRODUCTION

Special interest to the study of solid-state polymerization was encouraged after discovery of the Ziegler Natta catalyst to obtain crystalline polymers. In the solid state polymerization, the 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 one of the crystallographic axis of that monomer.[2–6] However, it was reported that only a few kinds of the monomer could yield crystalline polymer in solid-state polymerization [2,7–8] and most of the vinyl type monomer gave amorphous polymer. Some monomers with a suitable crystal structure [5] or modification in the monomer structure gave crystalline polymer. For example, we have previously reported [9] that in the polymerization of 3-aminocrtonamide by radiation, the monomer was polymerized by a condensation mechanism. The polymer obtained was crystalline and NH_3 molecules were produced as a side group.

The solid state polymerization of the diacetylene monomer lead to crystalline polymer by a 1,4-addition reaction.[8,10–12] The reaction was promoted by a special arrangement of the monomer molecules in the crystal matrix. The molecular arrangement was greatly affected by an R group connected to acetylene in the molecule. The polymerization was usually a topotactic type. However, the reactivity of disubstituted acetylene molecules is very low and no solid state polymerization has been reported. For example, Ziegler-type catalysts failed to polymerize 3-hexyne [13] because they were sterically hindered. However, a linear oligomer ($M_n = 724$) and cyclic trimer of the 3-hexyne mixture were obtained by the diarylcobalt catalyst.[14] The polymerization of 3-hexyne and 4-methyl-2-hexyne by Nb (III) and Ta (III) based salt has been reported.[15] High molecular weight ($M_w > 1 \times 10^6$) polymer of 2-hexyne by $MoCl_5$ and WCl_6 were reported.[15] These types of catalysts have been used to polymerize several disubstituted acetylene.[16–19] Acetylenedicarboxylic acid (ADCA) has not been polymerized before. However, Cataldo [20] reported the production of CO, CO_2, and soluble polyynes but no free acetylene in the anodic oxidation of this compound.

In this work, we are expecting a polycondensation type reaction by gamma-ray irradiation with the elimination of CO and/or CO_2 from the ADCA molecule. The kinetic of polymerization and product characterization will be studied.

EXPERIMENTAL

Material and Methods

Acetylenedicarboxylic acid was obtained from Aldrich Chemical Co. and purified by recrystallization in diethyl ether. Most of the solvents were Merck products and used without further purification. The purification of other solvents was done by distillation.

Co-60 Gamma irradiation was done in a 220 Model Gamma Cell of Atomic Energy of Canada Limited Co. The dose rate of the source during the experiments was 0.017 Mrad/h. UV spectra in DMSO were done on a Shimadzu 160 UV-spectrophotometer. IR spectra were obtained from Mattson 1000 spectrophotometer, using KBr pellets. DSC spectra were done on a TA 910 S model DSC with a heating rate of 10°C/min. DuPont 951 type TGA was used to investigate the thermal decomposition of the monomer and polymer under nitrogen atmosphere. The rate of heating was 10°C/min. Gel Permeation Chromotography (GPC) spectrum was done on a water 160 type GPC using THF as solvent. The viscosity average molecular weight, using Ubbelohde type of glass viscometer, were measured at 25°C in DMSO as solvent. The mass spectrometer used for direct pyrolysis experiment was a Balzers QMG 311 quadruple Mass Spectrometer. For the X-ray powder diffraction, the Enraf-Nonius diffractometer of FR 582 (CuK_{α}; kV and 20 mA), which was equipped with a Huber SMC 9000 Goniometer, was used.

Procedure

The solid state polymerization of ADCA, initiated by Co-60 γ-rays, was done under vacuum and in open atmosphere at room temperature. About 3–5 g of monomer sample was placed into an irradiation Pyrex glass tube and connected to a high vacuum system for 4–5 hours evacuation. The tube was then removed from the vacuum source by a sealed cutting and placed in the irradiation source at room temperature for the desired time. After irradiation, the tube was broken open. The monomer was extracted from the polymer by water extraction. The polymer was filtered and dried to a constant weight. The percent conversion of the monomer to polymer was calculated gravimetrically.

RESULT AND DISCUSSION

Solid State Polymerization of Acetylenedicarboxylic Acid

Radiation induced solid state polymerization of ADCA under vacuum and in open atmosphere gave gray colored powder polymers, which were insoluble in most common solvents but partially soluble in DMSO and THF. The percent conversions of monomer to polymer against total irradiation

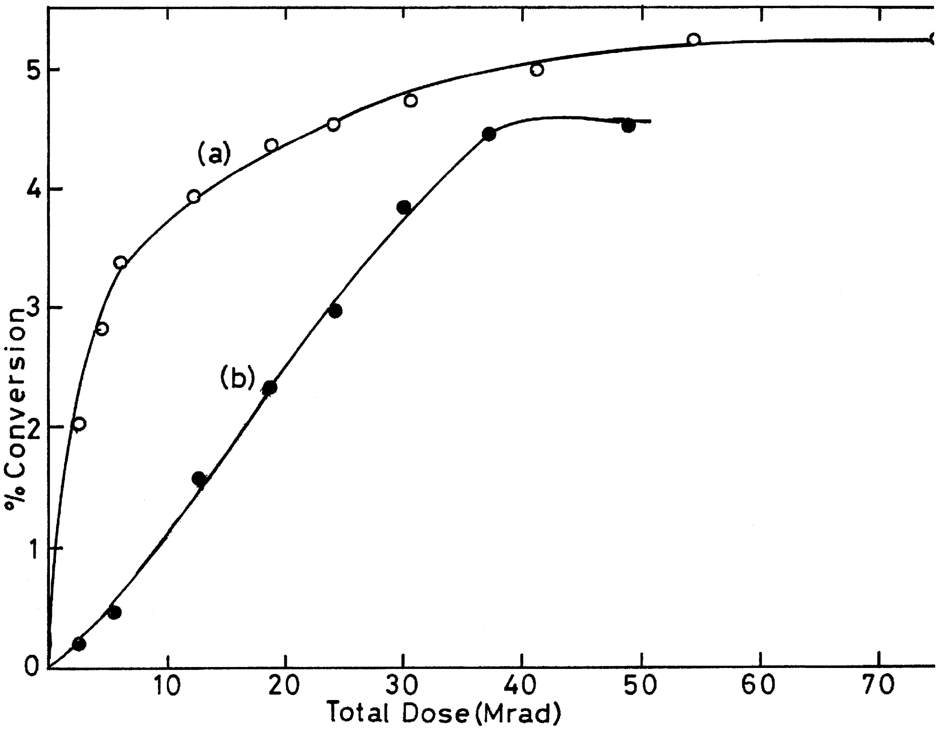


Figure 1. Radiation induced solid state polymerization of acetylenedicarboxylic acid (a) under vacuum and (b) in open atmosphere.

doses are plotted in Fig. 1 for the polymerization (a) under vacuum and (b) in open atmosphere. No polymer could be obtained for about the first 100 hours irradiation for polymerization in vacuum and much longer for that in open atmosphere. However, the scale used for radiation dose in Fig. 1 is not permitting the observation of the induction period clearly. The kinetic curves show a S-type autocatalytic mechanism, which is very common for radiation induced polymerization. The initial rate is slow and the percent conversion, after an induction period, first increased linearly with a constant rate, then the rate increased up to about 4–5% conversion. The percent conversion levelled off at a limiting value of about 5–5.5%. The limiting conversion can be expected to be higher if the dose rate of radiation source was higher. In the presence of oxygen (Fig. 1b), the rate of polymerization is slower and the induction period longer. The conversion percent after 15 days (6 Mrad) of irradiation is only 0.4%, which was 2.7% after 10 days (4 Mrad) irradiation under vacuum condition. Therefore, there is a retarding effect of oxygen. Thus, the polymerization is most probably a radical type.

For the polymerization process in the solid matrix, the monomer molecules have to be in such an orientation that they will be suitable for an addition reaction. If the active side of monomers is more than van der Walls distance apart from each other, the addition will not be possible.[6] In this case, energy has to be given to change the orientation of the molecules by overcoming the lattice energy of the monomer crystal and putting the molecules in a more favorable orientation for the addition reaction. This is one of the reasons for the induction period observed in the kinetic curve (Fig. 1). In other cases, the steric hindrances of the molecule may prevent an additional reaction. A type of condensation process can overcome this. A small fragment from the monomer molecule is broken away by radiation, and now the rest of the molecule can give an addition reaction. In fact, this last mechanism reported before for 3-aminocrotonamide [9,21] is also followed for polymerization of ADCA. The limiting conversion is related to the crystal structure of the monomer, which is investigated by X-ray.

Since the polymer is insoluble in most common solvents, the molecular weight of only the soluble fractions in DMSO could be measured by viscosity methods. The results are presented in Table 1. The intrinsic viscosities are largest when the rate of conversion slows down near the limiting conversion. When reaching the limiting conversion, the average molecular weight decreases with further irradiation due to the formation of shorter polymer chains and the degradation in longer chains. This is a general trend in radiation-induced polymerization. The GPC gave a monomodel distribution of molecular weight. However, detail work could not be carried out because of the insolubility of the polymer.

Infrared Spectral Investigation

The FTIR spectra of (a) monomer; (b) polymer obtained in open atmosphere irradiation and; (c) polymer obtained under vacuum irradiation is given in Fig. 2. The peaks in the monomer spectrum (Fig. 2b) are assigned as: 3640–2800 cm^{-1} to OH; 2400–2270 cm^{-1} to $C{\equiv}C$; 1710 cm^{-1} to C=O. The peaks around and smaller than 1000 cm^{-1} mostly represent the hydrogen bonding and resonance structures. The broad OH peak extending between 3640−2800 cm^{-1} indicates strong hydrogen bonding. It is most

Table 1. The Intrinsic Viscosities of Some Poly(ADCA) Samples

Radiation Dose (Mrad)	Intrinsic Viscosity (In Vacuum)	Intrinsic Viscosity (Open to Atmosphere)
4.02	0.076	–
18.25	0.698	0.540
48.68	–	0.170
73.02	0.308	–

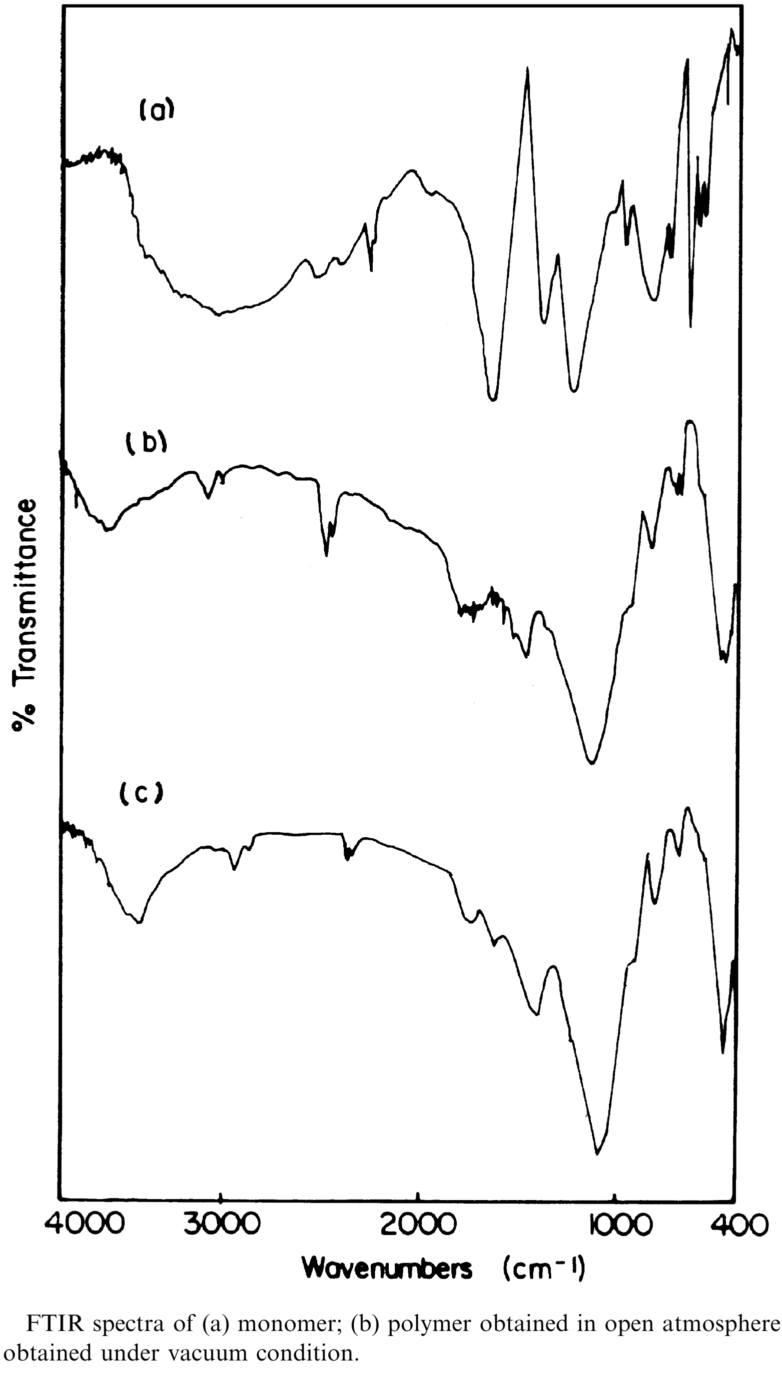


Figure 2. FTIR spectra of (a) monomer; (b) polymer obtained in open atmosphere, and (c) polymer obtained under vacuum condition.

probably due to the dimerization of molecules by the hydrogen bonding of $C{=}O\cdots H{-}O$. After polymerization, this peak disappeared, replacing a relatively weaker peak at 3600 cm^{-1} corresponding to OH without the hydrogen bonding (Fig. 2b and c). The second peak in this area (about 2900 cm^{-1}) shows C-H formation in the polymer. The acetylene peak at 2400–2270 cm^{-1} is quite weak because of the high symmetry in the monomer molecular structure, which reduces the dipole character of this bond. Since carbons in $C{\equiv}C$ and carboxylic functional groups are sp and sp^2 hybrid configurations, respectively, the molecule is planar. It has both a center of symmetry and a reflection mirror perpendicular to the plane of molecule. After the irradiation of the sample, modification takes place in the structure of the molecule with the splitting of CO and/or CO_2 fragments. The acetylene groups are now not quite symmetrical, and an increase in dipole will be observed. However, the direct involvement of $C{\equiv}C$ in polymerization reduces its concentration. Therefore, peak intensity due to acetylene in the polymer spectra (Fig. 2b and 2c) is low. In the polymer spectrum, a broad intense peak at around 1100 cm^{-1} corresponding to C-O-C ether group formed after polymerization takes place. The peak of C=O disappeared in its position and a relatively weak peak at 1660 cm^{-1} shows the newly formed C=C and C=O coincided. The C=C group is most likely existing in side group cyclization.

UV Investigation

The UV spectra of (a) monomer, and (b) polymer obtained by irradiation under vacuum are given in Fig. 3. The UV spectrum of polymer obtained by irradiation in open atmosphere is identical to that corresponding polymer obtained under vacuum. The absorbance at 291 nm in UV spectrum of monomer (Fig. 3a) corresponds to acetylene bond. The peak position shifted to 293 nm in polymer UV-spectrum (Fig. 3b) and a shoulder formed on the peak. These spectra are similar to that of poly (2-hexyne).[15] The result shows the C=C=C type bonding in the polymer chain. If this is an indication of C=C=C bonding in the main chain, the polymer would be expected to be conductive. However, the polymer obtained is not conductive, and most probably this type of bonding is on the side chain cycle groups rather than in the main polymer chain.

Thermal Investigation

The DSC thermogram of the monomer taken under N_2 atmosphere is shown in Fig. 4. There is a sharp exothermic peak at 204.8°C. No melting peak could be observed up to 300°C studied in this work. However, Benghiant et al. [22] have reported a melting point of 175°C for ADCA. They obtained anhydrous crystals by the slow evaporation from nitromethane solution. They also reported that the crystal was monoclinic with cell

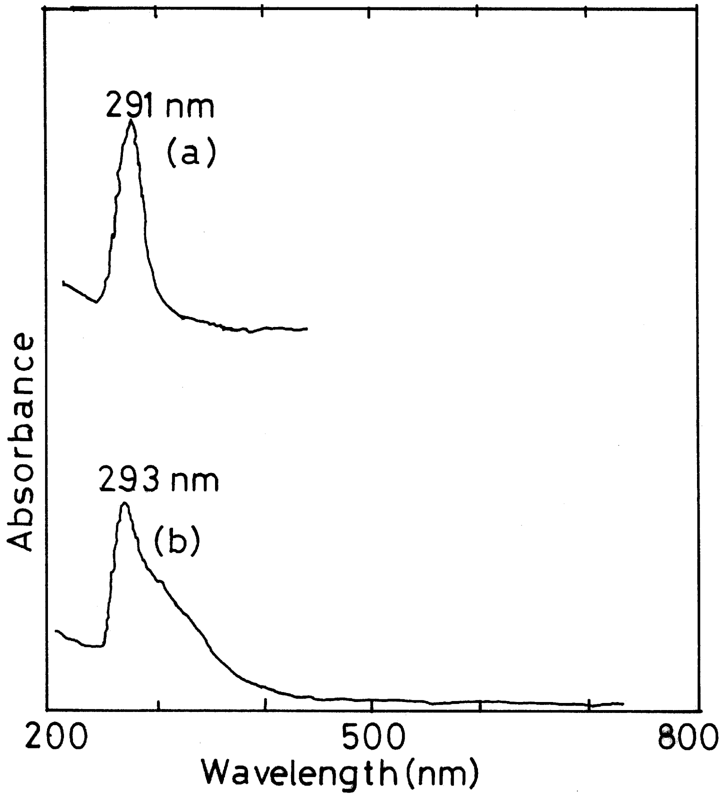


Figure 3. The UV spectra of (a) monomer, and (b) polymer obtained by irradiation under vacuum condition.

parameters of a = 14.894 A; b = 6.420 A; c = 4.862; z = 4 and space group was $P2_1/n$. In this study, we recrystallized the compound from diethylether. Therefore, the crystal structures and thermal behavior of the crystal could be different. We measured the melting point by a conventional method as 179°C, which could not be seen in the DSC thermogram. The peak obtained is most probably due to the splitting off CO and/or CO_2 from the molecule. This will be clarified better with results of thermal behavior (TGA) of samples and mass spectrum. The DSC thermogram of polymer obtained under vacuum is given in Fig. 5. The DSC thermogram of polymer obtained by irradiation in open atmosphere was identical to that under vacuum. The thermogram shows a T_g at 157°C, with no melting or observable decomposition up to 350°C. The high T_g indicates a rigid structure of polymer.

In order to understand the thermal behavior of monomer and polymer better, TGA thermograms of monomer and polymer were taken. The TGA thermogram of monomer is given in Fig. 6. 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

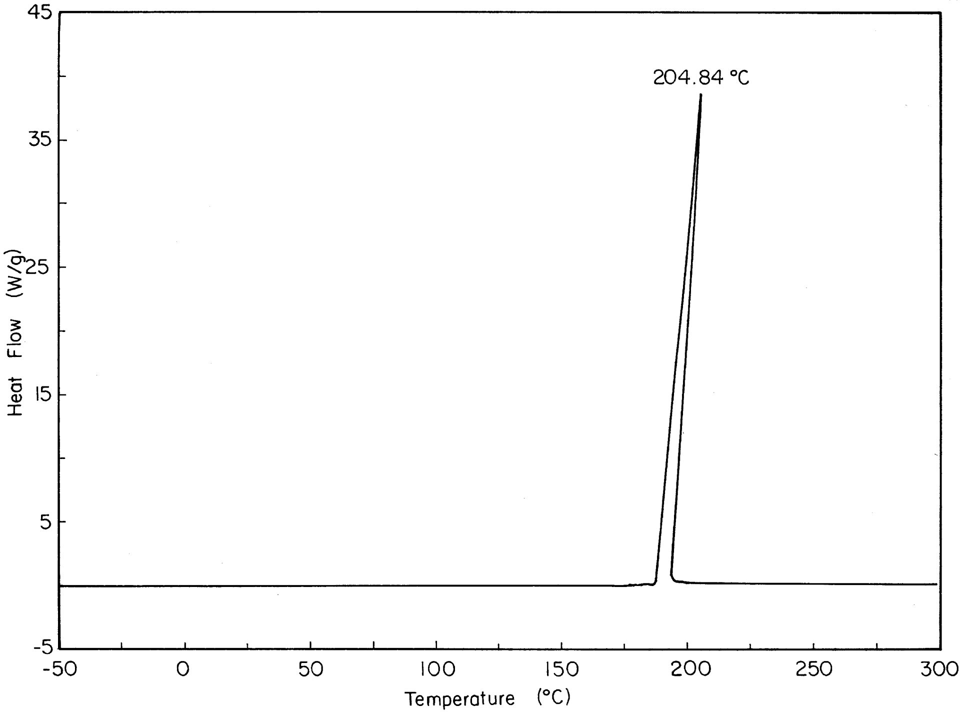


Figure 4. The DSC thermogram of monomer.

thermogram is observed at 226°C. The residual monomer left after about 250°C is about 11%, which remained constant up to 350°C studied. Most probably the initial weight loss (about 10%) is due to the CO and/or CO_2 evolution, which corresponds to about 1 mole per 3 mols 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 (about 11%) that remained as residual after heat treatment.

The TGA thermogram of polymer is shown in Fig. 7. Polymer obtained under different conditions gives an almost identical TGA thermogram. In this case, decomposition started at about 125°C and accelerated at 150°C. The maximum decomposition temperature is 214.8°C. The decomposition was almost completed at 220°C and continued with a slower rate up to 370°C. The weight remaining at about 370°C is 91.3%. This shows that the polymer loses some side groups in the form of CO and/or OH resulting with rigid side group aromatization.

In order to understand the thermal decomposition of polymer better, a polymer sample was heated in a muffle furnace up to 1200°C. The weight lost of the polymer was checked at each of 50°C temperature increments and the FTIR spectrum at each temperature was also taken. The weight loss of the polymer was about 12% in 200 to 300°C temperature ranges and remained

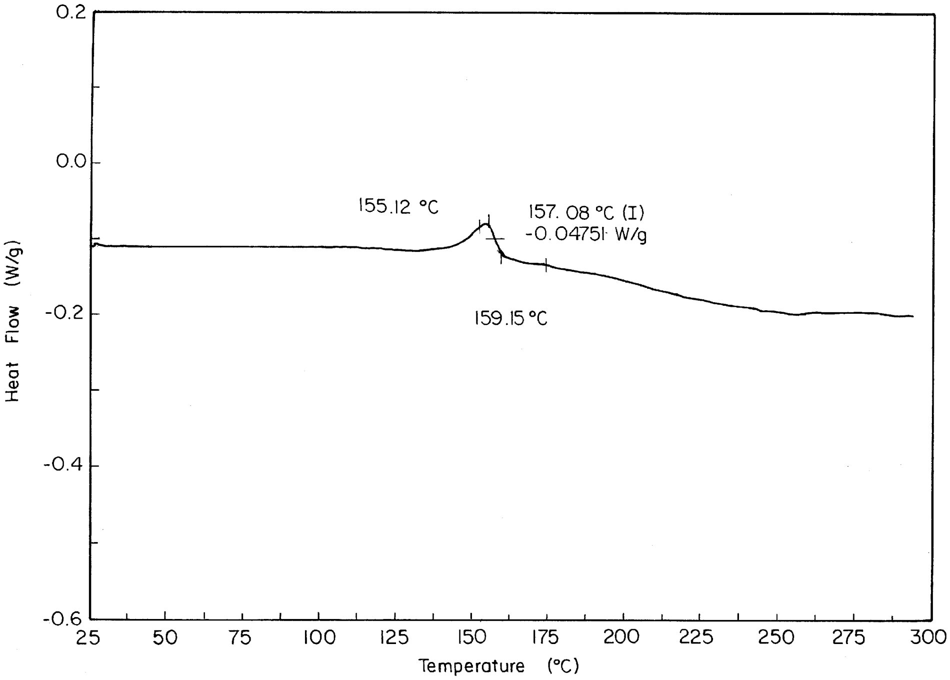


Figure 5. The DSC thermogram of polymer.

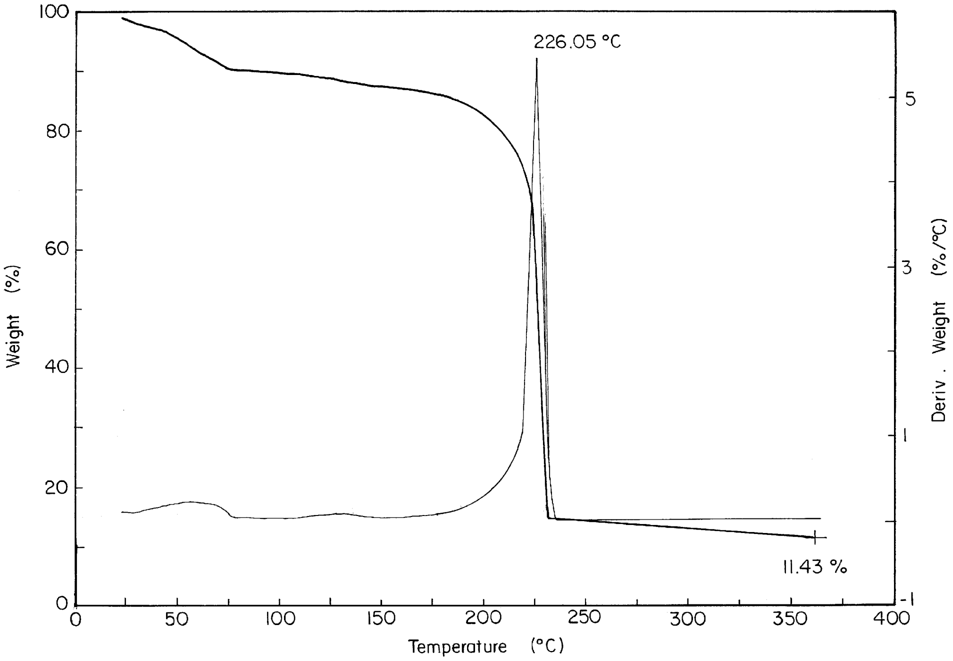


Figure 6. The TGA thermogram of monomer.

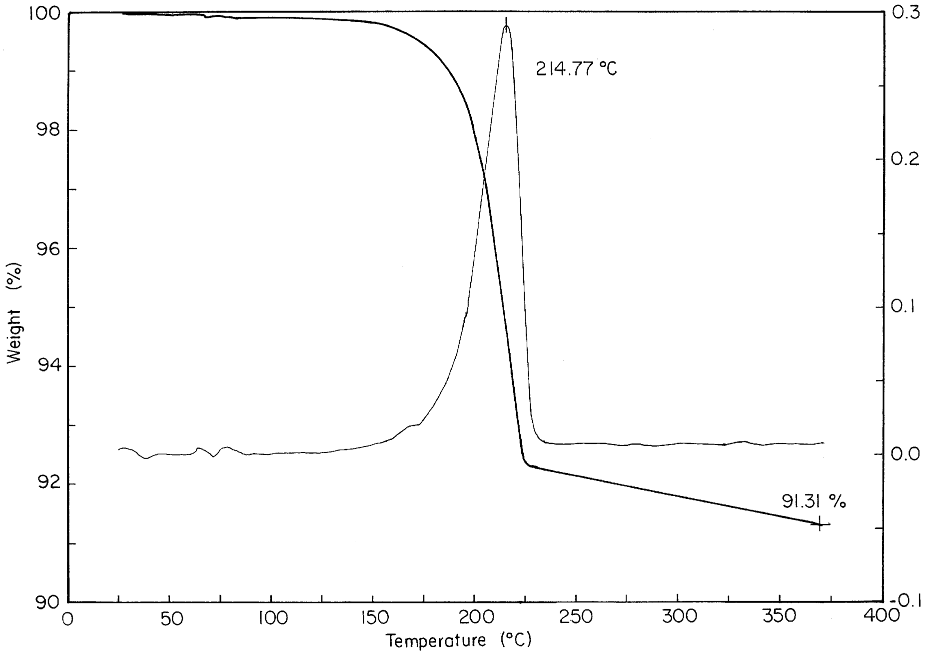


Figure 7. The TGA thermogram of polymer.

constant up to 1200°C. The FTIR spectra of the polymer sample heated for 20 min at each of (a) 1000°C, (b) 1100°C, and (c) 1200°C are given in Fig. 8. The FTIR spectra taken showed that the etheric, -C-O-C-, peak at about 1000 cm^{-1} disappeared after weight loss and side group aromatization took place.

Mass Spectral Analysis

The mass spectrum of monomer with a 70 eV electron impact is given in Fig. 9. The CO peak in the monomer structure is the base line. Therefore, the breaking of CO from the molecule can take place easily when the sample is irradiated. Since the monomer fragment is not observed in the spectrum, the monomer is unstable under these conditions. The peaks at 71.83, 75.83, and 77.09 amu are the monomer fragments after CO_2 evolution, and the peak at 93.84 corresponds to the monomer after evolution of CO. The acetylene bond gives polymerization and side group cyclization.

The mass spectrum of polymer is given in Fig. 10. In the polymer mass spectrum, the peak at 17 amu shows the evolution of OH group. This can be due to the oxygen in side group cyclization (etheric bond) or nonhydrogen bonded OH that was observed in FTIR spectrum. The base peak of 44 amu shows CO_2 evolution from the COOH side group in the polymer or the etheric

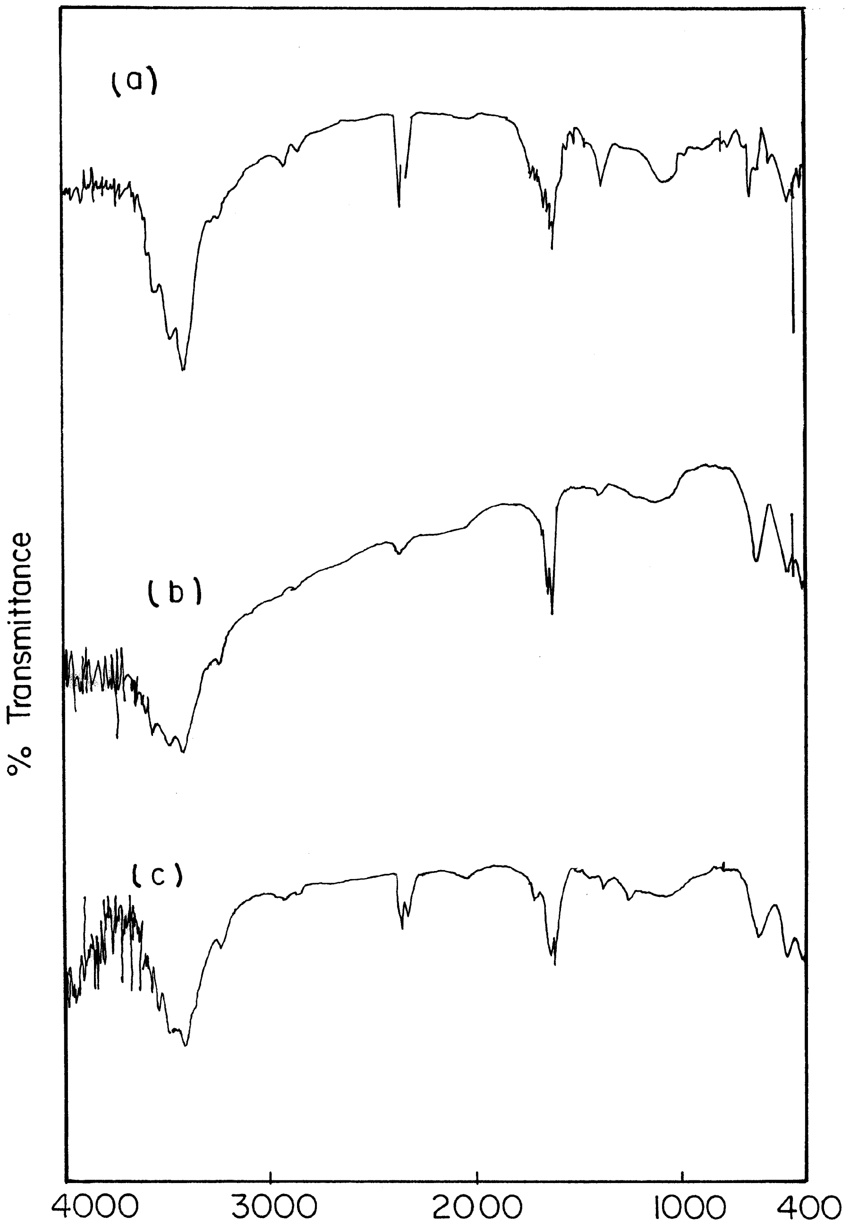


Figure 8. The FTIR spectra of polymer sample heated for 20 min at each of (a) 1000°C, (b) 1100°C, and (c) 1200°C.

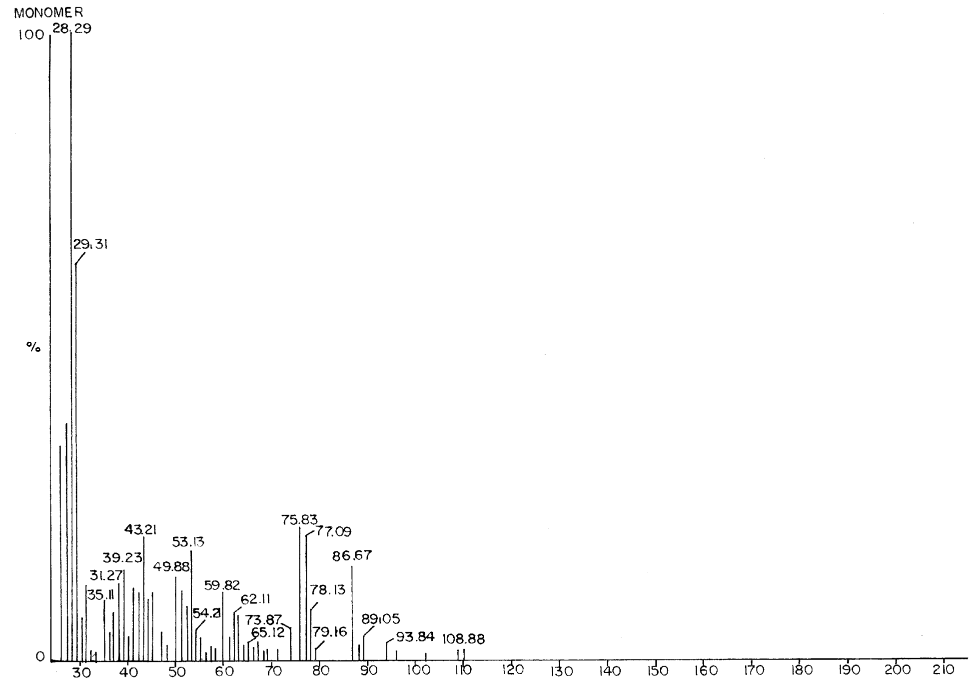
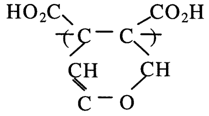


Figure 9. The mass spectrum of monomer with a 70 eV electron impact.

side group fragmented further. The results are supporting the conclusion derived from thermal investigation. When the polymer is annealed at higher temperatures, the etheric bond disappeared from the FTIR spectrum. Since the monomer fragment exists in the polymer mass spectrum at 114 amu, this is assigned to the end group of polymer. Different types of polymer fragments can be assigned from the mass spectrum of polymer. One example is as follows:



X-Ray Investigation

The powder X-ray pattern of ADCA is given in Fig. 11. The calculated and observed d-spacing were compared by the least square analysis of 23 observed reflections. The cell parameters are as follows:

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

Figure 10. The mass spectrum of polymer with a 70 eV electron impact.

These results agree well with the cell parameters reported by Benghiant.[22]

The polymer samples obtained under different conditions were mostly amorphous with various amounts of crystallinity. However, the polymer obtained under vacuum irradiation of 37.8 Mrad total dose was highly crystalline. The X-ray pattern of that sample is shown in Fig. 12. The powdered X-ray pattern was satisfactorily indexed using monomer cell parameters in least square treatment. The cell parameters for polymer were as follows:

$a = 15.155$ A; $b = 6.455$ A; $c = 4.862$ A; $\beta = 91.65$

The similarity between monomer and polymer structures showed that the polymerization follows a topotactic reaction mechanism. Even for an amorphous polymer structure, the observed orientation in polymer was similar to that in monomer.

The powder X-ray patterns of residual monomer after separation of polymer and that of mixture of polymer–monomer after irradiation at different total doses and under vacuum or in open atmosphere were also taken. Each of the spectrum was identical to that of the monomer. This showed that the monomer retains its crystal structure and only the monomer molecules, which gives CO, can polymerize.

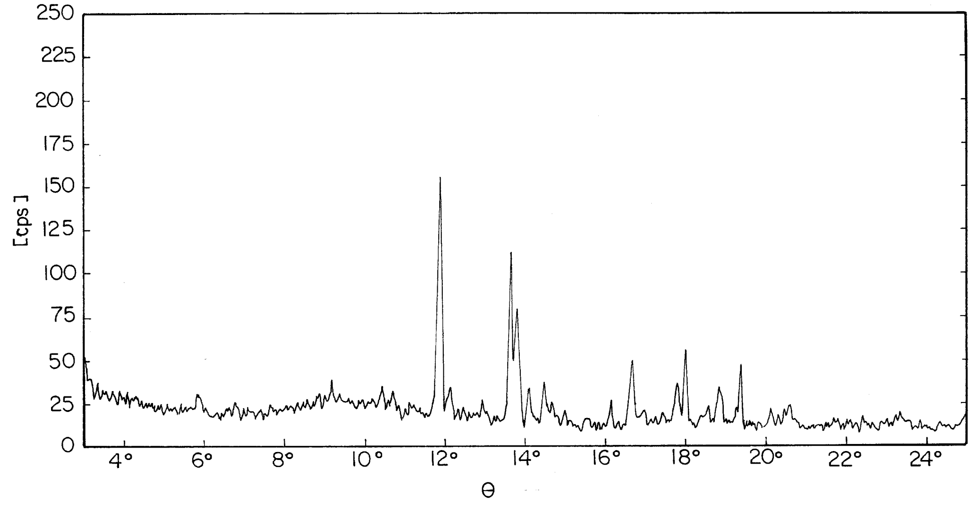


Figure 11. The powder X-ray pattern of acetylenedicarboxylic acid.

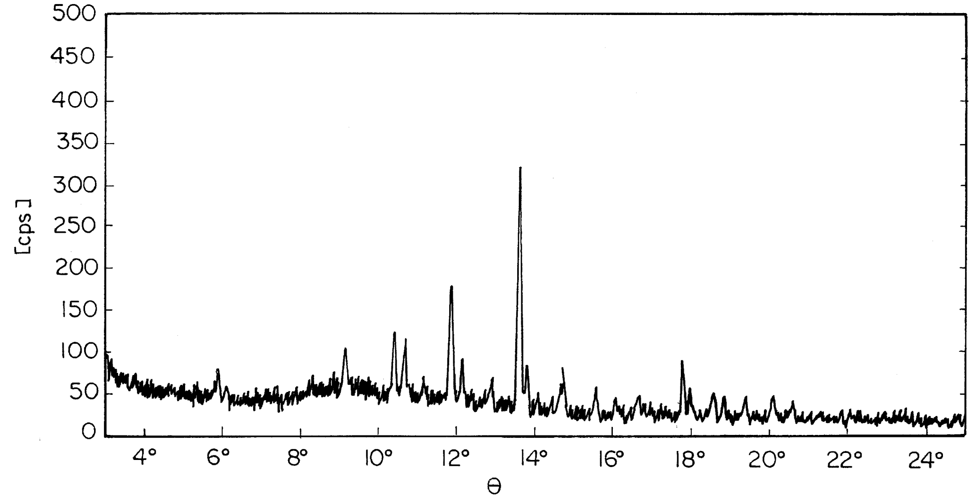


Figure 12. The X-ray pattern of polymer sample obtained in vacuum by 3.5 month's gamma irradiation.

CONCLUSION

In this work, it was shown that the radiation induced solid–state polymerization of ADCA can be carried out. However, the percent conversion was very low for the dose rate of radiation studied. Most probably, at higher dose rates, the limiting conversion might increase because of the easy fragmentation of carbon monoxide. The following conclusions can be derived from the this work:

ADCA can be polymerized by a condensation mechanism with the splitting of CO.

FTIR spectra showed that the monomer forms dimers in its structure, but after polymerization, the hydrogen bonding is not observed.

The UV spectral results showed that in the polymer structure, there are conjugated double and/or triple bonds.

The DSC thermogram of polymer showed a high T_g value (157°C) for polymer. The thermogram of monomer did not give a melting peak, but an exothermic peak, which is most probably due to the splitting of CO.

TGA thermogram of monomer showed initial splitting of CO and/or CO_2 before the main decomposition of the molecule. TGA thermogram of polymer indicated rearrangement in the side group cyclization resulting with a very stable polymer product, which could be stable up to 1200°C.

Mass analysis supported results obtained from thermal analysis. Initially the CO and/or CO_2 are removed from the monomer by radiation, then polymerization starts and progresses. In the polymer, the OH group is split with thermal treatment and rearranged in cyclic side groups.

X-ray results showed a high crystallinity of some polymer products and the retention of the monomer structure after polymerization.

The GPC and viscosity molecular weight determination showed formation of polymers with relatively high molecular weights. The molecular weight distribution seems to be monomodel.

In this work, the NMR investigation was also carried out, but consistent results could not be obtained because of the some experimental difficulties. The NMR could give valuable information for the structure of the polymer. Therefore, work on this monomer will be continued in the future using radiation of high doses and detailed NMR work.

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