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POLYMERIZATION OF 1-ETHYNYL-1-CYCLOHEXANOL BY RADIATION, ELECTROINITIATION, AND CHEMICAL CATALYSTS

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ABSTRACT

Solid-state polymerization of 1-ethynyl-1-cyclohexanol was carried out by irradiation in vacuum and in open air at 20°C. Radiation-induced polymerization was also done in a benzene solution. The products were mixtures of oligomers and polymers. IR, NMR, UV, and x-ray investigations showed the initial formation of trimer, oligomer, and polymer. The polymer fraction increased with an increase of conversion. Electro-initiated polymerization gave soluble and insoluble fractions. The soluble fraction was an ether. However, the results were not reproducible. No polymers were obtained with *n*-butyllithium and borontrifluoride etherate as chemical catalysts.

INTRODUCTION

The homopolymerization of 1-ethynyl-1-cyclohexanol (EC) has not been studied before. Hoene [1] reported the copolymerization of EC and cyclopentadiene in xylene at 200–300°C. Dimerization of EC was carried out using nickel [2] and rhodium [3] metal complex catalysts. Carusi et al. [4] trimerized EC with organometallic complexes of nickel. The product was shown by MS, IR, and NMR investigations to be a linear trimer in the presence of bisphosphine nickel(II) complexes.

Quelette [5] and Hearn [6] showed by NMR investigation that the cyclohexanol in EC has a chair conformation and the ethynyl group is mostly in the axial form.

In this work the polymerization of EC was carried out by radiation to investigate (a) the crystal structure effect on the solid-state polymerization of EC, (b) the nature of the product obtained, and (c) the reaction kinetics. Polymerization was also tried by electroinitiation and chemical catalysts to investigate a possible mechanism of reaction. The conductivity properties of the polymer samples will be the subject of another paper.

EXPERIMENTAL

1-Ethynyl-1-cyclohexanol obtained from Fluka was "purum" grade and used for polymerization without further purification. Single crystal growth was tried from common organic solvents and water. However, no single crystal suitable for x-ray diffraction studies could be obtained. All the solvents were purified by distillation before use.

The x-ray diffraction spectra of powdered samples of monomer and polymer were taken on a powder diffractometer using CuK_α radiation.

Monomer samples of about 1–3 g were placed in Pyrex tubes and connected to the vacuum line. They were evacuated for 6–7 h at a reduced pressure of 10^{-4} to 10^{-5} torr. After evacuation, the tubes were sealed off and irradiated in a Co-60 gamma-ray source at a dose rate of 0.06 Mrad/h for the desired periods. Irradiation in air was done with samples that were not evacuated. Irradiation in benzene solution was done with 3 mL of 10% (w/v) EC (saturated solution) in Pyrex tubes which had been evacuated similarly. After the desired irradiation times (in-source polymerization), the samples were first dissolved in a small amount of ethanol and then precipitated in triply distilled water. The degree of conversion was found gravimetrically.

The cyclic voltammogram and electroinitiated polymerizations were carried out by a procedure described before [7] using acetonitrile as solvent and tetrabutylammonium tetrafluoroborate (TBAFB) as electrolyte under nitrogen atmosphere. Polymerizations by borontrifluoride etherate and *n*-butyllithium were also described before [8].

The IR spectra of the monomer and the polymers were taken in the form of KBr pellets or in NaCl cells using CCl_4 as a solvent. The NMR spectra of samples were taken by employing TMS as the internal standard and deuterated chloroform as the solvent. The UV spectra of the samples were taken from their acetonitrile solutions.

RESULTS AND DISCUSSION

Polymerization of EC

Solid-state in-source polymerization of EC was carried out at 20°C either under vacuum or open to the air. The conversion vs irradiation time is plotted in Fig. 1. The conversions with respect to time for both cases are almost linear, then

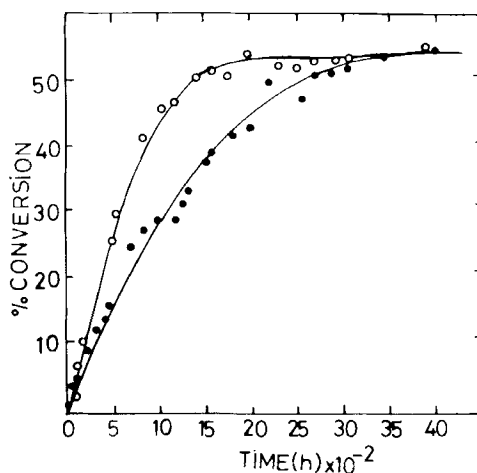


FIG. 1. Conversion vs time for radiation-induced solid-state polymerization of EC at 20°C in vacuum (●) and in open air (○).

slow down and reach a limiting conversion of about 50%. The rate of polymerization is higher for irradiation in open air than in a vacuum. The products obtained were yellow solid powders which become darker with an increase in irradiation time. They are partially soluble in common organic solvents but insoluble in water. The insoluble fraction increases with an increase of irradiation time. The softening temperature of the products was about 60–70°C. The reason for limiting conversion is due to the crystal structure of monomer, which has to be verified by further work. However, similar observations have been reported for some other monomers [9, 10].

In-source polymerization in benzene was carried out to eliminate the crystal structure effect. The percent conversion against irradiation time is plotted in Fig. 2. The percent conversion increases almost linearly up to 30%, the rate slows down up to about 40%, then increases again and reaches to about 80% in 4000 h irradiation time. Thus, the conversion vs time curve shows a sigmoidal shape with an inflection point around 40% conversion. The polymer properties are similar to those of samples obtained in bulk polymerization. The difference in limiting conversion (50% for solid-state and 80% for solution polymerization after 4000 h, which may reach 100% if irradiated further) can be attributed to the crystal structure effect in solid-state polymerization [9, 10]. The break in the kinetic curve between 30–40% conversion for solution polymerization is most probably related to the diffusion rate of monomer molecules in a benzene solution, but it may be a more complicated process which has to be investigated further. In this case, a very small amount of trimer was observed even at low conversions, e.g., the molecular weight for a sample obtained after 5% conversion was about 2500, which is much larger than the molecular weight of the trimer.

The polymerization was also carried out using initiators like butyllithium and borontrifluoride etherate. However, no polymer was obtained with either of these catalysts.

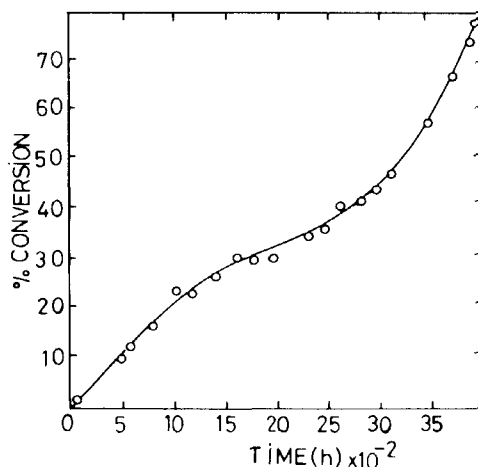


FIG. 2. Conversion vs time for radiation-induced polymerization of EC in benzene solution at 20°C.

The oxidation or reduction peaks from a cyclic voltammogram could not be observed. However, some polymeric material was obtained by electrochemical initiation at constant potential. The product was partially soluble in common organic solvents. The results were not reproducible in terms of percent conversion, and therefore kinetic studies could not be made. This will be investigated further in the future.

Molecular Weight

The molecular weight of insoluble fractions (insoluble in all the common organic solvents tried at temperatures up to about 50°C) could not be determined. The molecular weight of soluble fractions, after separation of any insoluble fraction by filtration, was determined by the cryoscopic method using benzene as a solvent. Most of the soluble fractions obtained under all polymerization conditions studied in the solid state gave a molecular weight equal to that of a trimer. The trimer obtained from benzene solution was in small quantities at low conversions. However, molecular weights up to 5500 were measured for some fractions of products obtained in solid-state polymerization in vacuum and in solution. The insoluble fraction increased with irradiation time. After about 32% conversion in vacuum polymerization, the product was almost completely insoluble. An efficient fractionation could not be done because both crystallinity, which was not the same for all types of polymerizations, and molecular weight cause a decrease in solubility. The products from polymerization in air were insoluble (high molecular weight or/and crosslinked) even at lower conversions.

IR Spectral Investigation

The IR spectra of EC monomer and the polymers obtained under different conditions are shown in Fig. 3. The IR peaks in the monomer spectrum (Fig. 3a)

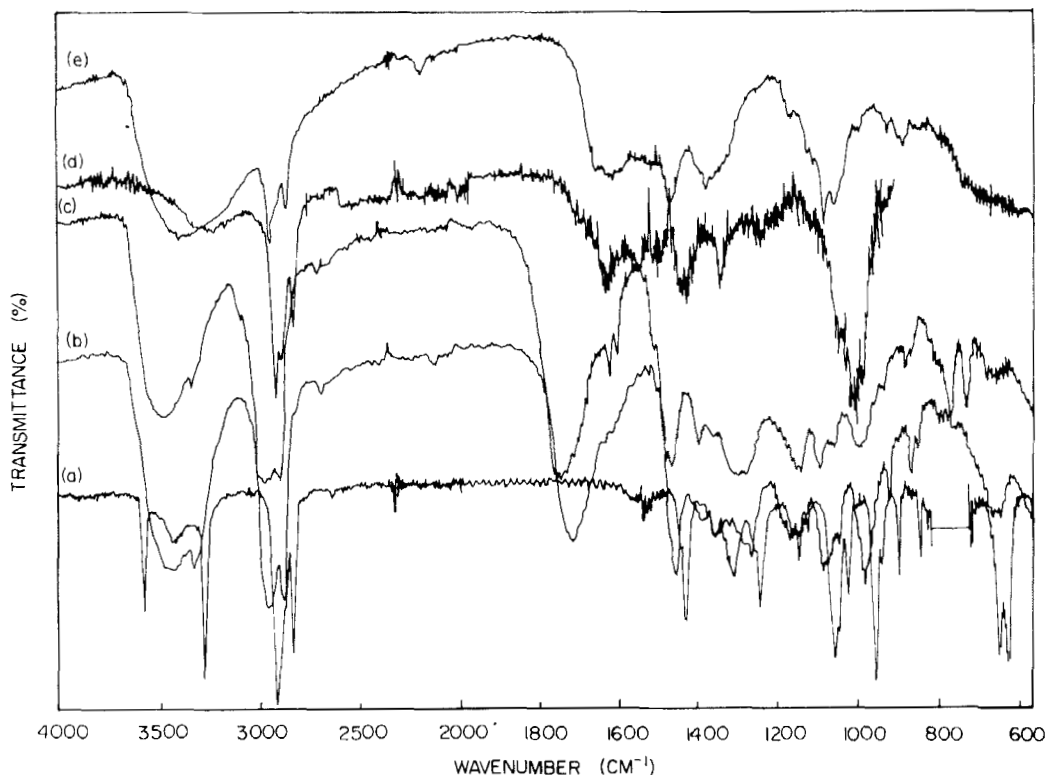


FIG. 3. The IR spectra of (a) monomer, (b) radiation-induced polymer in vacuum, (c) radiation-induced polymer in open air, (d) electroinitiated polymer for 24 h electrolysis, and (e) electroinitiated polymer for 48 h electrolysis.

are assigned to different functional groups as follows; $-\text{C}\equiv\text{C}-\text{H}$ at 3280 cm^{-1} ; hydrogen-bonded OH at 3575 cm^{-1} ; cyclohexane at $2895\text{--}2910\text{ cm}^{-1}$; $-\text{C}-\text{C}-\text{R}$ at 2650 and 2150 cm^{-1} (weak bands); $-\text{CH}_2$ at 1432 cm^{-1} ; $-\text{OH}$ groups at 1310 cm^{-1} . In the spectra of polymers, the doublet peaks at $2890\text{--}3000\text{ cm}^{-1}$ corresponding to cyclohexane do not change much. The small changes in position and peak shape are due to the different conformational form related mostly to the molecular weight. The $-\text{OH}$ peaks at 1250 , 1325 , and 1360 cm^{-1} become broader in radiation-induced polymer, but modification is greater in the spectrum of polymer (Fig. 3d for 24 h electrolysis and Fig. 3e for 48 h electrolysis) obtained by electroinitiation. The OH peak at 3575 cm^{-1} becomes broader and overlaps to the $-\text{C}\equiv\text{C}-\text{H}$ peak at 3280 cm^{-1} which can still be observed distinctly in the spectrum of polymers obtained by radiation (Figs. 3b and c), but not in the spectrum of electroinitiated polymer (Figs. 3d and e). The strong peak around $900\text{--}1000\text{ cm}^{-1}$ in the spectra of electroinitiated products (Fig. 3d and e) shows $-\text{O}-$ linkages.

The IR peaks of the acetylinic group, $-\text{C}\equiv\text{C}-\text{H}$, in the monomer spectrum are retained in the spectra of polymer samples, but with decreased intensity. A new peak at $1670\text{--}1790\text{ cm}^{-1}$, corresponding to conjugated double bond of $-\text{C}=\overset{\diagup}{\text{C}}-\text{C}\equiv\text{C}-$, appeared in the spectra of the polymer samples (Figs. 3b and c)

obtained by radiation. The broad nature of the peaks is typical for polymeric materials. The additional peak at 1640 cm^{-1} shows the presence of $-\text{C}=\text{C}-$ non-conjugated bonds in the polymer.

The IR spectra shows that EC irradiated with gamma rays gives products with conjugated double and triple bonds. The soluble product gives the same IR spectrum as the insoluble fraction. The product obtained from electrochemical initiation is different from that obtained by radiation. It can be concluded that the chain backbone of the polymer obtained by radiation contains vinylacetylinic bonds of

the $-\text{C}=\text{C}-\text{C}\equiv\text{C}-$ type. However, electroinitiated polymers have an ether-type backbone in addition to unsaturated bonds.

UV Spectral Investigation

The UV spectra of monomer and polymer in acetonitrile are shown in Fig. 4. The monomer gave a UV peak (Fig. 4a) at 211.8 nm which corresponds to the acetylinic chromophore $\text{H}-\text{C}\equiv\text{C}-\text{R}$. The UV spectrum for the sample obtained by radiation under vacuum (28.0% conversion) is shown in Fig. 4b. The peak at 234.8 nm in this spectrum shows the vinylacetylinic chromophore, $-\text{C}=\text{C}-\text{C}\equiv\text{C}-$. This peak becomes broader toward the higher wavelength region (Fig. 4c) with an increase of the percent conversion (39.2%). The peak broadening is attributed to the increase of the polymer fraction with an increase of conversion. The UV spectra for samples obtained from irradiation in open air and in benzene solution were similar. These results support the conclusion drawn for the IR investigation that the polymer backbone contains vinylacetylinic bonds.

NMR Spectral Investigation

The NMR spectra of monomer, radiation-induced polymer, and electroinitiated polymer are given in Fig. 5. The peaks in the NMR spectrum of the monomer (Fig. 5a) at 1.5 ppm correspond to cyclohexane, at 2.19 ppm to OH, and at 2.39 ppm to $-\text{C}\equiv\text{CH}$. The cyclohexane peak is retained in the spectra of the polymers. The $-\text{C}\equiv\text{CH}$ peak at 2.39 ppm is broadened and decreased in intensity in the spectrum of the radiation-induced polymer (Fig. 5b), but is shifted to 2.39–2.90 ppm as a broad peak in the spectrum of electroinitiated polymer (Fig. 5c). A new peak at 3.1–3.4 ppm, corresponding to the structure type $\text{R}-\text{CH}_2-\text{O}-\text{R}'$, appeared in the spectrum of the electroinitiated polymer. Another intense and broad peak at 0.8–0.1 ppm, corresponding to $-\text{CH}_3$, exists in this spectrum. Therefore, it can be concluded that R is cyclohexane and $\text{R}'-\text{CH}_3$ is the ether structure of $\text{R}-\text{CH}_2-\text{O}-\text{R}'$.

NMR spectral investigation shows that the product obtained by radiation contains both double and triple C–C bonds with no change in cyclohexane and OH. These observations support the vinylacetylinic structure elucidated in the other spectral investigations.

X-Ray Diffractational Investigation

The powder x-ray patterns of EC monomer, irradiated products, and electroinitiated products are shown in Figs. 6 and 7. The structure of EC has not been reported before, and the reflections in Fig. 6a for the monomer could not be indexed

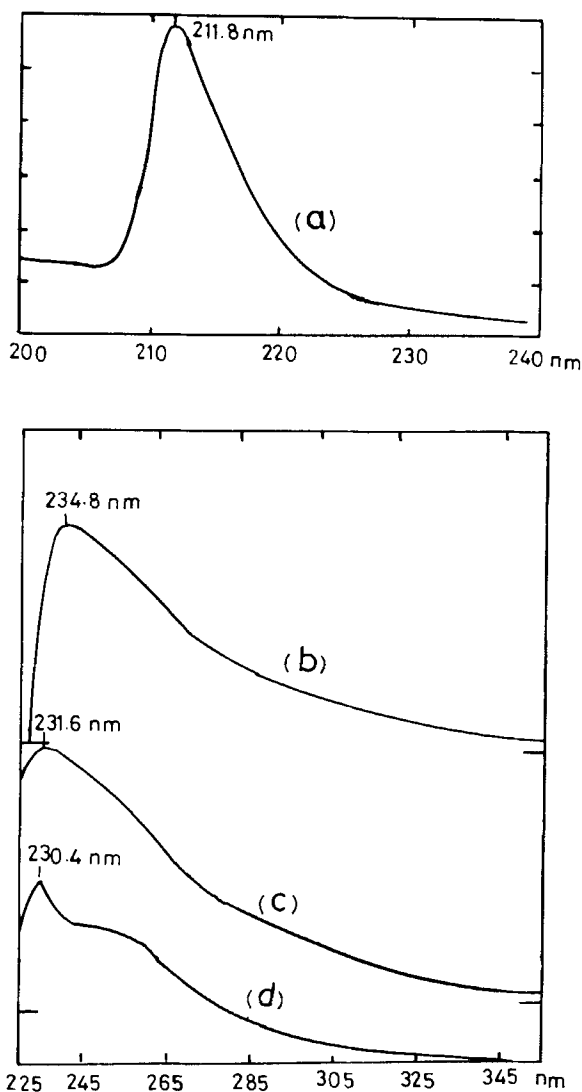


FIG. 4. The UV spectra of (a) monomer, (b) radiation-induced polymer (28.0% conversion) in vacuum, (c) radiation-induced polymer (39.2% conversion) in vacuum, and (d) in benzene solution (21.7% conversion).

with the available data. Figure 6b shows the spectrum of the polymer obtained by irradiation in vacuum; it has a conversion of 28%. The positions and intensities of the peaks are different from those of the monomer. The broad and low intensity peaks (counting rate is 4000 cpm in Fig. 6a and 1000 cpm in Fig. 6b) with a high background indicates the sample is a mixture of a simple crystalline compound and an amorphous polymer. This structure probably shows the trimer proved by molecular weight determination and spectroscopic methods (IR, NMR, and UV). The strongest peak of the monomer at $2\theta = 28.0$ ($d = 3.183 \text{ \AA}$) is also observed in the spectrum of the polymer (Fig. 6b), but much broadened. It is a typical polymer

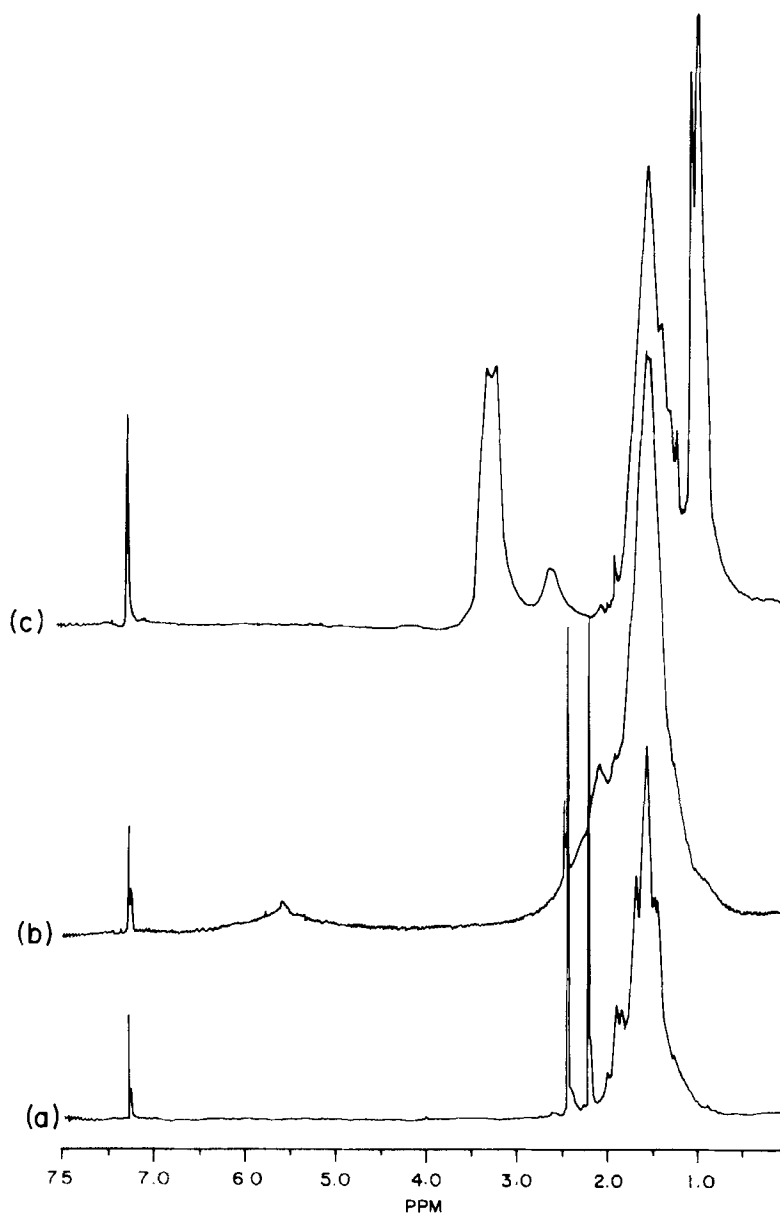


FIG. 5. The NMR spectra of (a) monomer, (b) radiation-induced polymer in vacuum, and (c) electroinitiated polymer.

diffraction peak and indicates that the direction of polymer propagation is in a certain crystallographic direction of monomer.

The x-ray powder spectrum of a polymer sample (with 38.3% conversion) obtained by irradiation in vacuum is shown in Fig. 7a, and that of a polymer obtained in open air (22.0% conversion) is shown in Fig. 7b. In both spectra the samples are amorphous polymers. Thus, the trimer observed at 28.0% conversion is almost completely changed to polymer at higher conversions (e.g., 38.3%). The

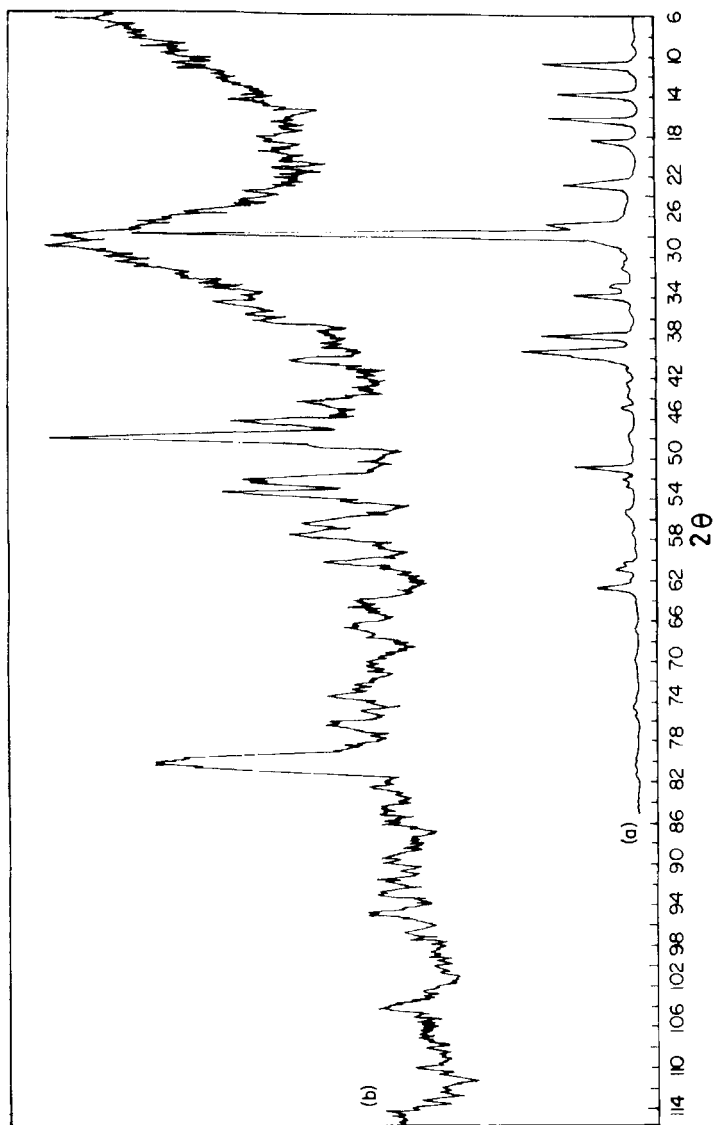


FIG. 6. The x-ray powder patterns of (a) monomer and (b) radiation-induced polymer (28.0% conversion) in vacuum ($\text{CuK}\alpha$, 35 kV, 15 mA).

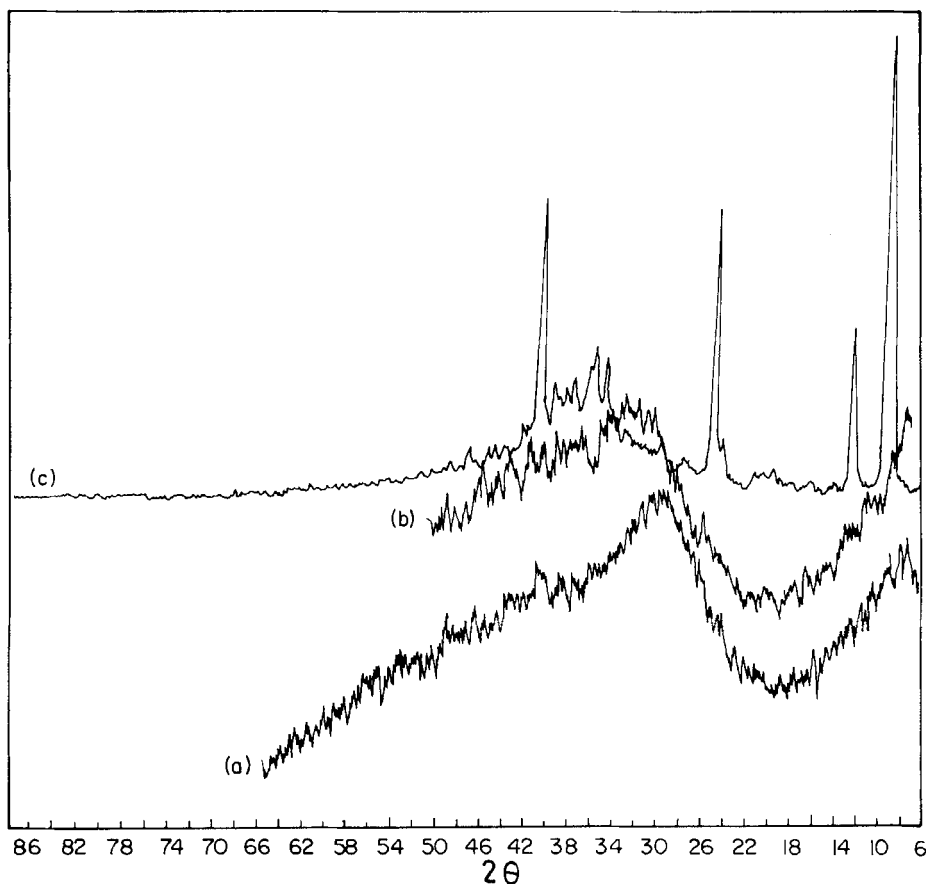


FIG. 7. The x-ray powder patterns of (a) radiation-induced polymer (38.3% conversion) in vacuum, (b) radiation-induced polymer (22.0%) in open air, and (c) electroinitiated polymer.

trimer was not observed as a product in open air irradiation at 22.0% conversion. Similar results were also observed for the product obtained when the sample was irradiated in a benzene solution.

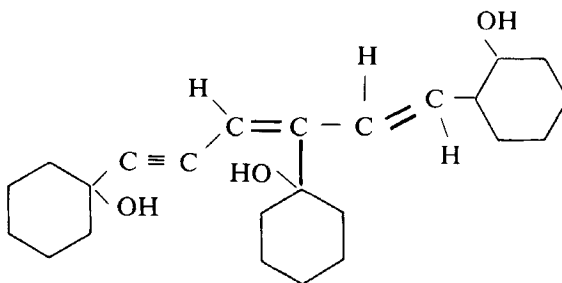
The x-ray diffraction spectrum of a soluble electroinitiated product is shown in Fig. 7c. Its spectrum is different from that of the monomer and trimer. Also, no polymer peaks or a high background count indicate that the soluble product obtained by electroinitiation is not a polymer. Therefore, the product is a relatively simple molecule which has been shown by IR and NMR spectral investigations to be an ether-type molecule.

CONCLUSION

EC was polymerized by radiation under various conditions. Polymerization in a benzene solution was carried out to eliminate the structural effect in solid-state polymerization which was expected to be unfavorable. Polymerization goes to al-

most 80–90% after 4000 h irradiation in benzene solution, whereas in the solid state it is limited to about 50% conversion. The products at lower conversions were mixtures of trimer, oligomers, and polymer.

The polymer fraction increased with an increase of conversion. However, the differences in both molecular weight and crystallinity make reproducible fractionation difficult. The structure of the trimer from the experimental investigation is



This structure is similar to that obtained by Carusi et al. [4]. The structure of monomer and trimer could not be determined from powder diffraction, but further research is in progress for structural analysis by x-ray diffraction and mass spectroscopy.

The polymerization of EC by electroinitiation at constant potential is not very promising. Although some insoluble, infusible products could be obtained in the bulk of electrolyte, the data were not reproducible. The soluble product, as shown by IR and NMR spectra, contain ether linkages and $-\text{CH}_3$ groups. The x-ray showed the product to be a crystalline simple compound.

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