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## POLYMERIZATION OF 4-VINYL-1-CYCLOHEXENE BY RADIATION AND CHEMICAL CATALYSTS

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### ABSTRACT

4-Vinyl-1-cyclohexene was polymerized by radiation at room temperature under vacuum and in atmospheric air. The change of percent conversion with irradiation time is almost linear up to limiting conversion, but it is S-type in atmospheric air. It was shown that the mechanism of polymerization is most probably ionic rather than free-radical. The cationic polymerization was carried out in dichloromethane solution at  $-8^{\circ}\text{C}$  using  $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$  as catalyst. The nature of the polymer obtained was investigated by UV, IR, and NMR spectroscopic methods, and the molecular weights by viscosity. Polymerization takes place by both linear addition of carbon-carbon double bonds and cyclopolymerization. The rate ratio of cyclization and linear propagation was calculated.

### INTRODUCTION

4-Vinyl-1-cyclohexene (4VCH) is a bifunctional monomer that has a vinyl group and a double bond in the ring. Therefore, it is a 1,5-diene-type molecule which can undergo cyclization reaction to give a cyclic polymer in addition to a linear polymer. The rate of polymerization will be

$$\text{Rate of cyclization} = k_c[\text{P}\cdot]$$

$$\text{Rate of linear propagation} = 2k_p[\text{P}\cdot][\text{M}]$$

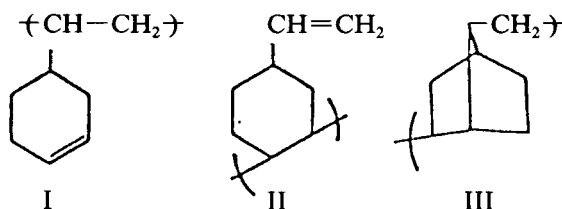
where  $k_c$  and  $k_p$  are rate constants, and  $[P\cdot]$  and  $[M]$  are the concentrations of the propagating chain and monomer, respectively. The factor 2 is due to the presence of two points of attack on the  $P\cdot$  radical. Linear propagation will give unsaturated polymer as in Structures I and II or cyclic polymer as in Structure III. If the mole fraction of unsaturated and cyclic fractions are  $f_u$  and  $f_c$ , the ratio will be

$$\frac{f_u}{f_c} = \frac{2k_p[M]}{k_c}$$

For  $f_c + f_u = 1$ , the equation can be rearranged to give

$$\frac{1}{f_c} = 1 + 2 \frac{k_p}{k_c} [M]$$

Thus, a plot of  $1/f_c$  against  $[M]$  should give a straight line with an intercept of 1 and a slope of  $2k_p/k_c$  [1].



The value of  $k_p/k_c$  found for 4VCH polymerization by Kawai and Katsuta [2] using  $\text{AlEt}_3\text{TiCl}_4$  in hexane at  $50^\circ\text{C}$  as the catalyst was 9.1. They concluded that Structure I was most probable. Butler and Miles [3] polymerized 4VCH by such different catalysts as  $\text{BF}_3(\text{g})$ ,  $\text{BF}_3(\text{Et})_2\text{O}$ , and Ziegler catalyst.  $\text{BF}_3$  polymerization at  $-70^\circ\text{C}$  gave 28% yield and 50% cyclization calculated from NMR results. They also reported 80% cyclization for polymerization with  $\text{BF}_3(\text{Et})_2\text{O}$ , and no polymer formation when  $n\text{-BuLi}$  and AIBN were used as the catalyst.

Mamedov and Abbasova [4] polymerized 4VCH in heptane at  $70^\circ\text{C}$  using  $\text{TiCl}_4\text{-iso-Bu}_2\text{AlCl}_4$  as catalyst and found 79% conversion. The polymerization of 4VCH has also been reported with  $\text{VCl}_4$  [5] and binary systems [6].

The copolymerization of 4VCH with *p*-chlorostyrene (28% highest yield and 17% cyclization) was reported by Kawai and Katsuta [2] and with maleic anhydride by Van Heiningen and Butler [7].

In the present work, 4VCH was polymerized by radiation under different conditions to investigate the kinetics and the mechanism of polymerization, comparing the results with chemically catalyzed polymerizations. The detailed kinetic study of polymerization by  $\text{BF}_3(\text{Et})_2\text{O}$  [3], which is also used in this study under different conditions (e.g., solvent and temperature), has not been reported before. The percent cyclization is measured from chemical experiments rather than from NMR spectra as has been reported before [3, 6]. This will give more accurate results for  $k_p/k_c$  values.

## EXPERIMENTAL

### Materials

Reagent-grade 4VCH (Aldrich Chemical Co.) was purified by  $\text{CaCl}_2$  drying overnight followed by vacuum distillation at  $60\text{--}65^\circ\text{C}$ . All solvents were purified by fractional distillation.

### Polymerization of 4VCH

For polymerization under vacuum, about 1–1.5 mL (0.8–1.2 g) samples were put into Pyrex tubes and connected to a high vacuum system. After evacuation for 4–5 hours at  $10^{-4}$ – $10^{-5}$  mmHg, the tubes were sealed off and placed in a Co-60 source with a dose rate of 0.5 MGy/h. The samples were irradiated for set times at room temperature. The tubes were then removed from the source, broken open, and the unpolymerized monomer was separated by freeze drying. Irradiation in open air at room temperature was similarly carried out, but without evacuation of the tubes.

Polymerization with  $\text{BF}_3(\text{Et})_2\text{O}$  was carried out in dichloromethane at  $-8^\circ\text{C}$ . Monomer (3 mL) and solvent (3 mL) were placed in a test tube, and nitrogen gas was passed through the mixture for several minutes. After cooling the mixture to  $-8^\circ\text{C}$  followed by the addition of catalyst solution (0.5 mL), the tubes were sealed and kept at a set ( $-8^\circ\text{C}$ ) temperature for the desired polymerization time (18 hours to 57 days). The mixtures were poured into 400–500 mL  $\text{CH}_3\text{OH}$  to precipitate the yellowish-white polymer as powders. The polymers were separated by filtration and dried to constant weight. The percent yields as  $\text{CH}_3\text{OH}$ -insoluble fractions were calculated gravimetrically. The polymer was then dissolved in a few milliliters of  $\text{CH}_2\text{Cl}_2$  and reprecipitated as a white precipitate from acetone. The percent yields as acetone-insoluble fractions were also calculated gravimetrically. The  $\text{CH}_3\text{OH}$ -soluble fraction was found by separation of the polymer from  $\text{CH}_3\text{OH}$  by freeze drying. The overall conversion is the sum of  $\text{CH}_3\text{OH}$ -soluble and -insoluble fractions.

### Polymer Characterization

The number of unsaturated bonds was determined by the Wijs method [8] to calculate the percent cyclization. A weight of polymer corresponding to 0.01–0.04 mmol monomer was dissolved in  $\text{CHCl}_3$  and combined with 20 mL of the standard Wijs solution (0.05:0.05 mol  $\text{I}_2:\text{Br}_2$  in 1 L glacial acetic acid). After the solutions were stored in the dark for about half an hour, 6 mL of 10% KI was added and the polymer solutions were titrated with a standard 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The same procedure was repeated for a blank solution, and the number of unsaturated bonds was calculated from the difference in the milliequivalents of  $\text{Na}_2\text{S}_2\text{O}_3$  used for the two titrations. The percent cyclization was calculated from the results.

The viscosities of the polymers (chloroform solutions) were measured at  $25^\circ\text{C}$  in a Ubbelohde viscometer.

The FT-IR spectra of the monomer in NaCl cells using  $\text{CH}_3\text{OH}$  as solvent and that of polymer as KBr pellets were taken with a Nicolet 510-FTIR.

The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra in  $\text{CDCl}_3$  and *d*-DMSO, using TMS as the internal standard, were taken from a Bruker Ac 80 FT NMR spectrometer.

The UV spectra of the polymers and monomer using cyclohexane were taken from a Hewlett-Packard 8452 A Diode Array Spectrophotometer.

## RESULTS AND DISCUSSION

### Polymerization of 4VCH by Radiation

The radiation-induced polymerization of 4VCH was carried out at room temperature by gamma irradiation under vacuum and in atmospheric air. The percent

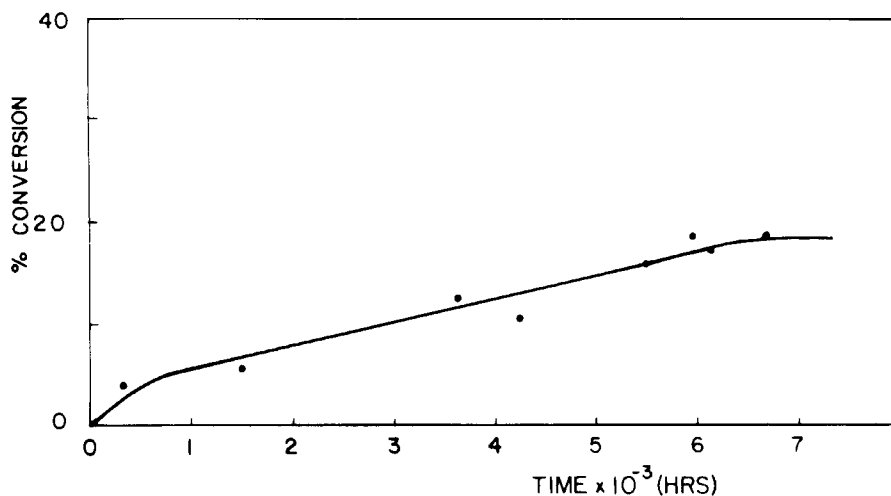


FIG. 1. Conversion vs irradiation time curve for the polymerization of 4-vinyl-1-cyclohexene (4VCH) initiated by Co-60 gamma rays under vacuum conditions and at room temperature.

conversion against time is plotted in Fig. 1. The percent conversion increased almost linearly with irradiation time, reaching about 19% conversion in 7000 hours for polymerization under vacuum (Fig. 1). An S-type relation was observed for polymerization in open air (Fig. 2). A limiting conversion of about 53% is reached after about 1500 hours. The products were yellowish-white solids with softening points

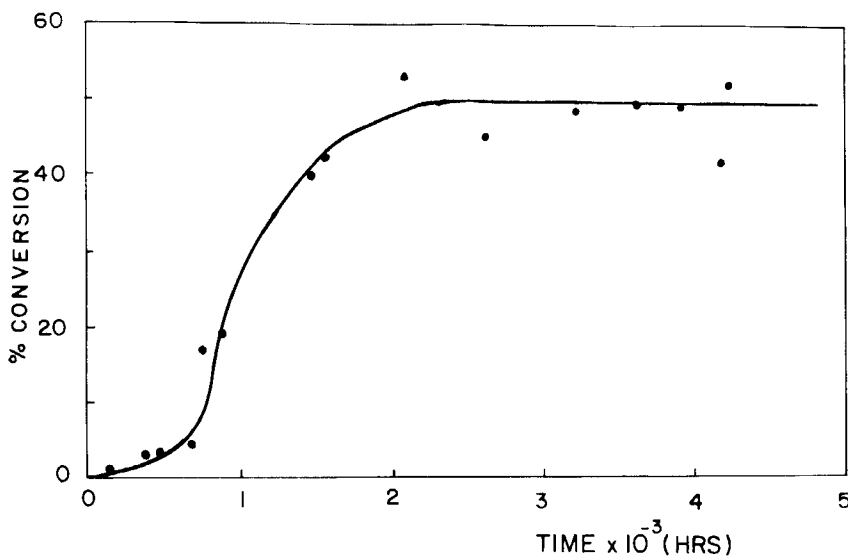


FIG. 2. Conversion vs irradiation time curve for the polymerization of 4VCH initiated by Co-60 gamma rays under air atmosphere at room temperature.

of 130°C; soluble in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$  but insoluble in methanol, acetone, and water. However, the solubility of polymer samples obtained under vacuum decreased in most solvents with increasing irradiation time. Therefore, the viscosity measurements were not reproducible. At low conversion (e.g., 4.5%), the polymers were soluble in methanol and gave  $[\eta]$  as 0.394 dL/g; up to 16% conversions, the polymer samples were soluble in  $\text{CCl}_4$  with  $[\eta]$  of 0.050 dL/g; at higher conversions (e.g., 19%) they were only soluble in THF which gave  $[\eta]$  of 0.059 dL/g.

The intrinsic viscosity  $[\eta]$  for polymer samples obtained by irradiation while open to air and measured in  $\text{CHCl}_3$  versus percent conversion are plotted in Fig. 3. The  $[\eta]$  increased with an increase of percent conversion, reaching a maximum value of about 0.085 dL/g at 50% conversion, then decreasing again. This behavior is a typical trend for radiation-induced polymerizations, giving an S-type kinetic curve. The maximum  $[\eta]$  corresponds to a conversion at which the rate of polymerization slows down and reaches a limiting value. Further irradiation at the limiting conversion may cause chain degradation and a decrease in  $[\eta]$ . The  $[\eta]$ s of the polymer samples obtained under vacuum were much larger than those obtained in atmospheric air.

#### Polymerization of 4VCH by $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$

The cationic polymerization of 4VCH was carried out in  $\text{CH}_2\text{Cl}_2$  at  $-8^\circ\text{C}$ , using  $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$  as a catalyst. The percent conversion against polymerization times for methanol insoluble and overall conversion are plotted in Fig. 4. The percent conversion increased at a high rate during the first several hours, then the increase continued linearly at a slower rate. The highest overall conversion after 57 days was 50%. The acetone-insoluble fraction showed a similar trend, reaching a maximum conversion of about 10% in 57 days. The overall, methanol-insoluble, and acetone-insoluble percent conversions are tabulated in Table 1.

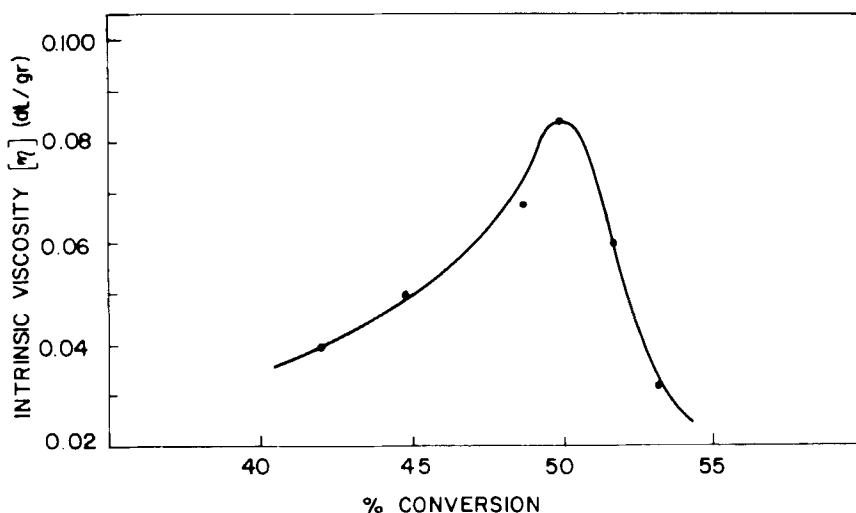


FIG. 3. Intrinsic viscosity,  $[\eta]$ , vs conversion curve for the polymerization of 4VCH initiated by Co-60 gamma rays under air atmosphere at room temperature.

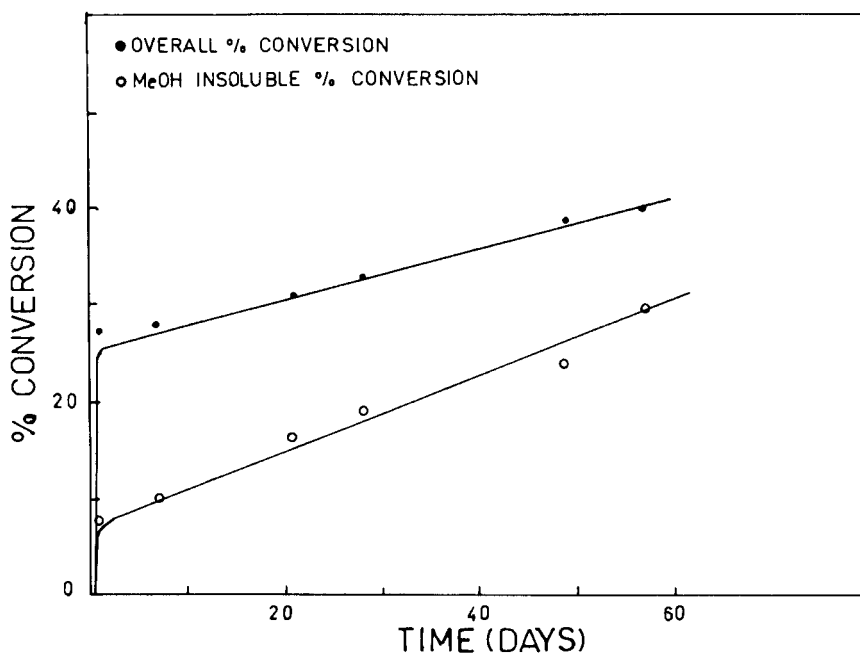


FIG. 4. Conversion vs time (days) for polymerization of 4VCH initiated by  $\text{BF}_3(\text{Et})_2\text{O}$  complex in  $\text{CH}_2\text{Cl}_2$  solution at  $-8^\circ\text{C}$ .

TABLE 1. Cationic Polymerization of 4VCH Initiated by  $\text{BF}_3(\text{Et})_2\text{O}$  Complex in  $\text{CH}_2\text{Cl}_2$  Solution at  $-8^\circ\text{C}^a$

Polymerization time, days	A	B	C	D	E
0.75	27.2	7.7	—	1.1	—
7	27.7	10.2	0.035	2.8	0.044
21	30.9	16.6	0.023	4.9	0.040
28	32.4	19.2	0.029	6.9	0.032
49	38.9	23.4	0.037	9.8	0.040
57	40.0	25.7	0.040	10.4	0.049

<sup>a</sup>A = % overall conversion.

B = % methanol-insoluble fraction.

C =  $[\eta]$  of methanol-insoluble fraction.

D = % acetone-insoluble fraction.

E =  $[\eta]$  of acetone-insoluble fraction.

The intrinsic viscosities were measured for acetone-soluble and -insoluble fractions in  $\text{CHCl}_3$  at  $25^\circ\text{C}$ . The results are given in Table 1. The  $[\eta]$ s for methanol-soluble fractions were in the range of 0.02 dL/g. The  $[\eta]$ s against overall percent conversion for acetone-insoluble fractions are plotted in Fig. 5. In this case,  $[\eta]$  passed through a minimum instead of the maximum observed for radiation-induced polymerization. Even though the changes in  $[\eta]$  are not large, it is still not easy to explain the observed behavior. Polymerization reactions leading to cyclization or linear addition probably have some effect on this behavior.

### Cyclopolymerization of 4VCH

The amount of cyclization was measured by determination of residual unsaturation in the polymer samples. This was done by addition of  $\text{I}_2$  to the unsaturated bonds and titration of excess  $\text{I}_2$  with a standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The percent cyclizations determined experimentally were 67–74% for radiation-induced polymerization (irradiation time, 930 to 4240 hours) in atmospheric air, 58–61% for cationic polymerization, and 43–51% for acetone-soluble fractions obtained from cationic polymerization. The plot of  $1/f_c$  (where  $f_c$  is the fraction of cyclization) against  $M$  (concentration of monomer) is given in Fig. 6. Straight lines were obtained in all cases. The intercepts are close to unity, and the slopes give  $k_p/k_c$  values of 2.2, 2.3, and 8.8, corresponding to radiation polymerization in atmospheric air (Fig. 6a), acetone-insoluble fraction (Fig. 6b), and acetone-soluble fraction of cationic polymerization (Fig. 6c).

The FT-IR spectra of the monomer and the polymers (Fig. 7), obtained under different conditions, are compared to find possible mechanisms of polymerization.

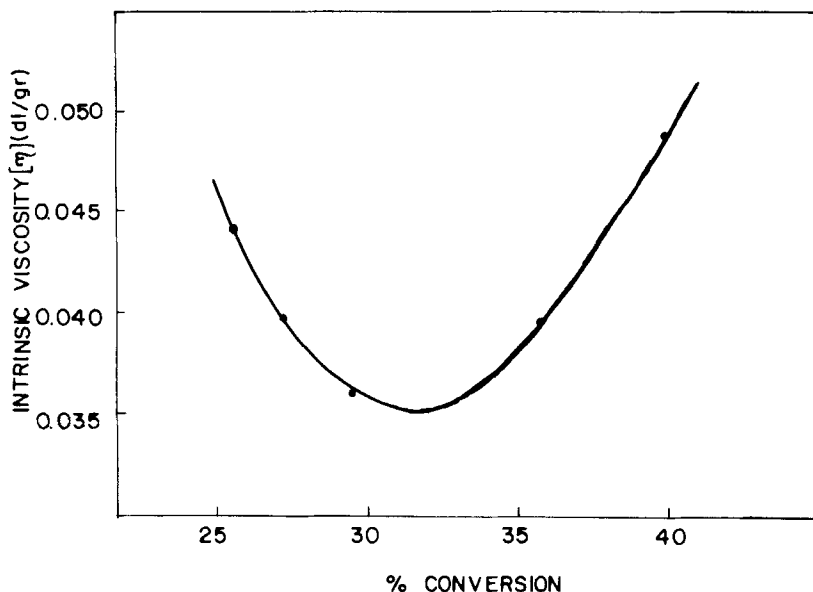


FIG. 5. Intrinsic viscosity,  $[\eta]$ , vs conversion curve for polymerization of 4VCH initiated by  $\text{BF}_3(\text{Et})_2\text{O}$  complex in  $\text{CH}_2\text{Cl}_2$  solution at  $-8^\circ\text{C}$  for acetone-insoluble fraction.



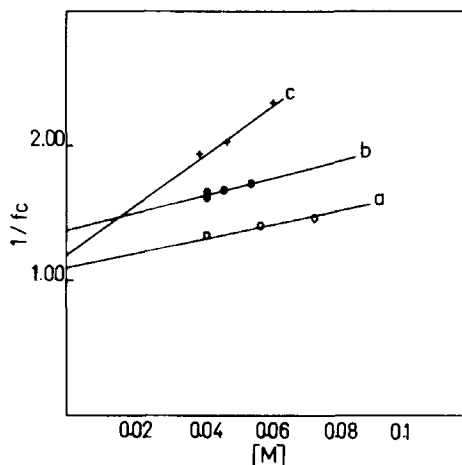


FIG. 6.  $1/f_c$  vs  $[M]$  graphs for polymers obtained by (a) radiation under air atmosphere at room temperature, (b)  $\text{BF}_3(\text{Et})_2\text{O}$  complex in  $\text{CH}_2\text{Cl}_2$  solution at  $-8^\circ\text{C}$  with respect to acetone-insoluble fraction, (c)  $\text{BF}_3(\text{Et})_2\text{O}$  complex in  $\text{CH}_2\text{Cl}_2$  solution at  $-8^\circ\text{C}$  with respect to acetone-soluble fraction.

The peaks in the monomer spectrum (Fig. 7a) correspond to different functional groups as follow:  $3100\text{ cm}^{-1}$  to  $=\text{CH}$  ( $sp^2$ ),  $2900\text{--}3000\text{ cm}^{-1}$  to  $-\text{CH}$  ( $sp^3$ ) in cyclohexene,  $1625\text{ cm}^{-1}$  to  $\text{C}=\text{C}$  in both vinyl and cyclohexene,  $1450\text{ cm}^{-1}$  to  $-\text{CH}_2$ ,  $1100\text{--}1200\text{ cm}^{-1}$  to  $\text{C}-\text{C}$ , and  $913$  and  $1000\text{ cm}^{-1}$  to  $\text{C}=\text{C}$  in vinyl group.

The FT-IR spectra of the polymers obtained for different irradiation times are the same. Therefore, the mechanism of reaction (linear addition or cyclopolymerization) does not change with time of irradiation. The FT-IR spectrum of the polymer obtained by radiation under vacuum is given in Fig. 7(b). When compared with the monomer spectrum, the peaks at  $2900\text{--}3100\text{ cm}^{-1}$  corresponding to  $=\text{C}-\text{H}$  and the vinyl peaks at  $1650$ ,  $913$ , and  $1000\text{ cm}^{-1}$  retain their position, but with decreased intensity. The relative intensity of the  $-\text{CH}_2$  peak at  $1450\text{ cm}^{-1}$  is increased. Thus, the polymerization propagates through the vinyl group or the  $\text{C}=\text{C}$  bond in cyclohexene. The products may have both linear or cyclic chain structures. However, from the extended spectrum it is observed that the relative intensity of the  $913\text{ cm}^{-1}$  ( $\text{C}=\text{C}$  in vinyl group) band decreased more than that of the  $990\text{ cm}^{-1}$  (corresponding to  $\text{C}=\text{C}$ ) band in the cyclohexene. Therefore, the vinyl group is used in both linear and cyclopolymerization while the  $\text{C}=\text{C}$  in cyclohexene is used only in cyclopolymerization alone, leading to Structures I and III. This would be expected from thermodynamic considerations. The intensity of the two peaks in the  $600\text{--}800\text{ cm}^{-1}$  region, corresponding to  $\text{C}=\text{C}$  in cyclohexene, has also decreased a little in the polymer spectrum.

The FT-IR spectrum of the radiation-induced polymer in atmospheric air (Fig. 7c) is quite different from that obtained under vacuum. In this case the intensities of the peaks at  $3100$ ,  $1650$ ,  $1000$ , and  $913\text{ cm}^{-1}$ , corresponding to the  $\text{C}=\text{C}$  group, are decreased more. There are two new strong peaks at  $3400$  and  $1720\text{ cm}^{-1}$  which can show the oxidation of double bonds to give  $\text{C}=\text{O}$  and  $\text{C}-\text{OH}$  groups or

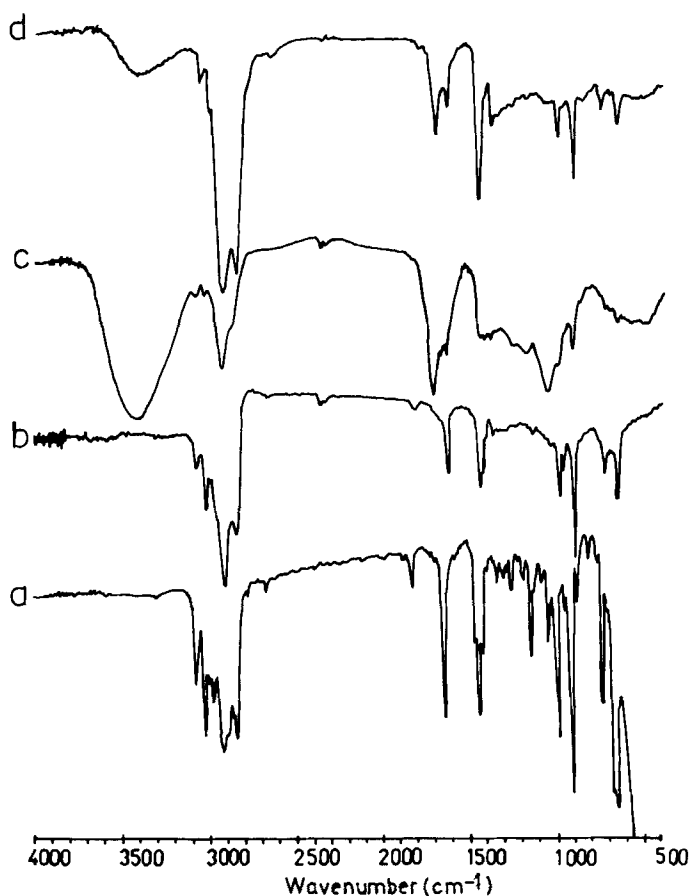


FIG. 7. FT-IR spectra of (a) monomer, (b) radiation-induced polymer in vacuum, (c) radiation-induced polymer in air, and (d) chemically catalyzed polymer by  $\text{BF}_3(\text{Et})_2\text{O}$  complex in  $\text{CH}_2\text{Cl}_2$  solution.

cyclopolymerization that give poly(2-vinyl norbornane) or poly(norbornylene)-type products.

The FT-IR spectra of the polymer samples obtained by  $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$  are given in Fig. 7(d). A broad peak at  $3500\text{ cm}^{-1}$  and a sharp intense peak at  $1720\text{ cm}^{-1}$ , which are not observed in the spectrum of the monomer, appeared. The peaks corresponding to a vinyl group ( $\text{C}=\text{C}$  in cyclohexene) almost disappear. The new peaks most probably show poly(norbornylene) or poly(2-vinyl norbornane) as in the samples obtained by radiation in atmospheric air.

### NMR Spectral Investigation

The proton and carbon-13 spectra were also obtained in order to help understand the nature of the polymer and the mechanism of polymerization. The  $^1\text{H}$ -NMR spectra of monomer and polymers obtained under different conditions are

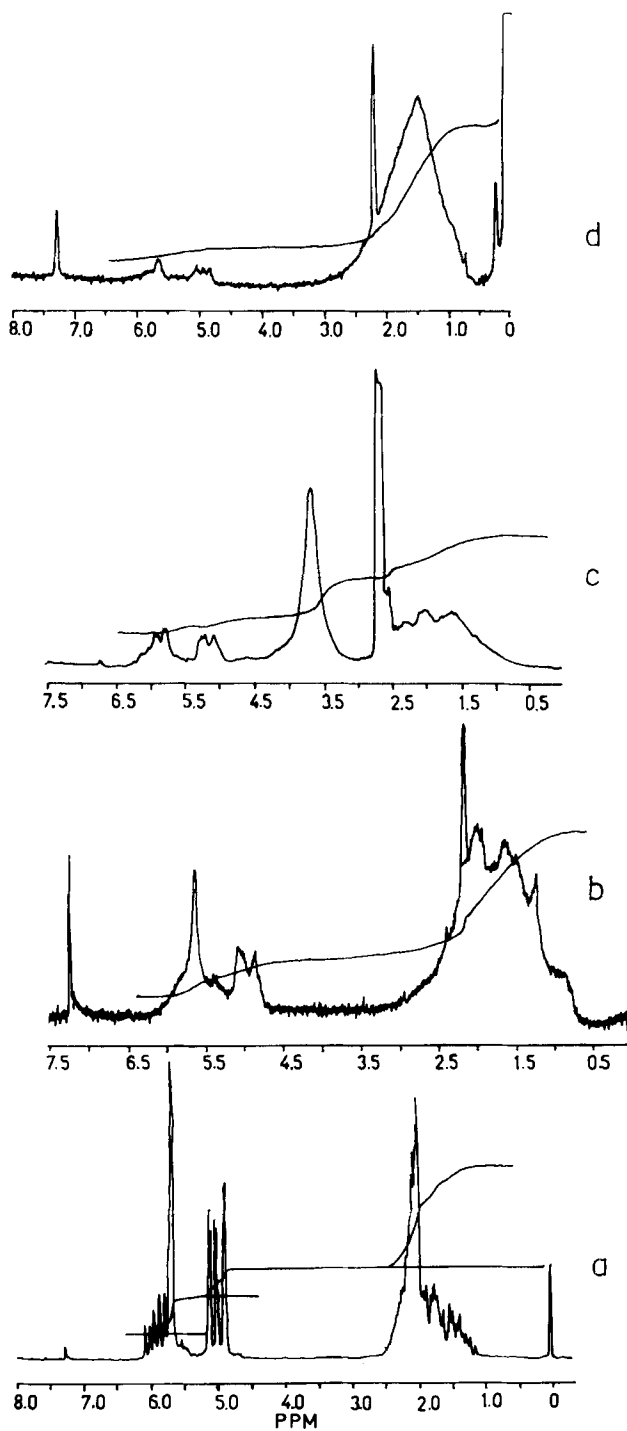


FIG. 8.  $^1\text{H-NMR}$  spectra of (a) monomer, (b) radiation-induced polymer in vacuum, (c) radiation-induced polymer in air, and (d) chemically catalyzed polymer by  $\text{BF}_3(\text{Et})_2\text{O}$  complex in  $\text{CH}_2\text{Cl}_2$  solution.

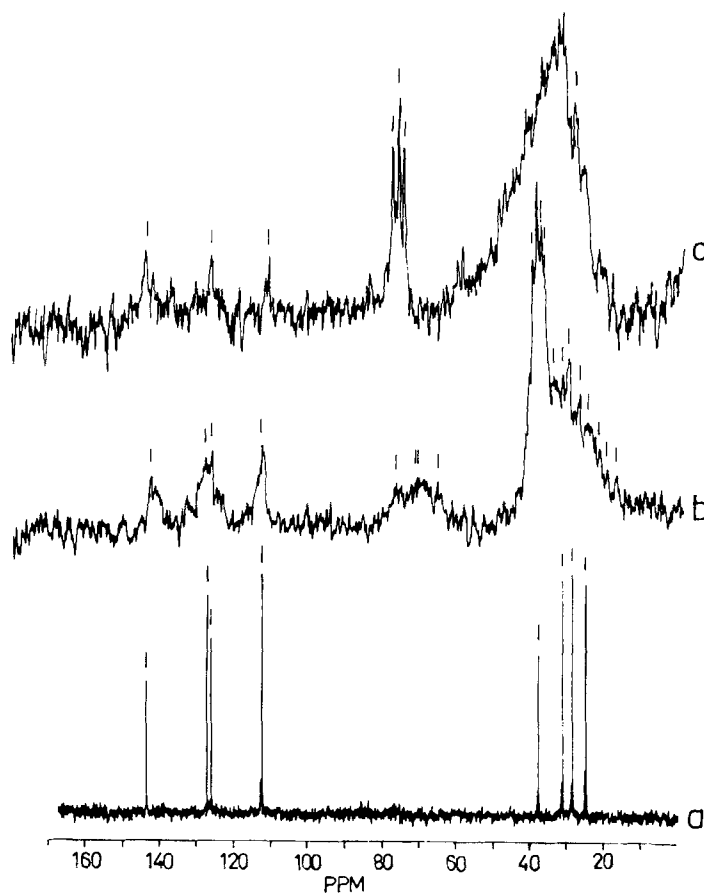


FIG. 9.  $^{13}\text{C}$ -NMR spectra of (a) monomer, (b) radiation-induced polymer in air, and (c) chemically catalyzed polymer by  $\text{BF}_3(\text{Et})_2\text{O}$  complex in  $\text{CH}_2\text{Cl}_2$  solution.

given in Fig. 8. The peaks in the  $^1\text{H}$ -NMR spectrum (Fig. 8a) of the monomer can be assigned as follows: 1.3–2.3 ppm to  $\text{CH}_2$ , 5.7–6.2 ppm to  $\text{CH}$  in cyclohexene, 4.8–5.2 ppm to  $=\text{CH}$  and  $=\text{CH}_2$  in the vinyl group, and 7.2 ppm to  $\text{CDCl}_3$ .

The  $^1\text{H}$ -NMR spectrum of the polymer obtained by radiation under vacuum is shown in Fig. 8(b). The peaks corresponding to all protons are retained in the polymer spectrum with some modification. The peaks corresponding to  $\text{CH}_2$  at 1.0–2.3 ppm became broader and more intense. This shows that the  $\text{C}=\text{C}$  bonds open to give more  $\text{CH}_2$  groups. The peaks for  $\text{CH}_3$  may also be present and covered by a broad peak at 1.0–2.3 ppm. Similarly, the cyclic polymer as norbornane may also be in this region. The peaks of unsaturated carbons at 4.8–5.2 and 5.7–6.2 ppm broaden and their intensity decreased.

The  $^1\text{H}$ -NMR spectrum of polymer obtained by radiation in atmospheric air in *d*-DMSO is given in Fig. 8(c). Most of the peaks of the monomer are retained, with the intensities much lower and broader. The additional peak at 3.0–4.0 ppm

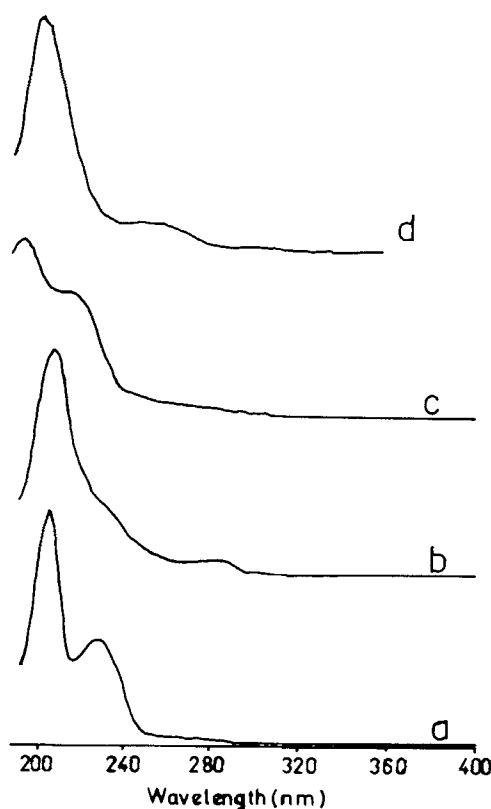


FIG. 10. UV spectra of (a) monomer, (b) radiation-induced polymer in vacuum, (c) radiation-induced polymer in air, and (d) chemically catalyzed polymer by  $\text{BF}_3(\text{Et})_2\text{O}$  complex in  $\text{CH}_2\text{Cl}_2$  solution.

may correspond to  $\text{CH}_2\text{O}$ , which agrees with the IR results showing oxygen might also enter into the molecule.

The  $^1\text{H-NMR}$  spectrum of the polymer obtained by cationic polymerization is shown in Fig. 8(d). As shown, the  $\text{CH}_2$  peak has become very intense and broad. The peaks of the unsaturated carbons retained their positions, but peak intensities decreased appreciably. Therefore, polymerization takes place by both linear addition and cyclopolymerization.

The  $^{13}\text{C-NMR}$  spectra of the monomer and the polymers are shown in Fig. 9. The peaks in the monomer spectrum (Fig. 9a) are assigned as follows: 24.8, 28.4, 30.9, and 37.6 ppm to cyclohexene; 112.2 ppm to  $=\text{CH}_2$  in the vinyl group; 125.9 and 126.7 ppm to  $\text{C}=\text{C}$  in cyclohexene; and 143.5 ppm to  $=\text{CH}$  in the vinyl group.

The  $^{13}\text{C-NMR}$  spectrum of the radiation-induced polymer in atmospheric air is shown in Fig. 9(b). The peaks corresponding to the unsaturated carbons almost retained their places, but with reduced intensity. The peak at 66–77 ppm corresponds to *d*-DMSO, which might also be overlapped by a peak corresponding to the norbornane structure.

The  $^{13}\text{C}$ -NMR spectrum of the polymer obtained by chemical catalyst is shown in Fig. 9(c). The peak at 78–75 ppm corresponds to  $\text{CDCl}_3$ . The peak of the  $\text{CH}_2$  group became more intense and broader, but those of the unsaturated carbons shifted a little from their positions and had a reduced intensity.

### UV Spectral Investigation

The UV spectra of the monomer and the polymers are given in Fig. 10. The monomer spectrum (Fig. 10a) has an intense peak at 204 nm and a weak peak at 225 nm. The intense peak shift to 198 nm for polymer was obtained by radiation under vacuum (Fig. 10b). For radiation-induced polymer in atmospheric air (Fig. 10c), an intense peak at 198 nm and a weak peak at 216 nm are observed. Similar peaks at 200 and 250 nm are observed for the chemical-catalyzed polymer (Fig. 10d). These results agree well with the IR and NMR results, showing that cyclopolymerization and linear addition coexist to give Structures I and III. The weak peak corresponding to unsaturated bonds shift positions with reduced intensity.

The spectral investigations show that 4VCH can polymerize by irradiation and cationic polymerization to give linear addition as Structure I and cyclopolymerization as Structure III. The presence of Structure II cannot be completely ruled out, but that probability is very small. If polymerization by radiation propagates by a radical mechanism, the rate should decrease in the presence of oxygen. However, the reverse was observed. The similarity of products created by cationic polymerization shows that the radiation-induced polymerization mechanism is most probably cationic.

### CONCLUSION

The polymerization of 4-vinyl-1-cyclohexene was carried out by radiation in vacuum and in the presence of atmospheric air. The high rate of polymerization in atmospheric air, which should be a scavenger for radicals and give similar product formation as a cationic chemical initiator, suggests a cationic mechanism of polymerization. Structural investigations by chemical determination of unsaturation and spectral analysis show that polymers obtained by both radiation and chemical initiation are mixtures of linear chains segments (Structure I) formed through double bond opening of vinyl groups and cyclic norbornane (Structure II) chain segments formed by both double bonds in the molecule.

The  $k_p/k_c$  values obtained in this work are smaller than the values reported by Kawai and Katsuta [2]. However, our double bond analysis by a chemical method should be more accurate than the one done by NMR spectral analysis [2].

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