A STUDY OF THE CYCLOHEXENE-FORMIC ACID COPOLYMERIZATION REACTION

by

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ABSTRACT

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While cyclohexene and formic acid are normally inert to polymerization, an unusual copolymerization reaction between them was reported recently when both iodine and free radical initiator are present. This reaction can lead to a copolymer whose repeat units are an unsaturated polyester and a polyalkene.

In the present study, the effect of systematically varying the cyclohexene, formic acid, iodine and *tert*-butylhydroperoxide concentrations on the copolymer yield, composition and extent of crosslinking was determined. The copolymer composition was determined by comparing the infrared absorption intensities of the ester and alkene groups with measurements on polymers in which the repeat units were only either polyester or polyalkene. The extent of crosslinking was determined by Soxhlet extraction of the polymer samples; the crosslinked polymer is insoluble in methylene chloride.

The results of this study showed that the extent of crosslinking in the copolymerization reaction could be reduced by raising the reactant concentration of iodine, formic acid or tert-butylhydroperoxide or by lowering the cyclohexene concentration. Increased polyester content was favored by lowering the cyclohexene concentration but was relatively uneffected by changing the other reactant concentrations. The polymers studied here had low molecular weights (800-1000) and had a solubility parameter of 8.6-10.0 in poorly hydrogen bonded solvents and 9.1-10.8 in moderately hydrogen bonded solvents.

Several possible mechanisms were considered for the copolymerization reaction. The results of this study and previous work support a mechanism in which the main step involves the formation of an allylic cyclohexenyl radical (probably as an iodine complex) by hydrogen atom abstraction from cyclohexene by iodine atoms. These radicals can then couple with each other to form a polyalkene or can couple with a formic acid radical to form a polyester.

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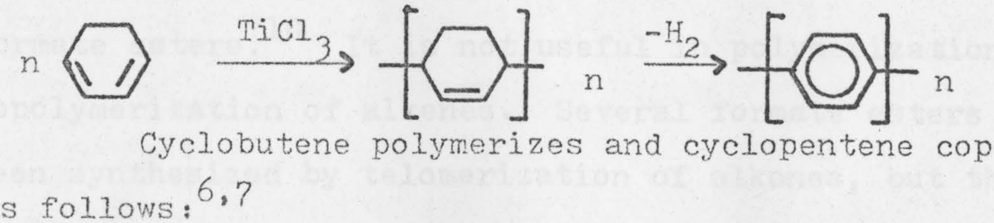
CHAPTER I

GENERAL INTRODUCTION AND HISTORICAL

Polymerization reactions are usually divided into two main types depending upon the polymerization process. These are chain-growth and step-growth polymerization. Any polymerization reaction can be subdivided into three stages: (1) initiation, in which the polymerization reaction begins; (2) propagation, wherein the main portion of the change from monomer to polymer occurs and the active species is called the growing polymer chain; and (3) termination where the growing polymer chain is converted into the more or less inactive final polymer and the reaction stops. In the step-growth process these three stages proceed at about the same specific rate and have about the same reaction mechanism while in the chain-growth process the specific rates and mechanisms of these three stages are different. Several other differences exist between chain-growth and step-growth processes. In the chain-growth process, both high molecular weight polymer and monomer exist during most of the reaction time while the monomer disappears early in the step-growth process and the main species present is the growing polymer chain. High molecular weights do not usually arise in the step-growth process until after long reaction times (an exception is the interfacial polymerization reactions) and the molecular weight distribution is broader than in the chain-growth process. The chain-growth process is usually a faster reaction. The empirical formula of the monomer and the polymer repeat unit are the same in the chain-growth process but differ by some small unit, usually H_2O or NH_3, in the step-growth process.

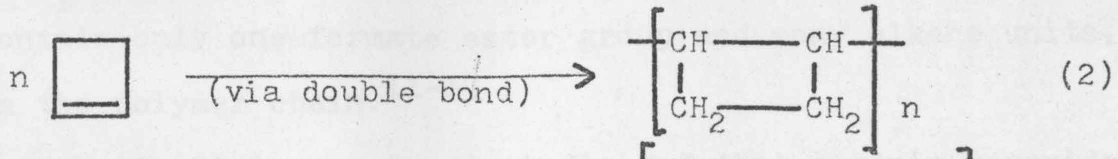
Examples of the chain-growth process include the polymerizations across the carbon-carbon double bonds in compounds such as styrene, vinyl acetate or acrylates and these reactions can proceed by free radical, cationic, anionic or heterogeneous initiation reactions. Certain ring-opening reactions, such as epoxide polymerization, are also chain-growth processes. The major examples of the step-growth process are polyesterification (such as the condensation of 4-hydroxycyclohexane carboxylic acid noted later and polyamide formation although reactions leading to polyurethanes, polyalkylenesulfides, polybenzyls and other polymers also occur in a step-wise manner.

The polymerization and copolymerization of cyclic alkenes have been reported. These reactions proceed by polymerization via the double bond[1,2] or by ring-opening reactions.[3,4] Cyclohexadiene polymerizes via the double bond in the presence of a Ziegler-Natta catalyst as follows:[5]

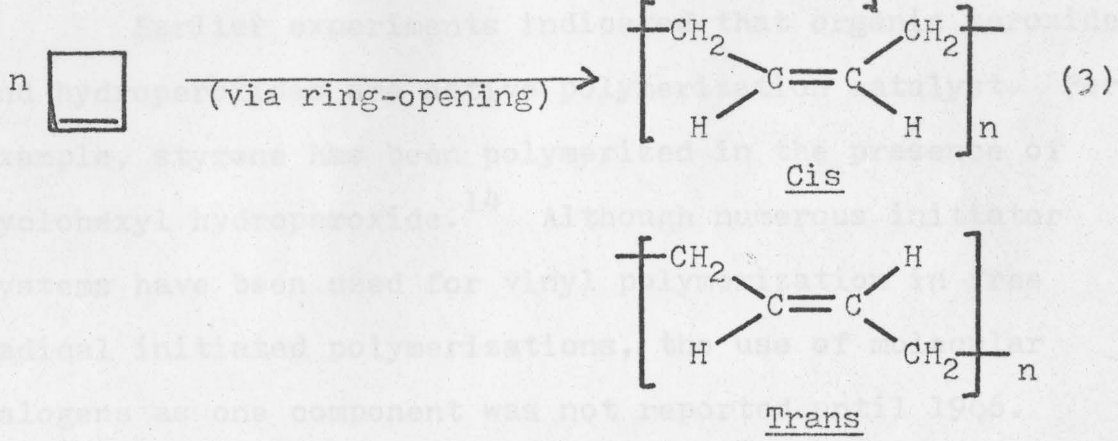


(1)

Cyclobutene polymerizes and cyclopentene copolymerizes as follows:[6,7]



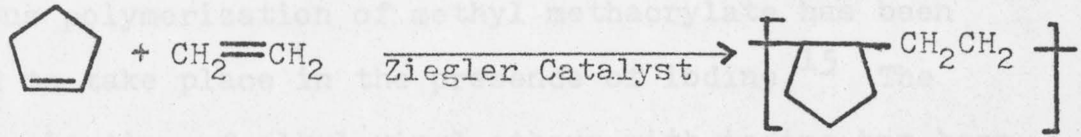
(2)



(3)

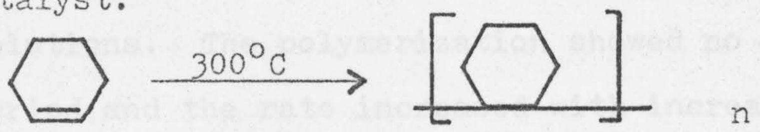
Cis

Trans



[8]

Other cycloolefins also polymerize by ring-opening, but cyclohexene is inert in these polymerization reactions. It has only been polymerized via the double bond under high pressure and temperature in the presence of a free radical catalyst.[9]



(5)

Similarly cyclohexene does not normally copolymerize. Thus the literature indicates that cyclohexene is inert in polymerization and copolymerization reactions.

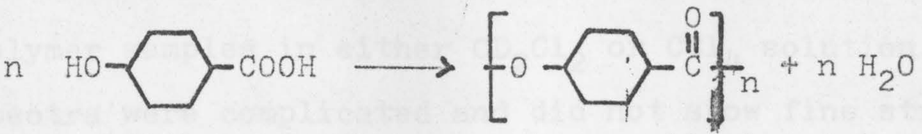
Formic acid is useful in ester synthesis because it can add readily to carbon-carbon double bonds to yield formate esters.[10] It is not useful in polymerization or copolymerization of alkenes. Several formate esters have been synthesized by telomerization of alkenes, but these contain only one formate ester group and many alkene units, in the polymer chain.[11-13]

Earlier experiments indicated that organic peroxide and hydroperoxides are active polymerization catalyst. For example, styrene has been polymerized in the presence of cyclohexyl hydroperoxide.[14] Although numerous initiator systems have been used for vinyl polymerization in free radical initiated polymerizations, the use of molecular halogens as one component was not reported until 1966. Aqueous polymerization of methyl methacrylate has been found to take place in the presence of iodine.[15] The polymerization of alkyl vinyl ethers with iodine has been claimed to proceed by a cationic mechanism.[16] The cocatalytic effect of hydrogen iodide on the polymerization of styrene by iodine has been studied kinetically by a dilatometric technique at 30°C in methylene chloride solutions. The polymerization showed no acceleration period and the rate increased with increasing hydrogen-iodide concentration for each given iodine concentration. The molecular weight of the polymers obtained decreases as the acid (HI) concentration increases.[17] The photopolymerization of methyl methacrylate, in the presence of iodine and triethylamine, was investigated to clarify the initiation mechanism in this system. It was confirmed that triethylaminehydroperoxide formed during the polymerization process, but did not act as a photosensitizer by itself,[18] because the exciting light was not absorbed by it.

In 1968, Silbert et al studied the reaction of alkyl and aryl peroxides and hydroperoxides with iodine to form alkyl or aryl iodides. With benzoyl peroxide they also observed some iodine-containing polymeric byproducts. These polymeric byproducts apparently were of the tetrahydroquater phenyl type.[19]

The 4-hydroxycyclohexanecarboxylic acids (cis and trans) are suitable monomers for the production of polymers, which are important model compounds for the copolymers of cyclohexane and formic acid.[20] 4-Hydroxycyclohexene-carboxylic acid is difficult to prepare and was first obtained by reduction of 4-keto-cyclohexene-1-carboxylic acid with sodium amalgam by Perkin.[20] This material (m.p. 120°C) was assumed to have the <u>trans</u>-configuration. The same acid has been made by Balav and Srol[21] by hydrogenation of p-hydroxybenzoic acid which gave a small quantity of the saturated <u>trans</u> form (m.p. 120°C) and excess of the <u>cis</u>-form (m.p. 152). Since the later compound readily lactonized on distillation it was assumed to be the <u>cis</u>-isomer.

Hunt and Cambell improved the synthesis of 4-hydroxycyclohexane-1-carboxylic acid.[22] The same acid has been made more recently by Noyce and Weingarton.[23] This acid could polymerize by losing water in a condensation reaction as shown below:



(6)

Although cyclohexene is usually inert in polymerizations, Gebelein[24] observed a polymerization reaction of cyclohexene in the presence of formic acid and iodine using a peroxide as a catalyst. The reaction appeared to proceed as follows:

(7)

No polymerization occurs if any one of these components is omitted. The polymer is an unsaturated polyester and appears to be poly (oxy-2-cyclohexen-1,4-enylcarbonyl.) The polymer found in the above reaction showed the following elemental analysis:[24]

Found: C, 68.35; H, 6.48; O (direct), 25.1.

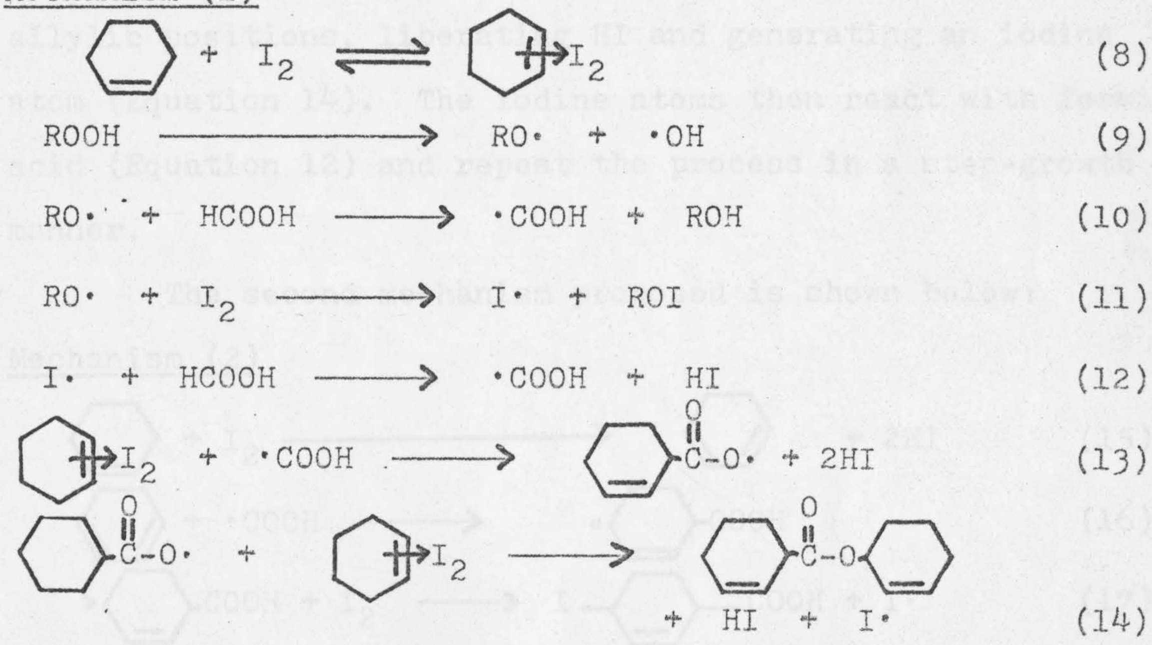
Calcd. for $C_7 8_8 O_2$: C, 67.73; H, 6.50; O, 25.78.

Infra red spectra (nujol mull on Beckman IR-5) showed absorption at about 1725 (ester C=O) 1600, 1160 (stretching C-O grouping) and 720cm^{-1} (cis-H-C=C-H alkene groups). The latter absorption occurs at the same place as the cis-H-C=C-H out-of-plane rocking in cyclohexane.[24] No absorption peaks due to cyclohexyliodide (approximately 650cm^{-1}) could be found in the spectra of these polymers. The polymers also showed a negative Beilstein test for halogen. The presence of unsaturation in the polymer was confirmed by bromine titration.[14]

Nuclear magnetic resonance spectra were run on polymer samples in either CD_2Cl_2 or CCl_4 solution. These spectra were complicated and did not show fine structure. Also it was difficult to distinguish individual protons due to overlaping peaks. The NMR spectra did not show any indication of congugation with a second double bond or with a carbonyl group. In addition, no formate or acid proton signals were present in NMR spectra.[24]

Two possible polymerization mechanisms were proposed by Gebelein.[24]

Mechanism (1)



$$ROOH \longrightarrow RO\cdot + \cdot OH \qquad (9)$$

$$RO\cdot + HCOOH \longrightarrow \cdot COOH + ROH \qquad (10)$$

$$RO\cdot + I_2 \longrightarrow I\cdot + ROI \qquad (11)$$

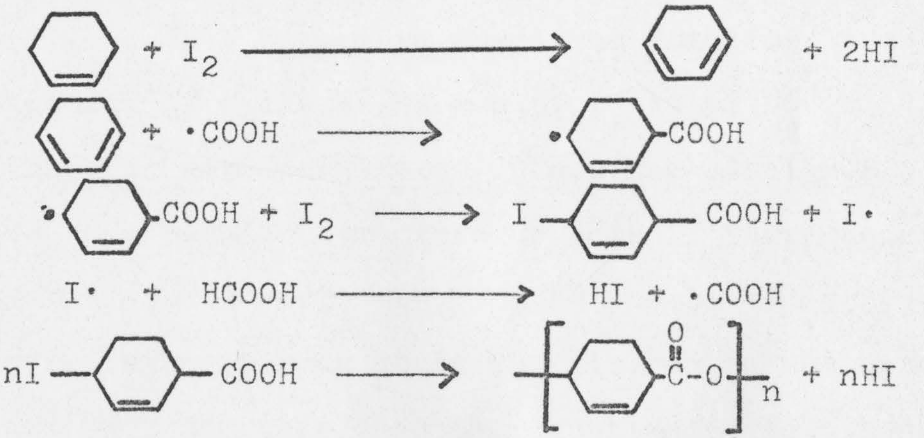
$$I\cdot + HCOOH \longrightarrow \cdot COOH + HI \qquad (12)$$

Equation 8 shows the complex formation between iodine and cyclohexene. Equation 9 describes the decomposition of the hydroperoxide into free radicals. (In the literature the hydroperoxides used included 2-cyclohexenylhydroperoxide, and tert-butyl hydroperoxide. Only the latter was used in the present study.) The resulting radical (either RO· or HO·) can then react with formic acid (Equation 10) or iodine (Equation 11) in the initiation step. Further reaction of the iodine atom with formic acid (Equation 12) is necessary to form the formic acid radical.

Equations 12 to 14 illustrate the growth of the polymer chain. The formic acid radical reacts with the cyclohexene-iodine complex to form HI and an ester group in the allylic position (Equation 13). The radical (Equation 13) then reacts with a second cyclohexene-iodine complex to form a polyester unit with fusion at the two allylic positions, liberating HI and generating an iodine atom (Equation 14). The iodine atoms then react with formic acid (Equation 12) and repeat the process in a step-growth manner.

The second mechanism proposed is shown below:

Mechanism (2)



(15)

(16)

(17)

(18)

(19)

The above scheme also involves free radical reactions but the polymer growth would still be stepwise. Equations 15 and 16 show the formation of 1,3-cyclohexadiene followed by a 1,4 addition of the formic acid free radical. Equation 17 shows the formation of 5-iodo-2-cyclohexene - carboxylic acid. Equation 18 is similar to Equation 12. Equation 19 shows the formation of polyester and hydroiodic acid, possibly by an ionic elimination reaction.

These mechanisms are discussed in more detail in Reference 24.

CHAPTER II

STATEMENT OF THE PROBLEM

Recently a polymerization reaction was reported in which a 1 to 1 copolymer of cyclohexene and formic acid was prepared.[24] Prior to this work there had been little reported polymerization studies involving either cyclohexene or formic acid.[9,11-13] The copolymerization reaction noted above required the presence of iodine and a free radical initiator, in addition to the cyclohexene and the formic acid, in order to form the copolymer. Many questions regarding this reaction remained unanswered.

Does this polymerization always lead to a 1 to 1 copolymer of formic acid and cyclohexene or can other ratios occur under some reaction conditions? What are the optimum conditions for forming the polymer? In the original work,[24] only a structure involving coupling at the allylic positions of cyclohexene was proposed although other structures were considered. Does the copolymer always have this regular structure or does it vary randomly among several structures? Can cyclohexene be homopolymerized to a poly (alkene) by a technique similar to the copolymerization reaction? Can this reaction be extended to alkenes other than cyclohexene? Finally, what is the actual reaction mechanism? Although two possible mechanisms have been proposed,[24] other mechanisms are possible. A study of the effect of reaction variables on the polymer structure could aid in deducing valuable information regarding the polymerization mechanism.

In this thesis the effect of varying the reactant concentration on polymer yield and properties are examined. The principal properties to be studied are the extent of crosslinking and copolymer composition. This latter property is to be investigated using an infrared spectrophotometric technique. Furthermore, a number of other important polymer properties such as the solubility parameter and the molecular weight are to determined in selected cases. All the information thus obtained will be used to deduce a probable reaction mechanism.

CHAPTER III

EXPERIMENTAL

Reagents

Since reproducibility of the experimental work with cyclohexene is important, all impurities had to be removed from the reactant. The following procedure was used to purify the cyclohexane.[25,26]

The cyclohexene, 1000 ml, (Baker Chemical Co.) was mixed with 10 - 25 g. of phosphorus pentoxide and refluxed for one day. After filtering, the cyclohexene was distilled in a nitrogen atmosphere using a vigreaux fractionating column. The distillation was conducted at 81°C and only the middle eighty percent fraction was retained for the polymerization reactions.

The formic acid (Eastman) used was 97% purity. The iodine was a resublimed grade (Fisher Scientific Co.). The <u>tert</u>-butylhydroperoxide (Matheson, Coleman & Bell) had 70% activity and was used without further purification.

Equipment

All glassware was cleaned and dried thoroughly. The following apparatus was used in the polymerization runs as a reaction vessel. The polymerization was run in a three-neck, 100 ml. flask which had standard taper joints. A Trubore stirrer with Teflon blade was placed in the center neck. The right hand side neck was fitted with a Y-adapter and held a water-jacketed condenser and (a 0-400°C) thermometer. The left hand neck was fitted with a 150 ml. dropping funnel. In most polymerization runs, the iodine and formic acid were placed in the flask and the cyclohexene and tert-butylhydroperoxide were placed in the dropping funnel.

A Calab flash-evaporator was used for evaporating methylene chloride and other solvents. Molecular weight determinations were run on a Perkin-Elmer-Hitachi Model 115, vapor phase osmometer. The instrument used for infrared spectral studies was a Beckman IR-5.

Polymerization Procedure

The reactant quantities employed in the individual runs as well as other characteristic data are summarized in Table 1. In all cases, a solution of tert-butylhydroperoxide in cyclohexene was added dropwise through the dropping-funnel over a known time period to a stirred mixture of iodine and formic acid in the reaction vessel. All polymerization reactions were run in the presence of air and sunlight. All reactions were exothermic and the temperature increase began within two minutes with the maximum temperature occurring within 3 to 10 minutes of the start of the cyclohexene addition. The temperature remained near the maximum for about five minutes then declimed. No additional heat was applied.

All free, undissolved iodine disappeared gradually when the mixture of cyclohexane and tert-butylhydroperoxide was added. Before the addition, the color of iodine in formic acid was light brown and the mixture was heterogeneous. After the addition started, the solution became dark brown and appeared homogeneous.

After the addition, the apparently homogeneous mixture was gradually cooled. The mixture was poured into methylene chloride. To this solution aqueous NaOH was added to remove excess formic acid. Next the mixture was washed twice with saturated Na_2SO_3 to remove any unreacted iodine. Then the organic layer was separated from the water layer. The resulting organic layer contained the polymer. The methylene chloride was removed using a flash evaporator.

The resulting oil was treated with warm acetone to isolate the insoluble polymer. The polymer was then washed with acetone and dried to give a black-brown solid.

Determination of Percent Crosslinked Polymer

Crosslinked polymers are generally insoluble in all common solvents. On this basis, the crosslinked polymer was isolated and its percentage determined. The following experimental procedure was used: a known amount of polymer was placed in a Soxhlet extractor-thimble and approximately

TABLE 1

Summary of Polymerization Reactions: Starting Conditions,
Yields, Percent Ester Formed and Percent Crosslinked Polymer

Run	Moles				Max. Temp. °C	Weight Polymer (g)	% Ester	% Crosslinked Polymer
	Cyclo-hexene	Formic Acid	Iodine	Hydro peroxide				
1	0.1	1.0	0.1	0.05	83	1.24	11	4 (a)
2	0.1	0.1	0.1	0.01	73	3.6	16	23 (a)
3	0.1	0.1	0.2	0.01	70	12	23	76 (a)
4	0.1	0.2	0.1	0.01	60	0.91	9	32 (b)
5	0.1	0.1	0.1	0.01	82	2.35	6	23 (a)
6	0.1	0.1 (c)	0.2	0.01	76	3.11	13	26 (a)
7	0.1	0.1	0.2	0.01	41	2.94	17	17 (b)
8	0.1	0.1	0.2	0.01	73	4.14	15	9 (b)
9	0.2	0.1	0.1	0.01	42	2.34	11	30 (b)
10	0.1	0.1	0.2	0.02	70	3.25	15	7 (b)

Table 1, continued

Run	Moles Cyclo-hexene	Formic Acid	Iodine	Hydro peroxide	Max. Temp. °C	Weight Polymer (g)	% Ester	% Crosslinked Polymer
11	0.1	0.1	0.2	0.05	112	3.57	13	4 (b)
12	0.1	0.5	0.2	0.01	62	4.42	9	25 (a)
13	0.1	0.25	0.2	0.01	63	10.2	12	42 (a)
14	0.2	0.1	0.2	0.01	98	6.3	6	24 (a)
15	0.05	0.05	0.15	0.05	52	4.35	8	38 (a)
16	0.2	0.05	0.05	0.01	40	0.90	9	56 (a)
17	0.2	0.1	0.05	0.01	29	0.30	5	10 (a)
18	0.1	0.0	0.1	0.01	66	3.15	--	6 (a)

(a) solvent was CH_2Cl_2

(b) solvent was C_6H_6

(c) 88% formic acid

500 ml methylene chloride (or benzene in some cases) was placed in a round bottomed flask and connected to the Soxhlet extractor. The flask was heated and the solid polymer was extracted over night. Most of the polymer dissolved in the solvent but some insoluble polymer remained in the thimble. The soluble polymer was isolated by removing the solvent using a flask evaporator (Calab). The resulting soluble polymer was dried in a vacuum oven. This dried soluble polymer was used in the spectroscopic determinations. The insoluble polymer in the thimble was also dried in a vacuum oven.

From the weight of the soluble and insoluble polymer, the percent crosslinked polymer was calculated as follows:

$$\%\text{ Crosslinked polymer} = \frac{\text{Wt. of insoluble polymer}}{\text{Total wt. of polymer}} \times 100 \qquad (20)$$

The percent crosslinked polymer in the different reactions is listed in Table 1.

Determination of Copolymer Composition

The copolymer formed in the polymerization reaction was an unsaturated polyester. The copolymer composition was expressed as percent ester by comparing the infrared absorption intensities of the ester and alkene groups.

In the actual experimental procedure, the infrared spectra (Beckman IR-5) were run using nujol mulls. The polymer compound (approximately 1 - 2 mg) was ground in 2 - 3 drops of nujol and the mull was spread on sodium chloride plates. The spectra showed absorption at about 1725 (ester C=O), 1600, 1160 (C-O stretching) and 720cm^{-1} (*cis*-H-C=C-H).

The percent ester was calculated using the peak intensities of the ester (1725cm^{-1}) and alkene (720cm^{-1}) adsorptions using the following equation:[27,28]

$$\%\ \text{Ester} = \frac{100\ E}{2.21\ A} \qquad (21)$$

In Equation 21, E is the absorbance of the ester peak, A is the absorbance of the alkene peak and 2.21 is the ratio of E/A for a 1 to 1 cyclohexene-formic acid copolymer.[27,28]

The percent ester in the copolymers was listed in Table 1. A typical sample calculation is shown below for Run No. 1 where E is 0.047 and A is 0.191.

$$\%\ \text{Ester} = \frac{100\ (0.047)}{2.21\ (0.191)} = 11.1\% \qquad (22)$$

Note that by this method of calculation, 100% ester would mean that the copolymer contained an equal number of cyclohexene and formic acid fragments. A copolymer with 3 cyclohexene units for each formic acid unit would have 50% ester.

Solubility Parameter Determination

The solubility characteristics of the cyclohexene-formic acid copolymer were studied and these results are summarized in Table 2. The main purpose of this study was to determine the solubility parameter of this polymer. The solubility parameter can be defined by Equation 23 for volatile liquids where δ is the solubility parameter, ΔH is the latent heat of vaporization, R is the gas constant, T is the absolute temperature, M is the molecular weight and D is the density of the liquid. The solubility parameter is also the square root of the cohesive energy density (CED). While the solubility parameter of a volatile liquid can be computed directly from the latent heat of vaporization, the solubility parameter of a non-volatile polymer must be determined by measuring the polymer solubility in various solvents. Hydrogen bonding complicates this determination and often the exact solubility parameter range observed varies with the hydrogen bonding tendency of the solvents. The solvents are normally grouped as poorly, moderately or strongly hydrogen bonded solvents. Tabulation of solubility parameters for solvents and common polymers are available.[29]

$$\delta = \frac{\Delta H - RT}{M/D} \qquad (23)$$

The experimental procedure used to obtain the data in Table 2 consisted in placing 0.1 g. polymer and 5 mls. solvent in a test tube, shaking vigorously and allowing to stand for several days with occassional shaking. The polymer sample used in these studies was CG-3150B which was a cyclohexene-formic acid copolymer that contained 63.2% ester. After about a week, the solutions were examined and residual solid was noted in all cases. Since the polymer was a dark brown, the more soluble samples were a darker brown solution. The solubility ranking of the 25 solvents was made visually from the lightest color (least soluble) to the darkest color (most soluble). These ranked samples were then subdivided into the four groups denoted by I, SS, S and VS in Table 2.

It is immediately apparent from Table 2 that the polymer is not appreciably soluble in a solvent with a solubility parameter below 8 or above 11, regardless of the solvent hydrogen bonding tendencies. The most favorable solvents, methylene chloride, chloroform, dichloroethane and benzene, are poorly hydrogen bonding solvents. In poorly hydrogen bonding solvents the solubility parameter range was 8.6 - 10.0 (as estimated by the S and VS results). With moderately hydrogen bonding solvents this solubility parameter range was 9.1 - 10.8. Appreciable polymer solubility was observed in only one strongly hydrogen bonding solvent, pyridine.

TABLE 2

Solubility of Polymer (CG 3150 B) in Solvents of Varying Solubility Parameter (δ)[27]

Name of Solvent (a)	δ (b)	Solubility (c)
Ethanol	12.7 (S)	I
Acetonitrile	11.9 (P)	I
Methanol	14.5 (S)	I
Pentane	7 (P)	I
Heptane	7.5 (P)	I
n-butanol	11.4 (S)	I
Cyclohexane	8.2 (P)	SS
DMSO	12 (M)	SS
Acetone	9.9 (M)	SS
Diethylether	7.4 (M)	SS
THF	9.1 (M)	S
Diethylacetamide	10.8 (M)	S
Toluene	8.9 (P)	S
Methyliodide	10.2 (M)	S
Carbontetrachloride	8.6 (P)	S
Carbondisulfide	10.0 (P)	S
Cyclohexanone	9.9 (M)	S
Chlorobenzene	9.5 (P)	S
Methylbenzoate	10.5 (M)	S
Cyclopentanone	10.4 (M)	VS
Pyridine	10.7 (S)	VS
Methylenechloride	9.7 (P)	VS
Dichloro Ethane	9.8 (P)	VS
Benzene	9.2 (P)	VS
Chloroform	9.3 (P)	VS

(a) Solvents are listed in order of increasing polymer solubility.

(b) (S) is strongly hydrogen bonded
(M) is moderately hydrogen bonded
(P) is poorly hydrogen bonded

(C) I - Insoluble
SS - slightly soluble
S - soluble
VS - very soluble

Molecular Weight Determination

Polymer number average molecular weights were determined using a Perkin-Elmer-Hitachi Model 115 vapor phase osmometer. This molecular weight method depends upon vapor pressure lowering by a solute and the actual measurements are differences in the rate of evaporation of a solution and a pure solvent sample. This quantity is termed $\Delta\Delta R$. Normally 4 or 5 benzene solutions of the polymer were used and the $\Delta\Delta R$ values were determined in increasing order of polymer concentration, c (in grams/1000 g. solvent). Values of $\Delta\Delta R/c$ were computed, plotted against c and the best straight line determined by the method of least squares. The value of the intercept at zero concentration represents the $\Delta\Delta R/c$ value at infinite dilution. The molecular weight, $\overline{M}_N$, is calculated from this value using Equation 24 where K is an instrument constant. The value of K was determined experimentally for each molecular weight determination using pure benzil as the calibration standard.

$$\overline{M}_N = \frac{K}{(\Delta\Delta R/c)\ \text{limit } c \rightarrow 0} \qquad (24)$$

The polymer molecular weights were found to be in the range of 800 to 1000.

Miscellaneous Polymer Properties

The polymer showed a negative Beilstein test for halogen. The infrared spectra of the polymers also showed the absence of peaks due to cyclohexyliodide (approximately 650cm^{-1}).

Capillary melting point studies showed that the polymer did not melt below 230°C. Above this temperature, it begins to melt with decomposition.

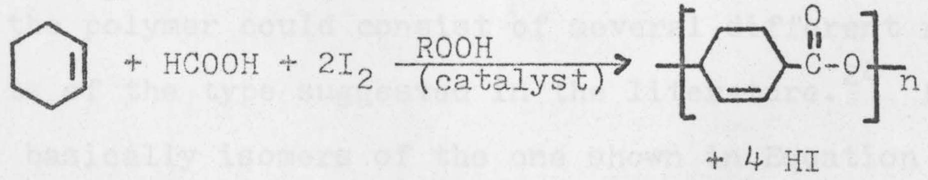
Usually the polymer was a light brown solid but sometimes it was a dark black-brown or a dark green solid.

CHAPTER IV

RESULTS AND DISCUSSION

Introduction

As noted in the historical section, copolymers of cyclohexene and formic acid have not been known until recently.[24] In addition, neither formic acid nor cyclohexene has been widely used alone in polymerization reactions. In a few cases, telomers have been made containing one formate group and several alkene units,[11-13] and cyclohexene has been homopolymerized across the double bond under conditions of high pressure and temperature.[9] The copolymerization reaction studied here does not involve this type of reaction since the final polymer still contains the double bond from the cyclohexene and does not contain any formate ester groups. This polymerization reaction requires the presence of both iodine and a free radical initiator in order to occur and appears to proceed by the following overall equation.

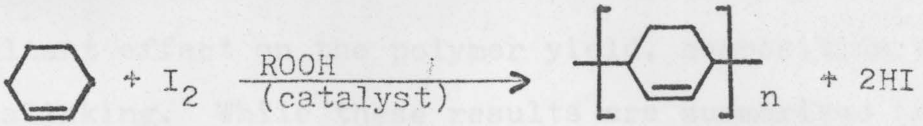


(25)

While the use of iodine in a free radical polymerization is unusual, there are several recent literature examples wherein iodine is directly involved as a free radical catalyst.[16-18] The role of iodine in this reaction does not appear to be as a catalyst but rather as a hydrogen atom abstractor from both the formic acid and the cyclohexene.

In addition, charge-transfer complexes between the cyclohexene and the iodine may play an important role in this reaction. Such complexes are known to occur.[30] There are strong indications that these complexes occur here also. All the copolymerization reactions of Table 1 were run by adding a cyclohexene-hydroperoxide solution to a heterogeneous, light brown-violet mixture of iodine and formic acid. This mixture rapidly changed to a deep red-brown color, presumably due to complex formation. Complex formation may also prevent an undesired electrophilic attack of formic acid on the double bond.

The purpose of the present study is to determine the effect of various reaction parameters on the polymer properties. The polymer structure shown in Equation 25 is an idealized one and may not occur in all cases. For example, additional attacks could still occur on this polymer chain leading to a crosslinked polymer structure or the polymer could consist of several different repeat units of the type suggested in the literature.[24] (These are basically isomers of the one shown in Equation 25.) In addition, the cyclohexene units could be joined to each other to form a polyalkene as shown in Equation 26. Run 18 of Table 1 showed the formation of such a polymer and additional examples have been observed.[27]



(26)

The result of Table 1 clearly show that most of the polymers studied consisted of mixtures of the repeat units from both Equations 25 and 26 since the percent ester ranged from about 5 to 20%. (The copolymer in Equation 25 contains 100% ester while the polymer in Equation 26 has 0% ester.) The results of Table 1 also indicate that the extent of crosslinking and the yield vary with the reactant concentration. These factors will be discussed more fully in the next section and the mechanistic implications will be discussed in the following section.

Effect of Variables on the Polymerization Reaction

The most obvious variables in this reaction are the concentrations of cyclohexene, formic acid, iodine and tert-butylhydroperoxide and the effect of varying these concentrations is the main subject of this study. The effect of different types of free radical initiator was not studied nor was the effect of agitation rate. (All reactions were run at about the same agitation rate of 300 RPM.) The possible effects of an inert atmosphere, external heat or additional light were excluded also. Some studies were made in varying the addition rate but these changes were relatively small. The basic approach used here involved the systematic variation of reactant concentration and observing the resultant effect on the polymer yield, composition and crosslinking. While these results are summarized in Table 1, the effect of each factor is best examined by isolating each variable separately. This has been done in Tables 3 - 9.

The effect of varying the formic acid and hydroperoxide concentrations, when the ratio of cyclohexene and iodine concentrations are held constant, will be examined and these results are summarized in Tables 3 and 4.

In Table 3, the cyclohexene:iodine ratio (=1) was held constant and only the amount of formic acid varied.

From Table 3 the following can be concluded. (1) If we increase the formic acid concentration we will get lower yields and a little more polyester. There is no significant effect on the extent of crosslinking.

In Table 4 the iodine and cyclohexane ratio was maintained constant (but at a value of 2) and the formic acid and hydroperoxide concentrations were varied.

The following conclusions can be made from the data of Table 4. (1) If the concentration of tert-butylhydroperoxide is raised, less crosslinking occurs in the polymer but there was no effect on the yield or copolymer composition. (2) The yield of polymer and amount of crosslinking appears to pass through a maximum on varying the formic acid concentration but there was no effect on the ester concentration.

TABLE 3

Effect of the Formic Acid Concentration on the Copolymer Composition, Yield and Percent Crosslinked Polymer at 0.1 mole Cyclohexene and 0.1 mole Iodine

Run No.	Moles of HCOOH	Moles of ROOH	g. Polymer	% Crosslinked Polymer	% Ester
14	0.1	0.01	6.3	24	6
5	0.1	0.01	2.4	23	6
2	0.1	0.01	3.6	23	16
4	0.2	0.01	0.9	32	9
1	1.0	0.05	1.2	4	11

TABLE 4

Effect of Formic Acid and *tert*-butylhydroperoxide Concentration on the Copolymer Composition, Yield and Percent Crosslinked Polymer at 0.2 moles Cyclohexene and 0.1 moles Iodine

Run No.	Moles of HCOOH	Moles of ROOH	g. Polymer	% Crosslinked Polymer	% Ester
7	0.1	0.01	2.94	17	17
6	0.1	0.01	3.11	26	13
8	0.1	0.01	4.14	9	15
10	0.1	0.02	3.25	7	15
11	0.1	0.05	3.57	4	13
13	0.25	0.01	10.2	42	12
12	0.5	0.01	4.42	25	9

In Table 5 the cyclohexene and formic acid ratio was maintained constant and the iodine and hydroperoxide concentrations were varied. From the data of Table 5, one can conclude the following. (1) If the concentration of iodine is raised, less crosslinking and slightly more ester in the polymer is observed but there is no appreciable effect on the yield. (2) If the concentration of hydroperoxide is raised, less crosslinking occurs but there is no appreciable effect on the yield and percent ester in the copolymer.

In Table 6 we maintain the concentration of cyclohexene constant and vary iodine/formic acid ratio and the concentration of hydroperoxide.

From the data of this table, the following facts become apparent. (1) Raising the concentration of the tert-butylhydroperoxide, produces less crosslinked polymer and there is no significant effect on the yield or copolymer composition. (2) Increasing the ratio of I_2/HCOOH we get a higher percent ester in the copolymer, a slightly higher yield and less crosslinking.

In the fifth case, the concentration of formic acid and the hydroperoxide were maintained at 0.1 and 0.01 moles,

TABLE 5

Effect of Iodine and tert-butylhydroperoxide Concentration on the Copolymer Composition, Yield and Percent Crosslinked Polymer at 0.1 moles Cyclohexene and 0.1 moles Formic Acid

Run No.	Moles of Iodine	Moles of ROOH	g. Polymer	% Crosslinked Polymer	% Ester
2	0.1	0.01	3.6	23	16
5	0.1	0.01	2.4	23	6
6	0.2	0.01	3.11	26	13
7	0.2	0.01	2.94	17	17
8	0.2	0.01	4.14	9	15
10	0.2	0.02	3.25	7	15
11	0.2	0.05	3.57	4	13

TABLE 6

Effect of Iodine-Formic Acid Ratio and tert-butylhydroperoxide Concentration on the Copolymer Composition, Yield and Percent Crosslinked Polymer at 0.1 mole Cyclohexene

Run No.	Mole Ratio I_2/HCOOH	Mole of ROOH	g. Polymer	% Crosslinked Polymer	% Ester
1	0.1	0.05	1.2	4	11
12	0.4	0.01	4.4	25	9
4	0.5	0.01	0.9	32	9
13	0.8	0.01	10.2	42	12
2	1.0	0.01	3.6	23	16
5	1.0	0.01	2.4	23	6
6	2.0	0.01	3.11	26	13
7	2.0	0.01	2.44	17	17
8	2.0	0.01	4.14	9	15
10	2.0	0.02	3.25	7	15
11	2.0	0.05	3.57	4	13

TABLE 7

Effect of Cyclohexene and Iodine Concentration on the Copolymer Composition, Yield and Percent Crosslinked Polymer at 0.1 moles Formic Acid and 0.01 moles <u>tert</u>-butylhydroperoxide

	Moles			%	
Run No.		I_2	g. Polymer	Crosslinked Polymer	% Ester
9	0.2	0.1	2.34	30	11
14	0.2	0.2	6.3	24	6
5	0.1	0.1	2.35	23	6
2	0.1	0.1	3.6	23	16
6	0.1	0.2	3.11	26	13
7	0.1	0.2	2.94	17	17
8	0.1	0.2	4.14	9	15

respectively. These results are summarized in Table 7. From the data of Table 7 we can conclude the following facts. (1) Increasing the iodine concentration, while holding the cyclohexene constant, has little effect on the copolymer yield, composition or crosslinking. (2) Raising the concentration of cyclohexene, at constant iodine concentration, results in more crosslinking but there was no appreciable effect on the yield or composition of the copolymer. (3) If the ratio of cyclohexene to iodine is raised, a copolymer with less ester and more crosslinking was obtained but there was no significant effect on the yield. Obviously this effect was due primarily to changing the cyclohexene concentration.

Finally, in the last two cases, the concentration of iodine is maintained at 0.1 and 0.2 moles and the <u>tert</u>-butyl-hydroperoxide concentration at 0.01 mole and the formic acid:cyclohexene ratio was varied. These results are summarized in Tables 8 and 9 it appears that the amount of ester in the polymer decreased as the formic acid:cyclohexene ratio increased. The effect on the yield or the amount of crosslinking were obscure.

These effects can be summarized as follows. (1) Increasing the cyclohexene concentration increases the extent of crosslinking but has little effect on the yield or composition. (2) Increasing the formic acid concentration appears to decrease the yield and the crosslinking but has little effect on the extent of ester formed. (3) Increasing the iodine concentration decreased the crosslinking, may increase the amount of ester in the copolymer but has little effect on the yield. (4) An increase in the amount of tert-butylhydroperoxide decreased the crosslinking but had no effect on yield or composition. (5) Increasing the iodine to formic acid ratio decreases the crosslinking, raises the percent ester but has no effect on the yield. (6) Raising the cyclohexene:iodine ratio increases the crosslinking and decreases the amount of ester in the polymer but did not effect the yield. Finally, (7) increasing the formic acid:cyclohexene ratio decreases the percent ester but the effect on the other properties is uncertain.

To prepare a copolymer with high ester content and low crosslinking, a low concentration of cyclohexene and high concentrations of formic acid, iodine and hydroperoxide

TABLE 8

Effect of the Formic Acid: Cyclohexene Ratio on the Copolymer Composition, Yield and Percent Crosslinked Polymer at 0.1 moles Iodine and 0.01 moles tert-butylhydroperoxide

Run No.	Ratio $HCOOH/C_6H_{10}$	g. Polymer	% Ester	% Crosslinked Polymer
9	0.5	2.34	11	30
2	1.0	3.6	16	23
5	1.0	2.35	6	23
4	2.0	0.91	9	32

TABLE 9

Effect of the Formic Acid: Cyclohexene Ratio on the Copolymer Composition, Yield and Percent Crosslinked Polymer at 0.2 moles Iodine and 0.01 moles *tert*-butylhydroperoxide

Run No.	Ratio $HCOOH/C_6H_{10}$	g. Polymer	% Ester	% Crosslinked Polymer
8	1.0	4.14	15	9
7	1.0	2.94	17	17
6	1.0	3.11	13	26
13	2.5	10.2	12	42
12	5.0	4.42	9	25

should be used. A high ratio of iodine to formic acid would also be preferred. This is essentially in agreement with the ratios shown in Equation 25 except that lower than stoichiometric amounts of cyclohexene would be preferred. The closest reactions to these criteria were Runs No. 10 and 11 of Table 1.

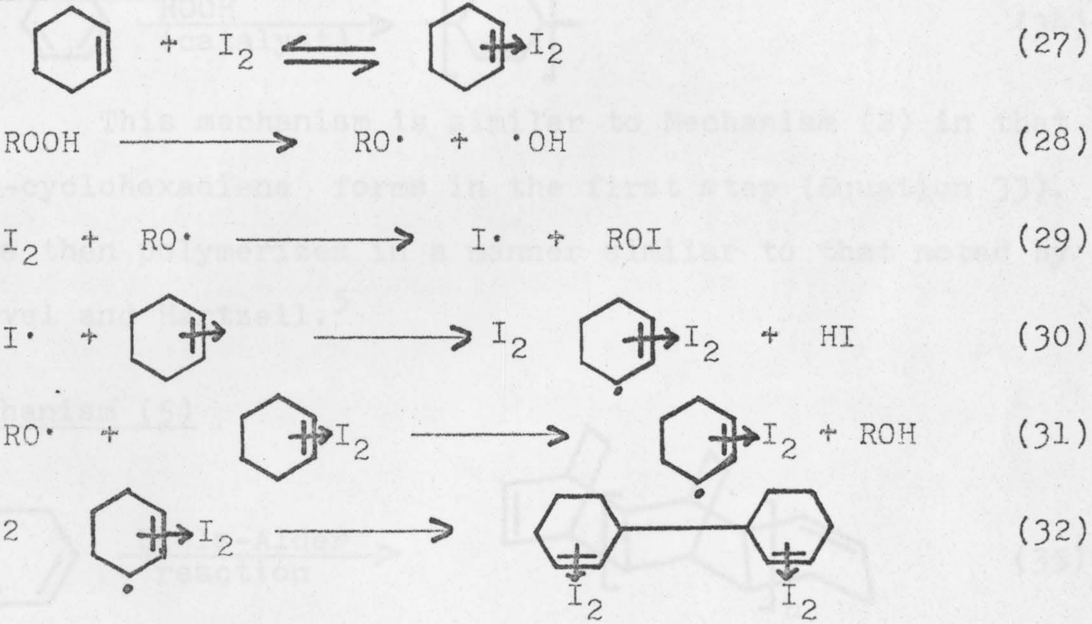
It is worth noting at this point that none of the factors studied had a great effect on the amount of ester in the copolymer and that this appears to be controlled by some factor other than the concentrations studied here. The agitation rate possibly is a strong controlling factor since the reaction mixture is heterogeneous during much of the reaction. Further study would be necessary to determine the extent of the effect of the agitation rate on the polymer properties.

Polymerization Mechanism

The mechanism of this polymerization appears to be a step-growth process involving free-radical reactions. The two suggested reaction mechanisms that appear in the literature[24] were discussed in the Historical Section. At this point, we will propose several other possible reaction mechanisms for the copolymerization of cyclohexene and formic acid and some possible mechanisms for the homopolymerization of cyclohexene. As many of these as possible will then be eliminated based on the experimental work in this study. The two mechanisms discussed in the Historical Section will be referred to as Mechanism (1) and Mechanism (2) in this section and will be compared against some new mechanisms here.

Three possible mechanisms can be proposed for the homopolymerization of cyclohexene. These will be examined first.

Mechanism (3)



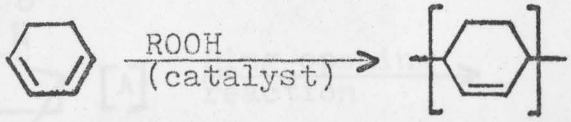
$$\mathrm{ROOH} \longrightarrow \mathrm{RO\cdot} + \mathrm{\cdot OH} \tag{28}$$

$$\mathrm{I_2} + \mathrm{RO\cdot} \longrightarrow \mathrm{I\cdot} + \mathrm{ROI} \tag{29}$$

Mechanism (3) is basically similar to Mechanisms (1) except formic acid is not used. The cyclohexene-iodine complex forms in Equation 27 and undergoes a hydrogen abstraction (Equation 30 or 31) by iodine atoms or alkoxy radicals formed in Equations 28 or 29 to give allylic cyclohexenyl radicals. These radicals in turn couple (Equation 32). Additional reactions analogous to Equation 30 or 31 thus would lead to a polymer with the structure given in Equation 26. Essentially the same reaction mechanism could be written involving abstraction reactions with uncomplexed cyclohexene.

Mechanism (4)

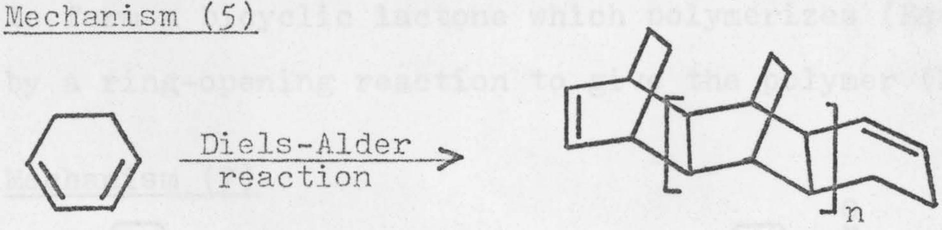
(33)



(34)

This mechanism is similar to Mechanism (2) in that 1,3-cyclohexadiene forms in the first step (Equation 33). This then polymerizes in a manner similar to that noted by Marvel and Hartzell.[5]

Mechanism (5)



(35)

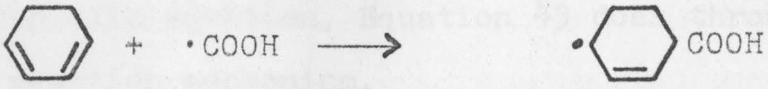
In Mechanism (5) the 1,3-cyclohexadiene (Equation 33) undergoes a Diels-Alder reaction and forms a bicyclic ladder polymer. While such a reaction is possible, the resulting polymer would not be unsaturated except at the end groups and is thus not similar to the polymers of Equation 26. This mechanism will not be considered further.

For the copolymerization reaction, two additional new mechanisms can be proposed. These are Mechanisms (6) and (7).

Mechanism (6)

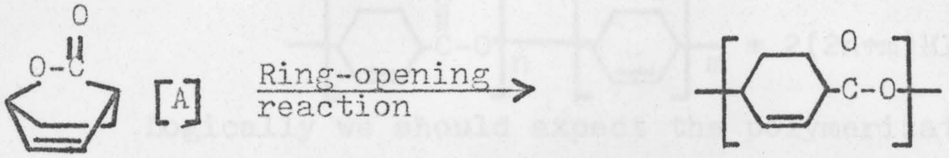
$$RO\cdot + HCOOH \longrightarrow \cdot COOH + ROH \qquad (36)$$

$$I\cdot + HCOOH \longrightarrow \cdot COOH + HI \qquad (37)$$



(38)

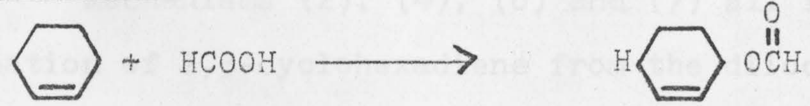
(39)



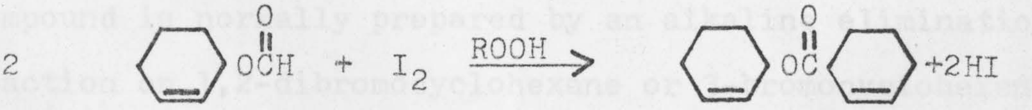
(40)

Mechanisms (6) is a variation of Mechanism (2). A formic acid radical forms (Equation 36 or 37) and adds 1,4 to 1,3-cyclohexadienes (from Equation 33) in Equation 38. The resulting radical reacts with iodine (Equation 39) to form a bicyclic lactone which polymerizes (Equation 40) by a ring-opening reaction to give the polymer (Equation 25).

Mechanism (7)



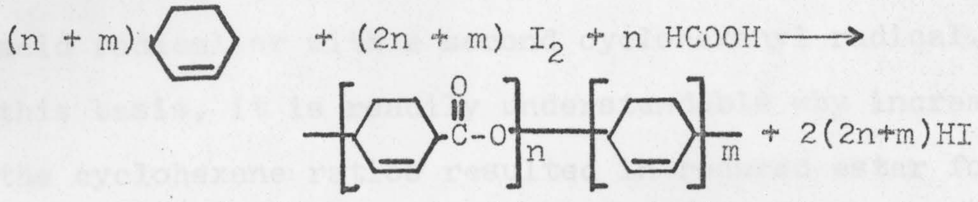
(41)



(42)

In Mechanism (7) the first step involves a simple 1,4-electrophilic addition of formic acid to 1,3 cyclohexadiene (Equation 41) followed by a free radical reaction (Equation 42) in which HI is eliminated. Repetition of the coupling reaction (Equation 42) would result in polymer (Equation 25).

In actual fact, the polymers reported in Table I are combinations of polyester and polyalkene repeat units. We can combine Equation 25 and 26 to get the overall copolymerization Equation 43. Even though this is not a mechanistic equation, Equation 43 does throw some light on the reaction mechanism.



(43)

Logically we should expect the polymerization reactions (Equation 43) to proceed by similar rather than dissimilar mechanisms. This essentially pairs Mechanism (1) with (3), (2) with (4) and (4) with (7). Mechanism (6) involves a ring-opening reaction to form the polyester and no analogous polyalkene forming reaction appears to exist. On this basis the Mechanism (6) seems less likely than the others.

Mechanisms (2), (4), (6) and (7) all involve the formation of 1,3-cyclohexadiene from the diiodide. This compound is normally prepared by an alkaline elimination reaction on 1,2-dibromocyclohexane or 3-bromocyclohexene. Since our reaction conditions are strongly acidic the formation of 1,3-cyclohexadiene does not appear probable. In addition, cyclic dienes appear to polymerize to yield products with two residual double bonds.[27] For these reasons Mechanisms (2), (4), (6) and (7) appear unlikely

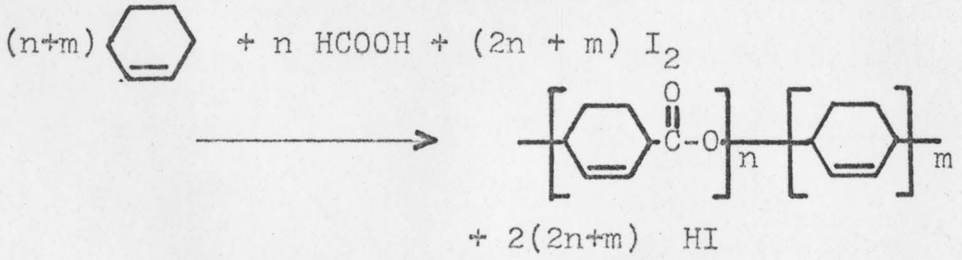
This leaves only the mechanism pair (1) and (3). Mechanism (1) is discussed throughly in the Historical Section and in the literature.[24] Mechanism (3) is basically the same reaction without coupling with the formic acid. In both cases, a cyclohexenyl radical (probably as an iodine complex) forms and either couples with a formic acid radical or with a second cyclohexenyl radical. On this basis, it is readily understandable why increasing the cyclohexene ratios resulted in reduced ester formation. Increasing the amount of cyclohexene would give rise to higher cyclohexenyl radical concentrations and favor Mechanism (3).

Mechanism (1) and (3) appear to be the most likely mechanisms for this copolymerization based on present knowledge. Additional experimental information that would be useful would include the independent synthesis of the possible intermediates in Mechanisms 1 - 7 and an examination of these under typical polymerization conditions to see whether the polymer actually forms.

CHAPTER V

SUMMARY

The effect of varying the reactant concentrations on the copolymerization of cyclohexene and formic acid, in the presence of iodine and tert-butylhydroperoxide, was studied. The polymer properties investigated most thoroughly were the yield, copolymer composition and extent of crosslinking. Some solubility parameter and molecular weight studies were also run. The basic polymerization reaction can be summarized by the equation below.



Experimentally, the polymer composition can be varied from completely polyester units to only polyalkene units. Most of the present studies involved copolymers with 20% or less polyester repeat units. These studies showed that increasing the cyclohexene concentration, relative to the iodine and formic acid concentration, decreased the amount of ester groups in the polymer. The extent of crosslinking was decreased when the concentrations of formic acid, iodine or hydroperoxide were increased or when the cyclohexene concentration was decreased.

The solubility parameter of these copolymers was found to be 8·6-10·0 in poorly hydrogen bonded solvents and 9·1-10·8 in moderately hydrogen bonded solvents. The polymers were not normally soluble in solvents which show strong hydrogen bonding. The polymer molecular weights were in the range of 800-1000.

Several possible polymerization reaction mechanism were proposed and compared to those in the literature.[24] The most reasonable reaction mechanism, based on currently available information, appears to involve the formation of allylic cyclohexenyl radicals (probably as iodine complexes) and the reaction of these with each other to form polyalkene or with a formic acid radical to form a polyester.

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