SYNTHESIS AND CYCLOPOLYMERIZATION OF DIMETHYLDIACRYLYLMETHANE

BY

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Submitted in partial fulfillment of the
requirements for the degree Master
of Science in the Chemistry Department
of the American University of Beirut
Beirut, Lebanon
January 1967

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ACKNOWLEDGMENT

The author wishes to thank Professor Aziz F. Abdul-Karim for suggesting this problem and for his interest and counsel throughout the work.

He also wishes to thank Professors Costas H. Issidorides and Makhluf J. Haddadin for their helpful advice and kind interest.

ABSTRACT

A new method for the preparation of dimethyldiacrylylmethane and its subsequent polymerization to polydimethyldiacrylylmethane is presented.

Dimethylmalonic acid was treated with excess thionyl chloride, and the product dimethylmalonyl dichloride was allowed to react with ethylene in the presence of aluminium chloride. The product obtained, after hydrolysis, was identified as 2,2-dimethyl-3-keto-5-chloropentanoic acid. This acid was allowed to react with thionyl chloride and the acid chloride formed was further made to react with ethylene in the presence of aluminium chloride to yield 1,7-dichloro-4,4-dimethylheptane-3,5-dione. Dehydrohalogenation of the β-diketone with potassium carbonate yielded the monomer, 4,4-dimethyl-1,6-heptadiene-3,5-dione (dimethyldiacrylylmethane), which with free radical initiation produced a white powdery soluble polymer, polydimethyldiacrylylmethane.

The polymer formed is sought to be a precursor of a polyquinoline derivative which is expected to be a thermally stable polymer.

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I. INTRODUCTION

A. Thermal Stability in Organic Polymers

A survey of the literature offers impressive evidence of the work that has been done in attempting to synthesize thermally stable polymers. Interest in this field has been stimulated by the wide variety of applications which such polymers may be made to serve in the world of today; applications that extend from simple household equipment to the more demanding and expanding fields of electronics and jets.

Natural and modified inorganic polymers, which possess outstanding thermal stability, have been used by man ever since he discovered how to make glass and pottery. In recent years an increasing number of investigators have been concerned with the synthesis and evaluation of a large number of inorganic "man-made" polymers. It is outside the scope of this study to go into this rapidly growing field of research.

In reviewing the extensive field of organic polymers, it is noticed that at least four approaches have been attempted to increase thermal stability.

The first involved replacing hydrogen atoms in organic molecules by halogens. Fluorine has been the most successful substituent. A large number of fluocarbon monomers have been

reported in the patent and published literature. Two fluorcarbon polymers, polytetrafluoroethylene and polytrifluorochloroethylene, have been of commercial importance since 1941.

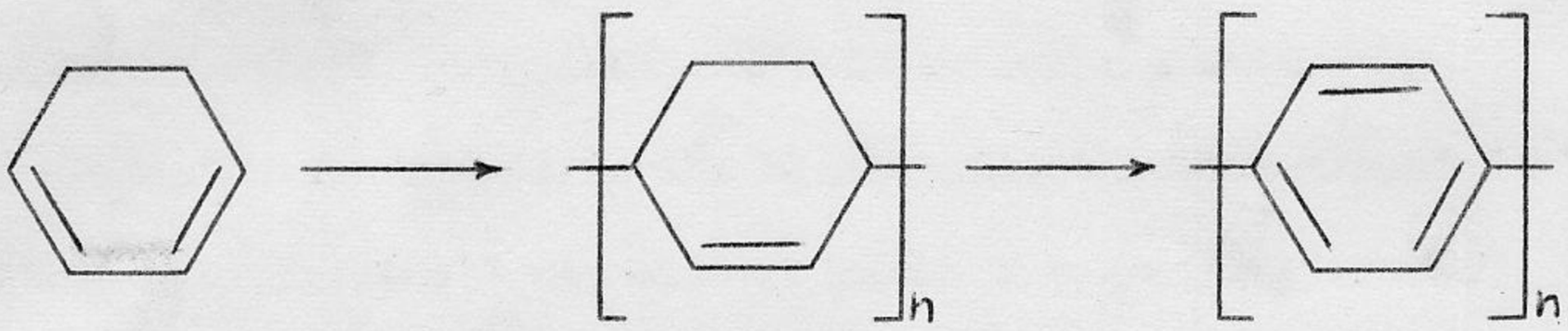
The second approach involved the hybridization of organic with inorganic molecules. Silicones came to commercial use in 1943, and within ten years, the literature listed a wide variety of products that ranged from liquids to oils, greases, resins and rubbery materials. This type of crossbreading has not been limited to silicon, but has been extended to a number of other elements such as boron, phosphorous, sulfur, nitrogen, tin, nickel, chromium and others.

The third approach involved the synthesis of coordination complex polymers. Tagging a metal ion to an organic molecule before or after polymerization is expected to confer higher thermal stability. While a number of chelate-type polymers have been synthesized[1-6], non as yet possess the properties needed for industrial applications.

The fourth approach, which is of direct interest to this investigation, involved the preparation of polyaromatics. It is well known that aromatic compounds such as benzene, pyridine, quinoline and others are produced in the destructive distillation of coal. The stability of these compounds at the high temperatures used in the distillation, led a number of investigators to search for methods leading to the synthesis of fully aromatic polymers.

The preparation of polyphenyl, for example, has been

attempted by several investigators. Edwards and Goldfinger[7] treated p-dichlorobenzene with a potassium-sodium alloy and obtained a non-linear polyphenyl of low molecular weight. In 1961 Marvel and Hassagawa[8] achieved partial success in preparing polyphenyl, by polymerizing 1,3-cyclohexadiene with a Ziegler-type catalyst and dehydrogenating the polymer with bromine.



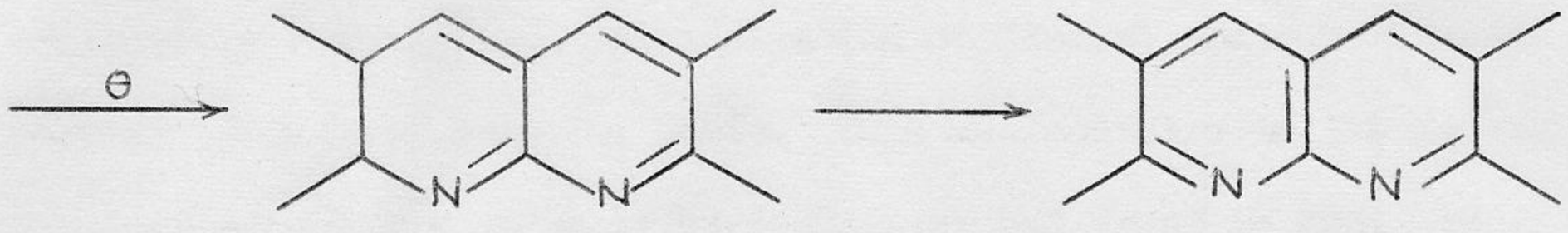
I II III

The product was stable for long hours at 400°C but was still too low in molecular weight (about 7600) to have practical applications.

More recently[9] polymers of this type were obtained from benzene homologs by using $AlCl_3$-$CuCl_2$ type catalyst. It was also claimed[10] that polyphenyls are produced by pyrolyzing benzene in tubes that reduce coking to a minimum.

Polypyridine is believed[11] to be formed by heating polyacrylonitrile over a Bunsen flame. The product undergoes a color change from white to black, and "the chemical changes which are believed to occur during this color transformation involve cyclization of the polymer through the nitrile groups followed by dehydrogenation and hence aromatization of the ring:"

IV V



VI VII

polypyridine, VII, has a high degree of thermal stability, but its low molecular weight, caused by the scission of the polymeric chains during heating, renders the black product of low tensile strength. Polypyridine[12] was also obtained by passing pyridine and chlorine through a SiO_2 tube at 800°C.

A large number of heterocyclic polyaromatic compounds have been synthesized and reported.[13-18] Although some have excellent thermal stability, yet their development to industrially useful products has been handicapped by their low molecular weights and, consequently, their poor mechanical properties.

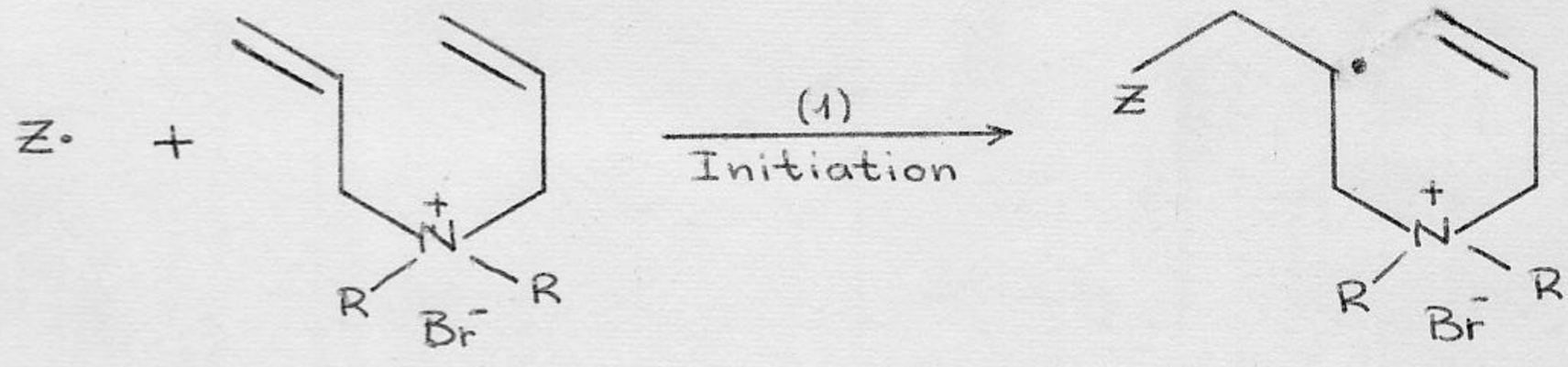
The synthesis of polyquinoline has not escaped the wide interest of Marvel and coworkers in polyaromatics. A promising approach was initiated around 1960. It involved the preparation and cyclopolymerization of a non-conjugated diolefin[19] followed by a series of reactions leading to the formation of polyquinoline.

B. Cyclopolymerization

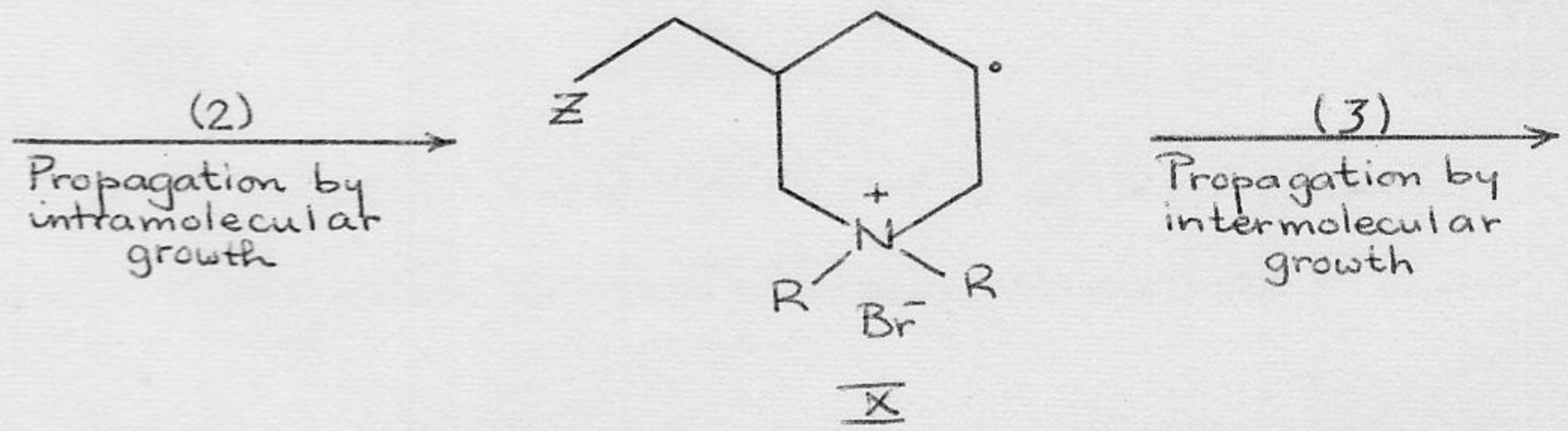
The use of cyclopolymerization to prepare linear polymers from non-conjugated diolefins has been well established. In 1951, Butler and Ingley[20], in studying the ion exchange properties of a

series of polymers, reported the formation of soluble and fusible polymers by free radical polymerization of diallyl and substituted diallyl quaternary ammonium salts. This was contrary to the generally accepted hypothesis advanced by Staudinger and Heuer in 1934, that polymerization of non-conjugated dienes result in crosslinked polymers. However, in this publication no attempt was made to explain the scheme by which such soluble polymers were produced.

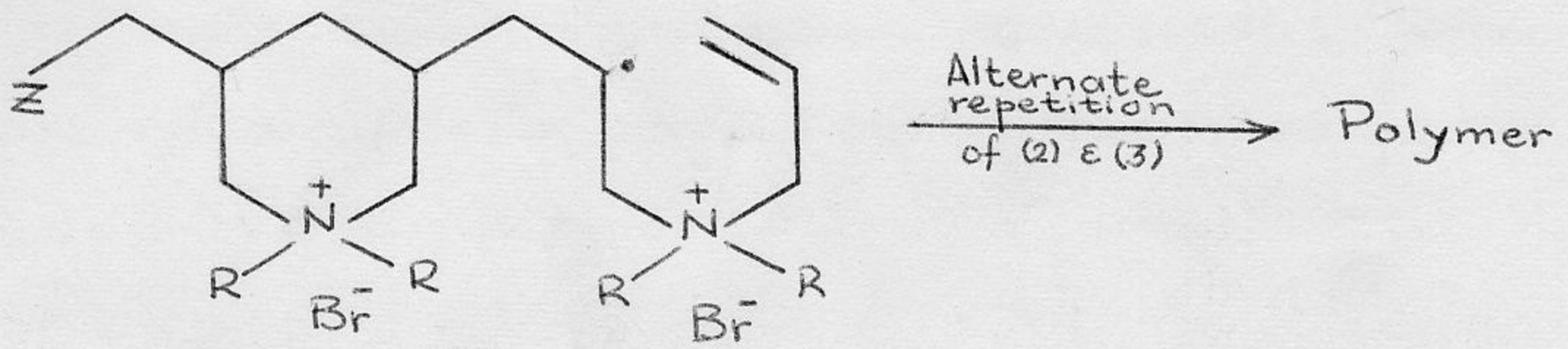
In 1953 Simpson et al[21] were the first to propose the concept of cyclopolymerization in trying to explain the formation of soluble and fusible polydiallylphthalate. Four years later Butler and Angelo[22] proposed a polymerization mechanism for the anomalous properties obtained by the polymerization of diallyl quaternary ammonium salts. According to this mechanism, diene monomers capable of forming six-membered ring systems by an intramolecular attack of a free radical on the terminal methylene of the second double bond within the same molecule can result in linear unsaturated polymers:



VIII IX



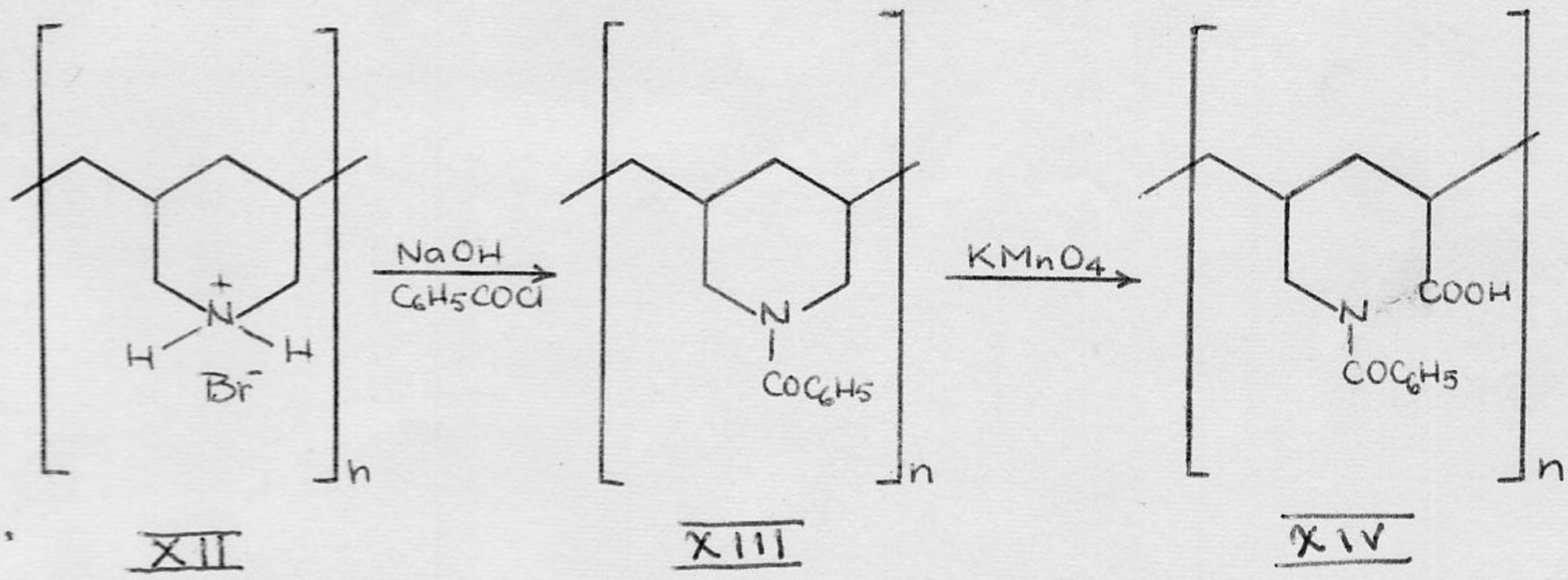
X



XI

This would involve a free radical attack on one of the double bonds followed by cyclization with the remaining favorably situated double bond within the same molecule. The resulting cyclic radical then attacks another molecule of monomer and repetition of the process results in the propagation of the chain.

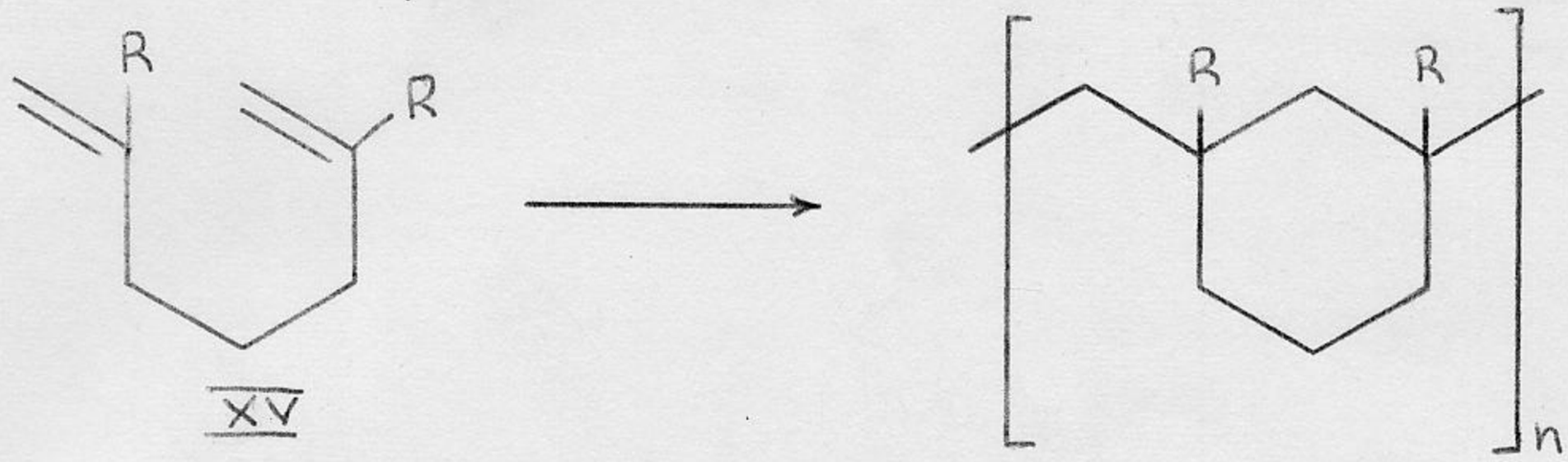
As further evidence of proving the proposed mechanism, representative polymers were degraded[23] to show conclusively the presence of the cyclic structure in the polymer chain. Polydiallylamine hydrobromide was degraded as follows:



XII XIII XIV

The structure of XIV was substantiated by ultimate analysis, potentiometric titration and infrared spectroscopic analysis.

Polymerization by such a mechanism has been extended to include a wide variety of non-conjugated dienes. Marvel and Vest[24] polymerized by free-radical initiation three 2,6-disubstituted 1,6-heptadienes, XVa, b, c, to soluble polymers.



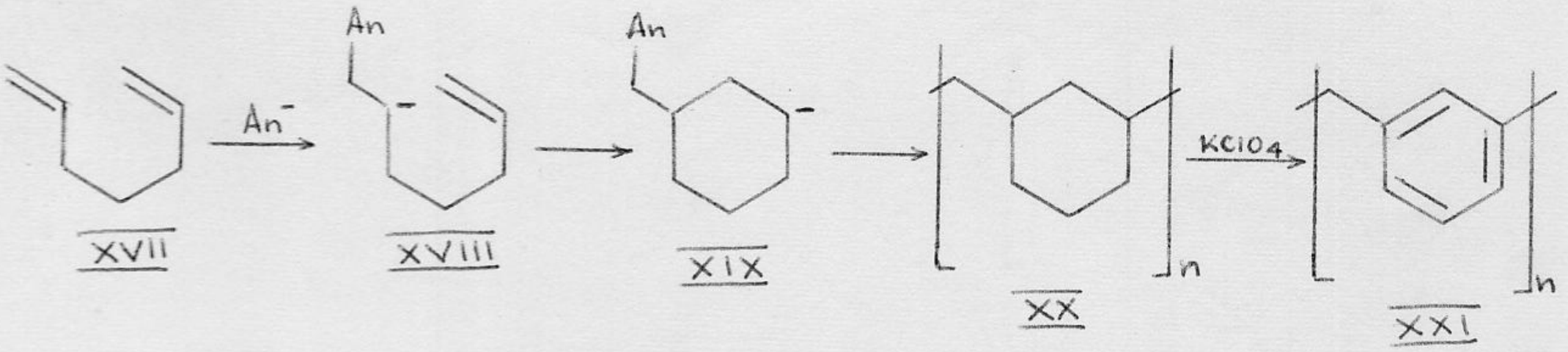
XV XVI

a. R = $CO_2C_2H_5$

b. R = CO_2CH_3

c. R = CO_2H

The polymers produced were soluble in such solvents as chloroform or benzene and showed no infrared absorption in the carbon-carbon double bond region. Marvel and Stille[25] described essentially saturated linear polymers from 1,6-heptadiene, XVII, by the use of triallyl aluminium-titanium tetrachloride catalyst.

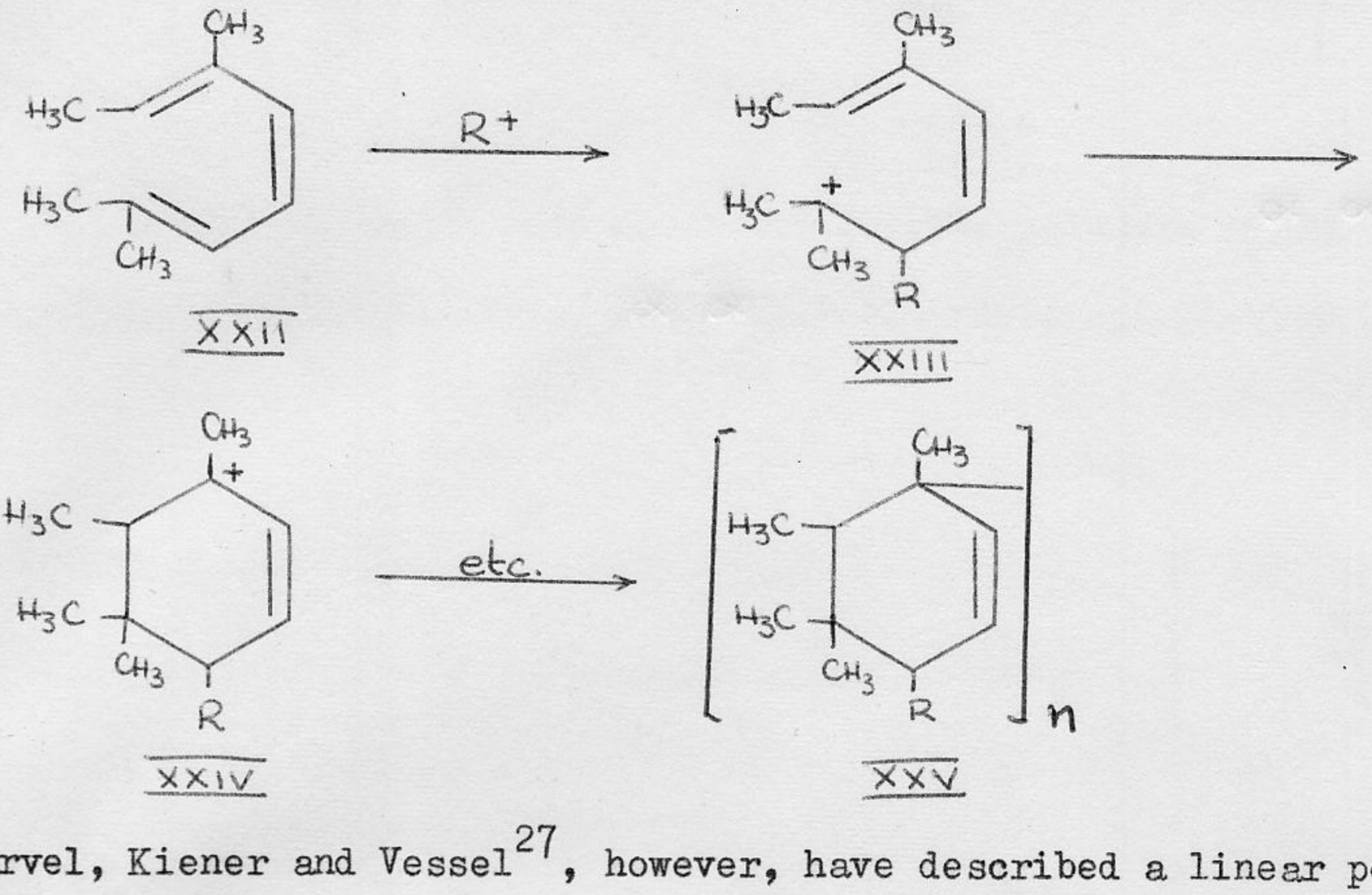


XVII XVIII XIX XX XXI

Here again, the presence of the six-membered ring in the polymer chain was proved conclusively by dehydrogenation with potassium perchlorate to yield aromatic structures which were demonstrated

by ultraviolet and infrared absorption spectra.

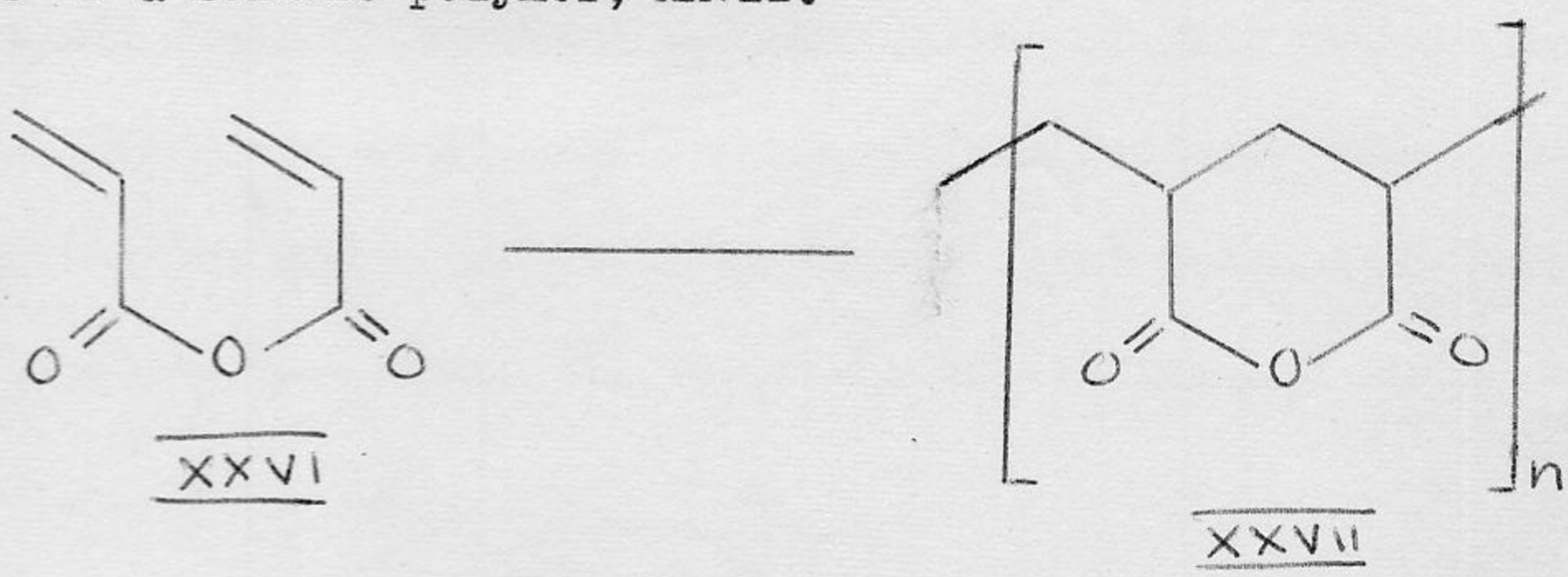
Jones[26] described a soluble polymer from alloocimene, XXII, and proposed the following mechanism for its cationic polymerization



XXII XXIII XXIV XXV

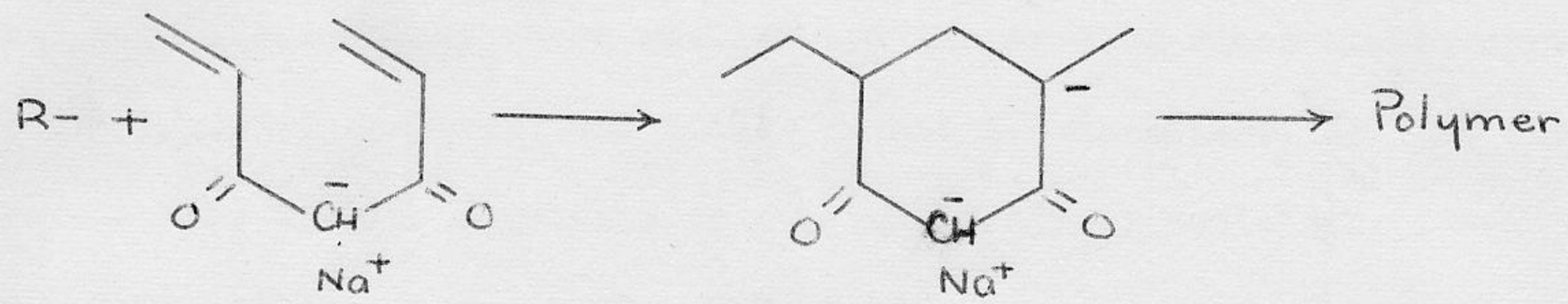
Marvel, Kiener and Vessel[27], however, have described a linear polymer from this monomer by Ziegler catalysis.

Crawshaw and Butler[28] and Jones[29], independently described polymerization of acrylic anhydride, XXVI, under a variety of conditions to a soluble polymer, XXVII.



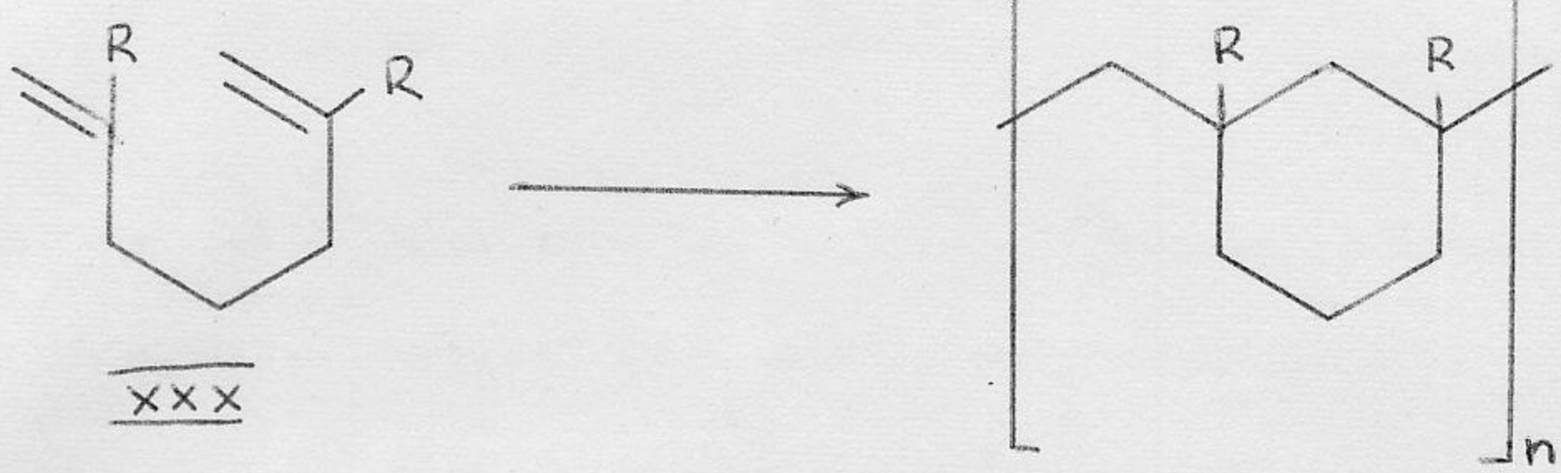
XXVI XXVII

Jones[30] isolated the sodium salt of poly-(diacrylylmethane), XXIX, which he attributed to anionic polymerization of the monomeric compound as it is formed.



XXVIII XXIX

Marvel and Vest[31] have described soluble polymers from α-α'-dimethylenepimelamide, XXXa, and α,α'-dimethylenepimelonitrile, XXXb,

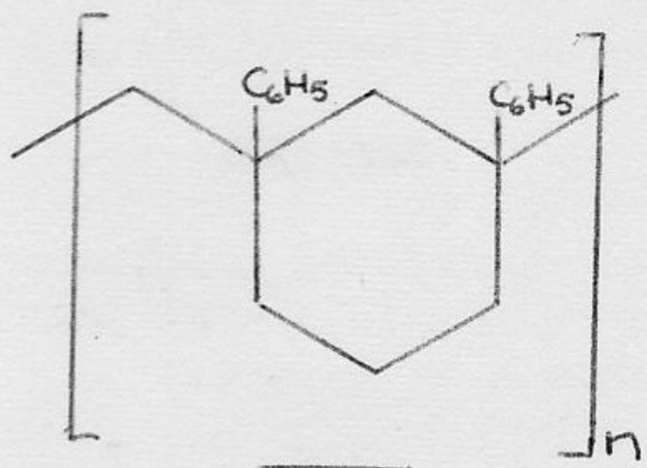


XXX XXXI

a. R = $CONH_2$

b. R = CN

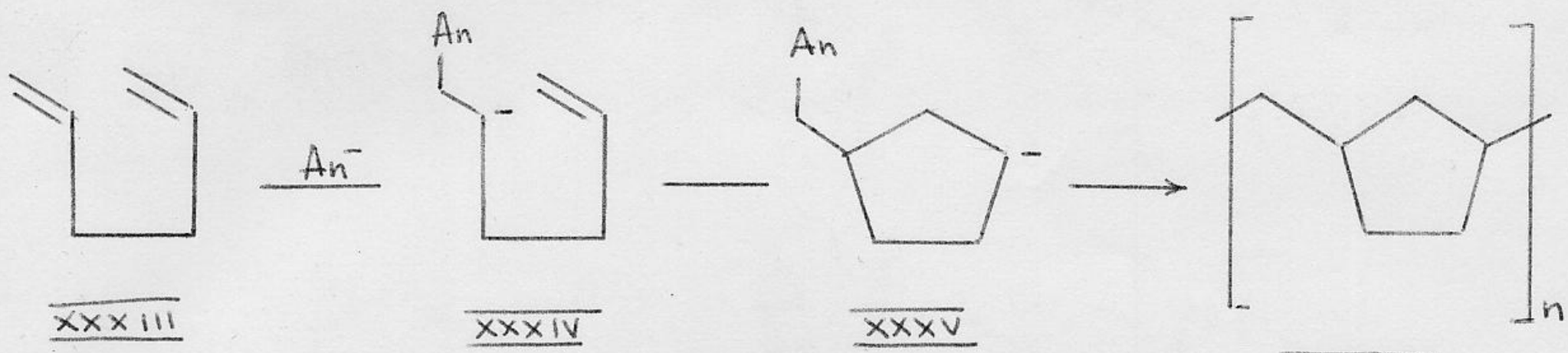
Marvel and Gall[32] reported the preparation of 2,6-diphenyl-1,6-heptadiene and Field[33] described polymerization of this monomer to a polymer, XXXII, having cyclic structures by free radical, cationic and anionic initiation and reported it to be the first polymer of this type to be polymerized using all the three initiation methods.



XXXII

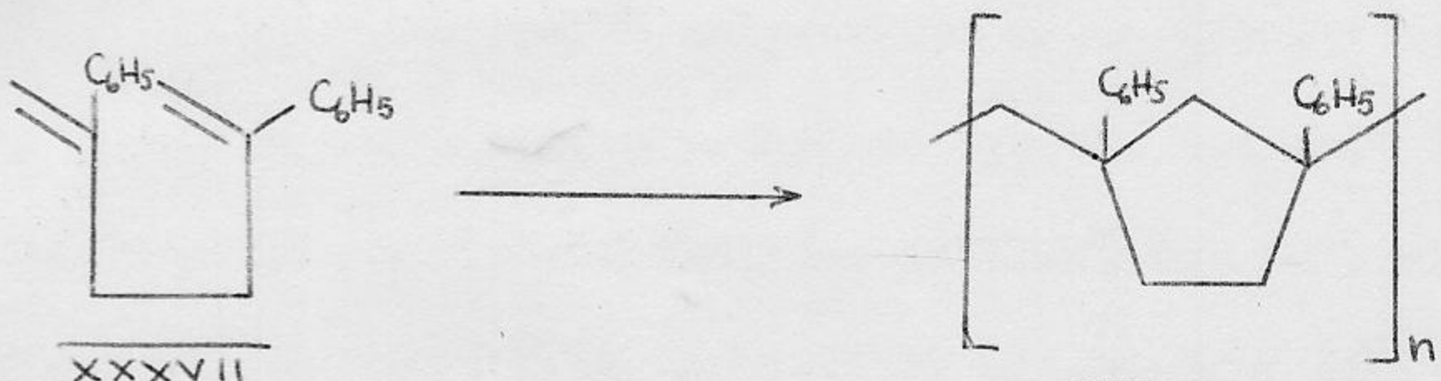
While cyclopolymerization reactions involving the formation of

six-membered ring structures have been extensively studied, there are well established cases where smaller and larger ring sizes are produced. It was reported by Marvel and Stille[25] that 1,5-hexadiene, XXXIII, was converted by Ziegler catalysis to a soluble polymer containing five-membered ring structure in 92 - 95% yield:



XXXIII XXXIV XXXV XXXVI

Marvel and Gall[32] also reported that 2,5-diphenyl-1,5-hexadiene, XXXVII, can be cyclopolymerized to a soluble polymer by Ziegler catalysts, cationic and free radical intiators.

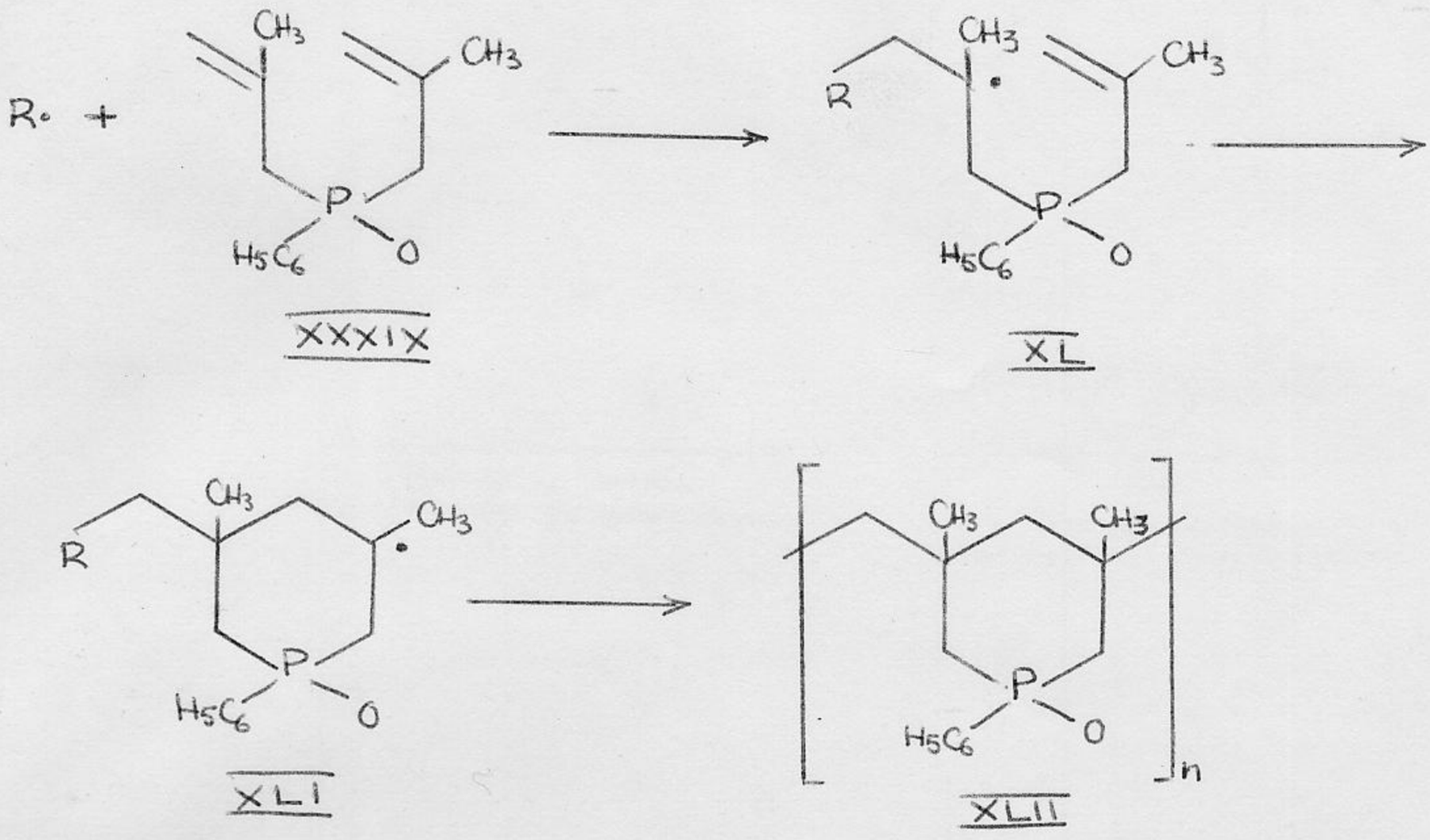


XXXVII XXXVIII

The formation of ring sizes greater than six was reported by Marvel and Garrison.[34] Olefins of the general formula $CH_2=CH-(CH_2)_n-CH=CH_2$, where n = 4, 5, 6, 7, 8, 9, 10, 11, 12, 14 and 18 were polymerized and in all cases polymers containing cyclic and open-chain recurring units were indicated.

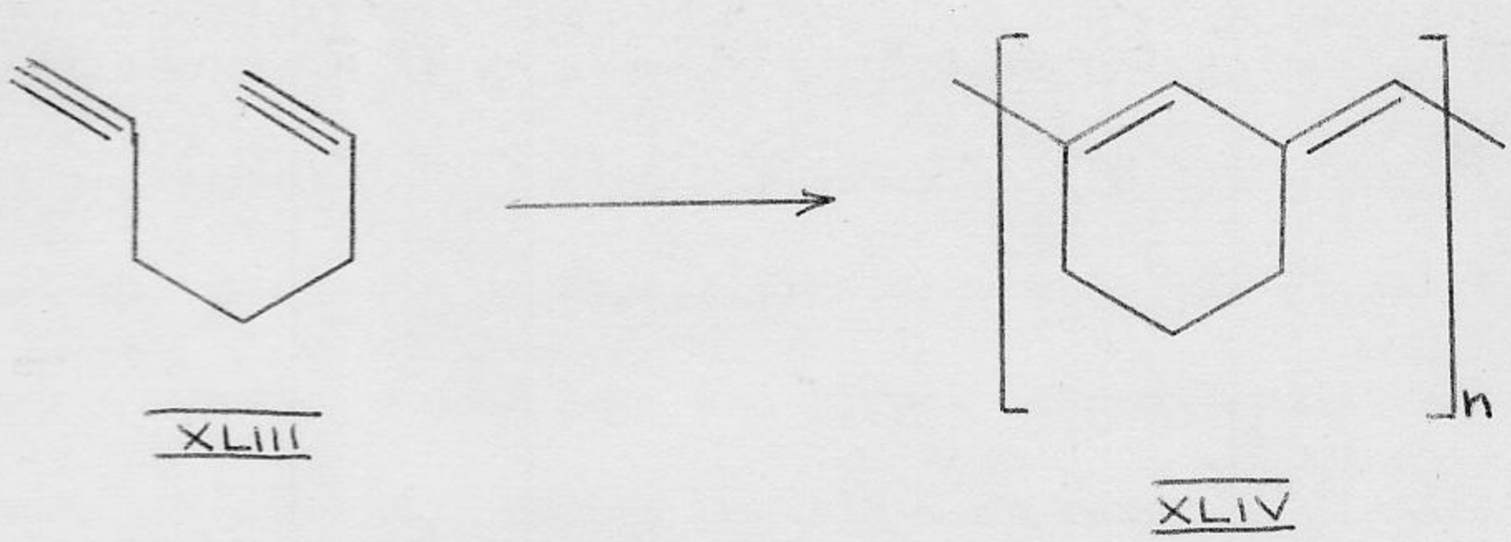
Polymerization reactions involving the formation of heterocyclic recurring units have been reported by a number of investigators.[29, 35-39]

Berlin and Butler[37] for instance polymerized dimethylallylphenylphosphine oxide, XXXIX, to a soluble polymer containing a phosphorus atom in the cyclic recurring unit.



XXXIX XL XLI XLII

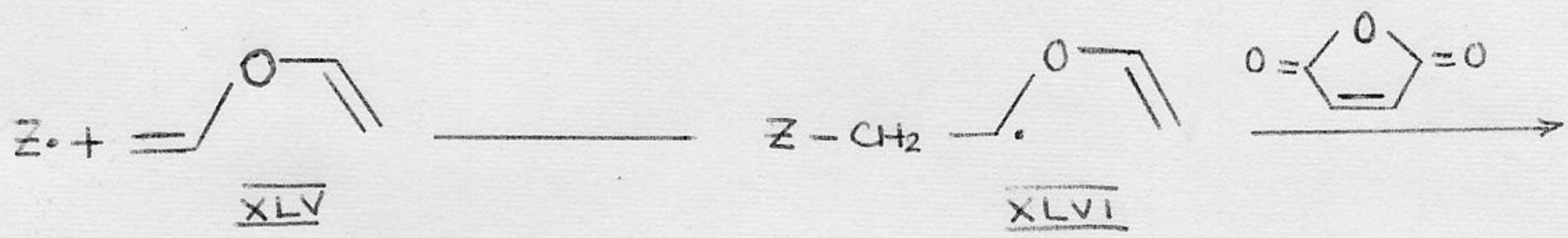
This type of polymerization was further extended to include diacetylenes. Stille and Frey[40] polymerized α,ω-diacetylenes to soluble polymers containing a methylene cyclohexene unit in the chain. The diacetylene, 1,6-heptadiyne, XXXXIII, was polymerized to produce a soluble polymer, XLIV, containing alternating double and single bonds along the backbone of the polymer chain.



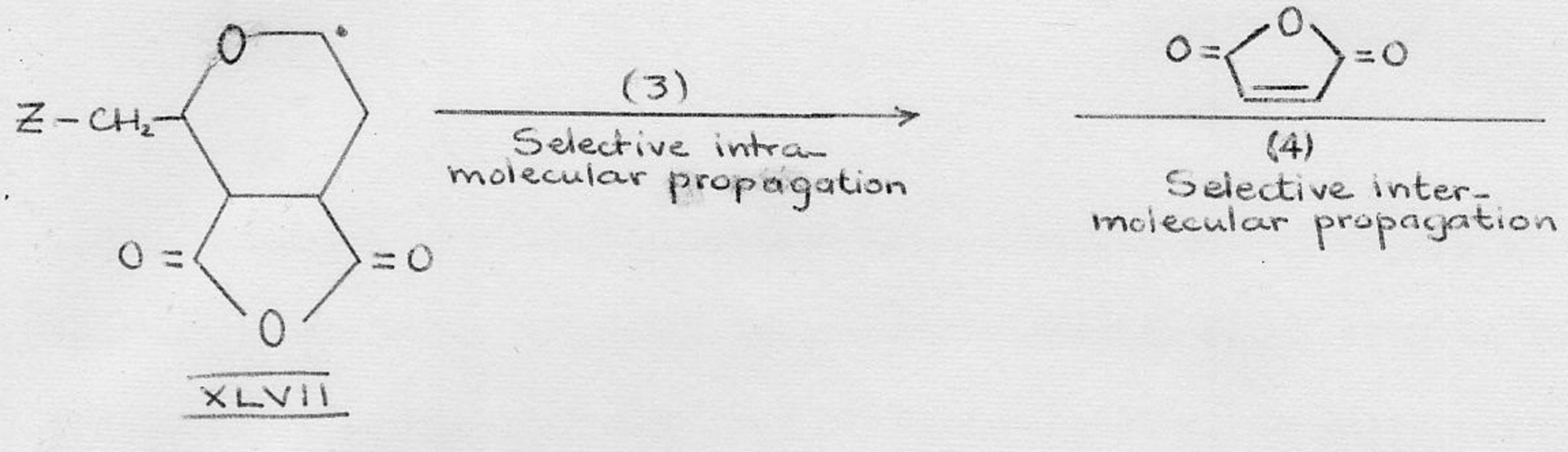
XLIII XLIV

Cyclopolymerization was also reported to be obtained from

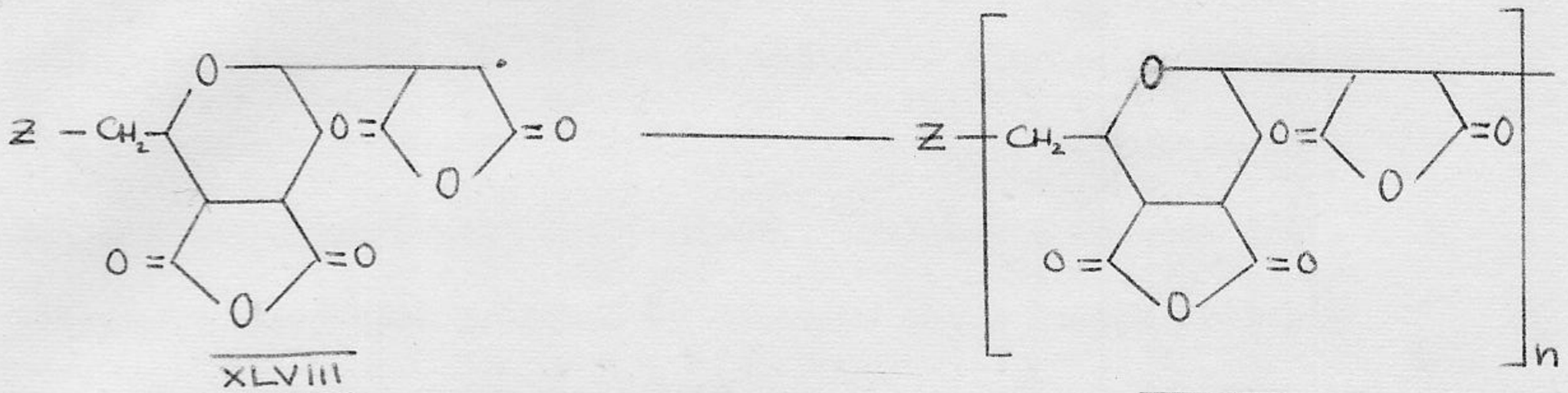
copolymerization reactions[41]; Divinyl ethers and maleic anhydride undergo free radical-catalyzed polymerization to produce soluble polymeric anhydrides containing the tetrahydropyran ring



XLV XLVI



XLVII

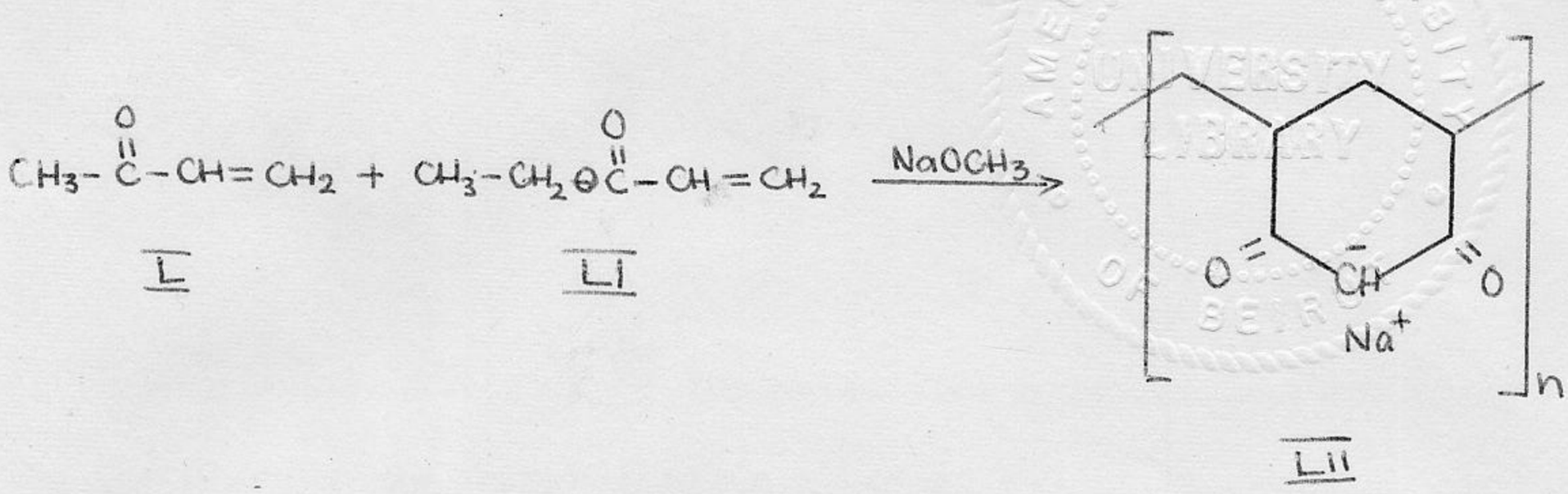


XLVIII XLIX

C. Previous Work Leading to this Study.

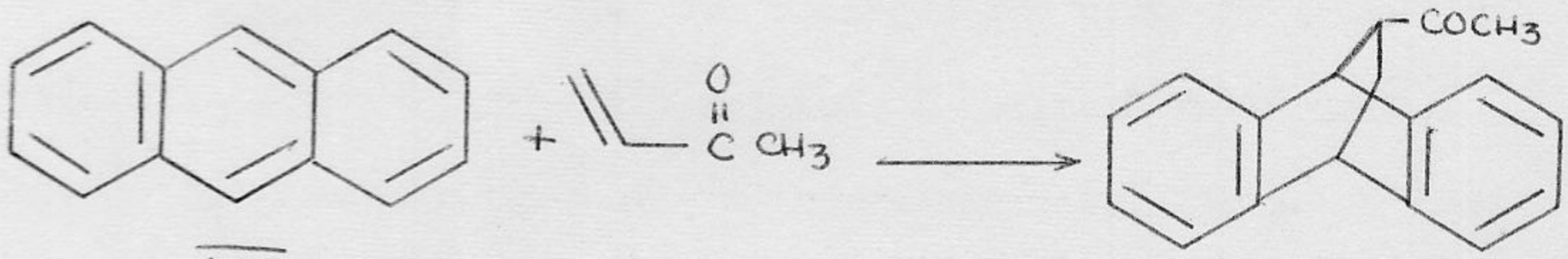
The research project under investigation was initiated by Marvel and coworkers in an attempt to prepare polyquinoline through the cyclopolymerization of diacrylylmethane. In 1958 Jones[30] attempted the synthesis of diacrylylmethane with the expectation that such a monomer should have the proper intramolecular spatial arrangement of its vinyl groups for six-membered-ring closure by a head-to-tail polymerization mechanism. He reported that the

acylation of methyl vinyl ketone with ethyl acrylate produced exclusively the homopolymer of diacrylylmethane. All attempts to isolate the monomer or its sodium salt failed.

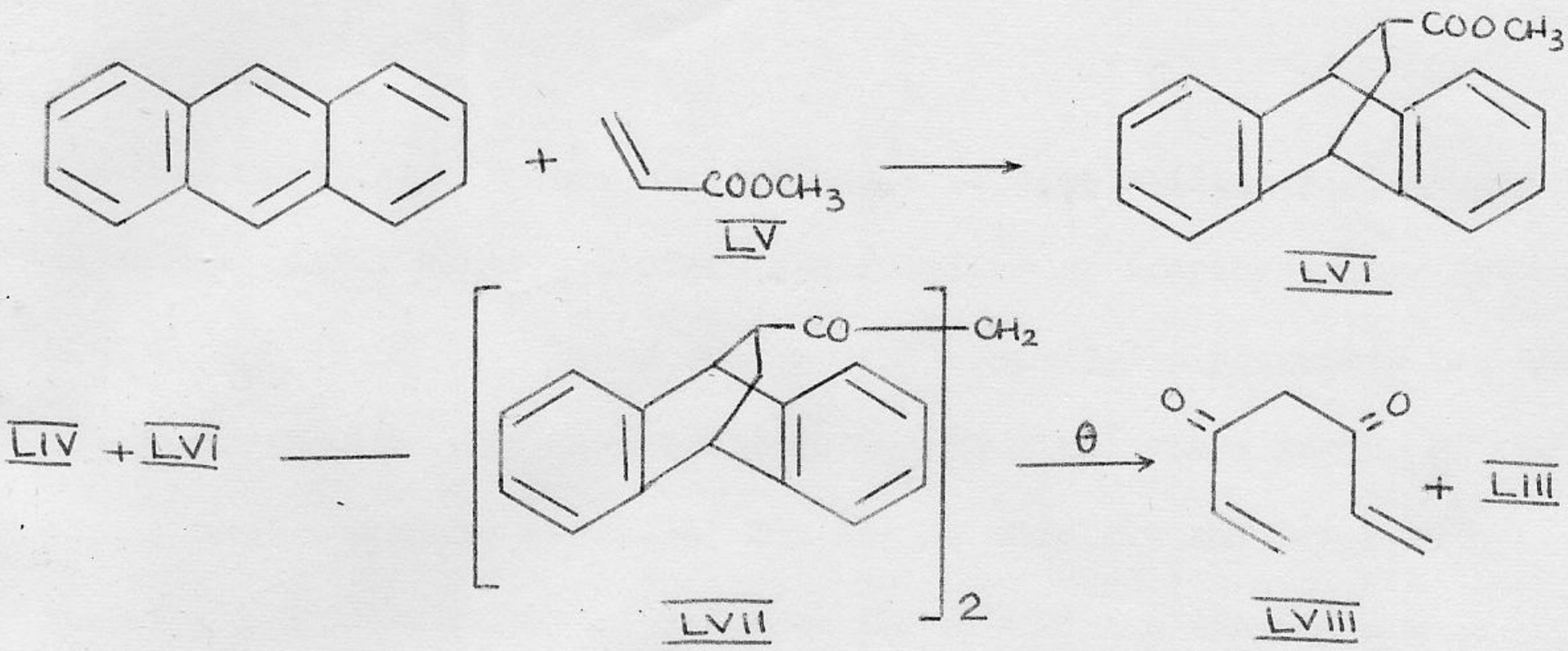


L LI LII

Jones assumed that diacrylylmethane homopolymerizes cyclically, as soon as it is formed, through an anionic mechanism which results in a soluble linear polymer composed of recurring diketone units whose structure is a resonance hybrid of methylene dihydroresorcinol. Otsu, Mulvaney and Marvel[42] in studying some of the reactions of the polymer contested Jones' conclusions. They believed that the polydiacrylylmethane prepared by Jones is not a homopolymer but probably a copolymer of the cyclic diketone with units of methyl vinyl ketone which is a component of the reaction mixture used in the preparation of the polymer. Hence efforts were directed toward the synthesis and subsequent polymerization of the pure monomer. Bloomfield[43,44], succeeded in synthesizing diacrylylmethane in good yields by a pyrolytic reverse Diels-Alder reaction.



LIII LIV



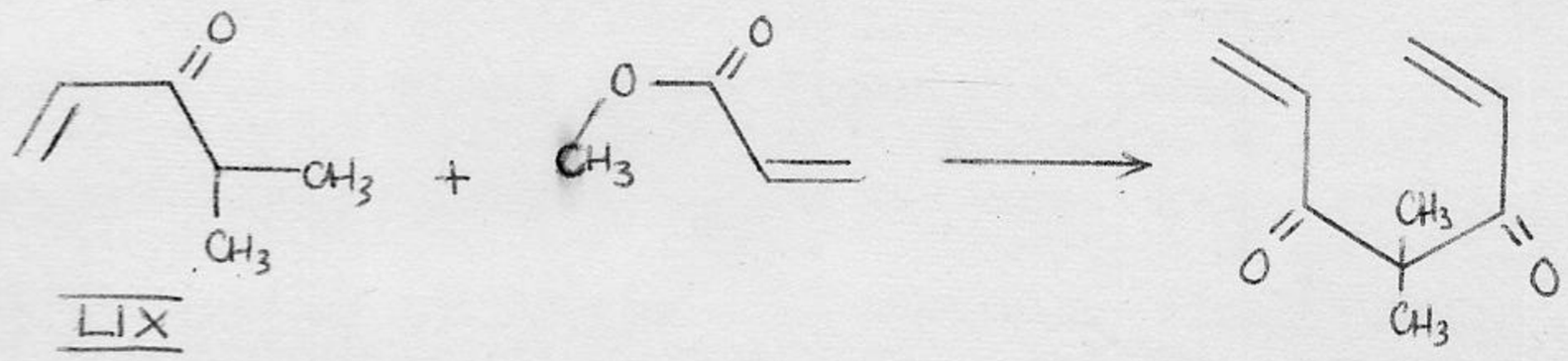
In a subsequent study[45] the method for synthesizing and purifying the monomer was improved and a study of its polymerization was undertaken. It has been found that free radical initiation of diacrylylmethane results in an insoluble product in very low yield. Anionic initiation with sodium methoxide gives a 90% yield of a yellow polymer which is soluble in water and a number of organic solvents. The polymer is a sodium salt of polydiacrylylmethane. When this salt is treated with acetic acid or methanol, a white insoluble intractable product is formed. It is believed that insolubility is due to crosslinking caused by side-reactions involving the active methylene group. This explanation is substantiated by nuclear magnetic resonance analysis of the monomer which shows that one ketone group is completely enolyzed, and by infrared analysis of the polymer which indicates the presence of an ether bond.

In 1962 work at A.U.B. was consequently directed toward the synthesis of dimethyldiacrylylmethane, a compound which cannot undergo enolization or other side reactions involving an active

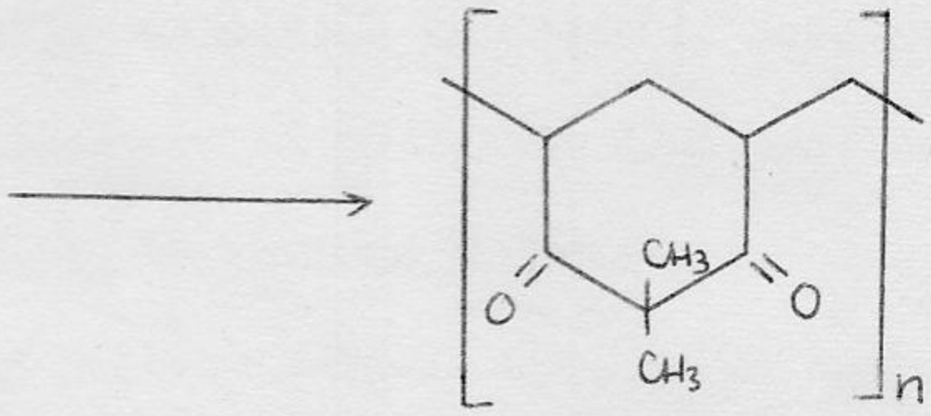
methylene group.

As a first approach, the synthesis of dimethyldiacrylylmethane was attempted by using a Claisen condensation of isopropylvinyl ketone with methyl acrylate. Bacon and Farmer[46] reported a procedure for the synthesis of vinylisopropyl carbinol in 20% yield via a series of complicated reactions involving the use of acrolein and Grignard reagent. After a number of attempts the method was dropped out as a means of getting the ketone in the yield and purity demanded by polymer reactions. Brown and Johnson[47] reported a procedure for preparing the ketone in an overall yield of 32%. Using a modification of this procedure, Saliba[48] succeeded in 1964 in preparing vinyl-isopropyl ketone in about 70% yield and high degree of purity.

Acylation of vinyl isopropyl ketone with methyl acrylate under inert atmosphere and in the presence of sodium methoxide at temperatures of -50° to -100°C gave polydimethyldiacrylylmethane in 21% yield.



LIX + CH_3 → LX



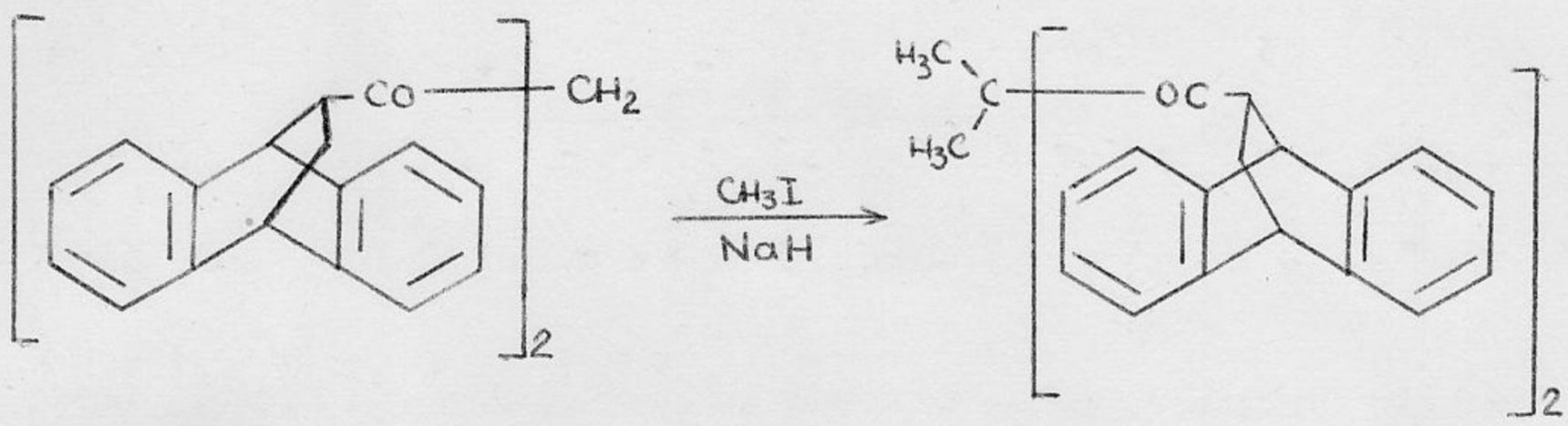
LXI

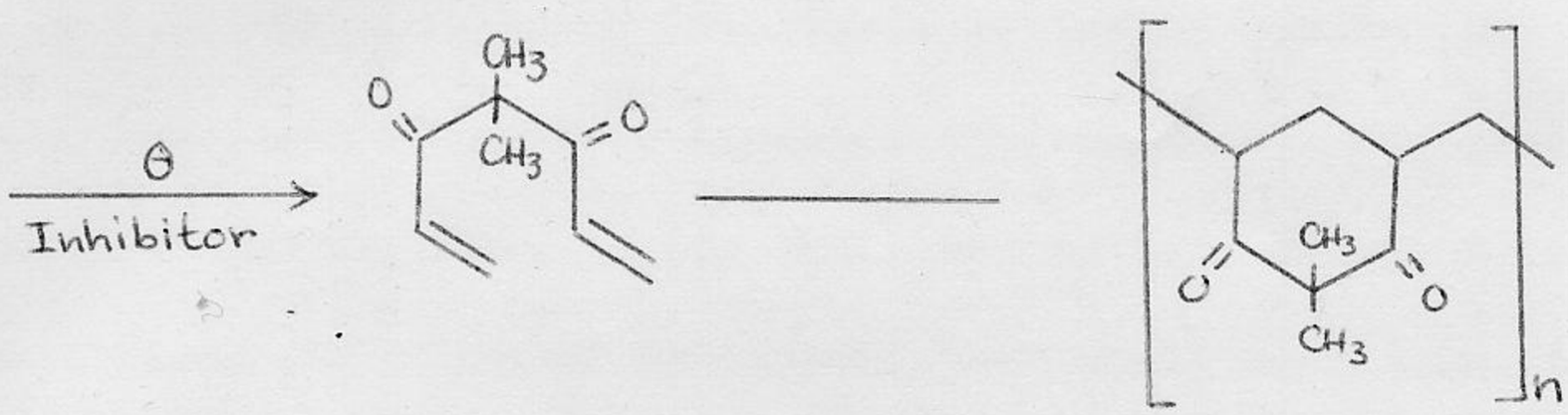
Evidently, in the presence of an anionic initiator such as sodium

methoxide, the beta-diketone monomer, LX, cyclopolymerizes as soon as it is formed to, LXI, Infra red analysis of the white powdery product shows excellent agreement with the postulated structure. Instrinsic viscosity in chloroform indicates a polymer of relatively high molecular weight.

Attempts to isolate the monomer, LX, and improve the yield are still in view and have been encouraged by a recent report[49] that acylation reactions involving the preparation of beta-diketones produced yields up to 83% when carried out in dry dimethyl sulfoxide and sodium hydride compared to yields up to 36% in toluene and sodium methoxide.

While work was in progress DeWinter and Marvel[50] reported the synthesis of dimethyldiacrylylmethane by exhaustive methylation of 1,3bis(9,10-dihydro-9,10-ethano anthracenyl-11)-1,3-propandione using methyl iodide and sodium hydride in 95% yield. Compound LXII, was pyrolyzed in the presence of tert-butyl hydroquinone to give the monomer LX, which is a pale yellow liquid with intense acrylic odor and lachrymatory properties, and was demonstrated by infra red and NMR spectroscopy and by elemental analysis. Dimethyldiacrylylmethane was found to polymerize slowly at room temperature to produce an insoluble intractable product. However, free radical polymerization at 65°C using 2,2'-azobis-isobutyronitrile as an initiator, in various organic solvents, yields up to 95% of a white powdery product soluble in a large number of organic solvents.





The cyclic structure LXI, was assigned to the polymer on the basis of absence of vinyl and enol absorption in the infrared spectrum and on the solubility of the polymer in many organic solvents. It is believed that some noncyclic polymer may be present since in reactions intended to increase the yield or the molecular weight of the polymer some insoluble portion was obtained due to crosslinking. Work on the conversion of the polymer to its dioxime, to be followed by other reactions leading to a ladder-type polymer were not very successful.

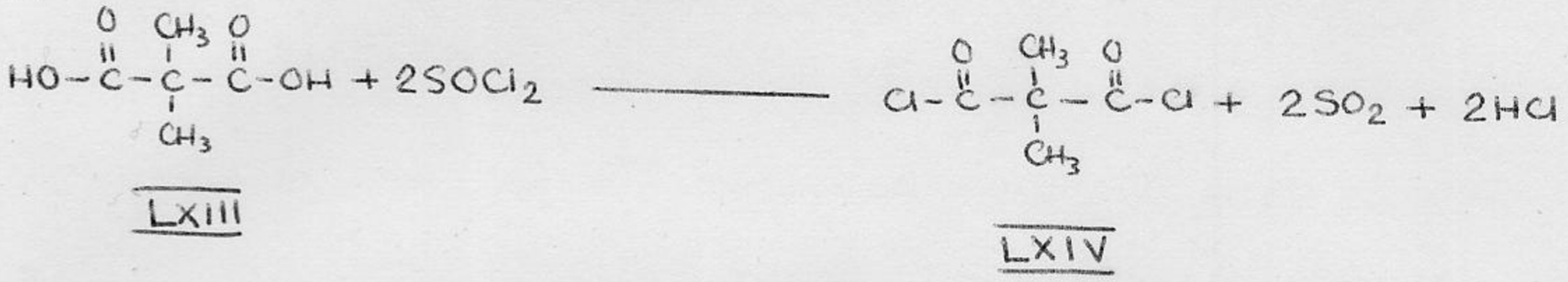
Definition of the Problem

The present investigation is another attempt aiming at the synthesis and cyclopolymerization of dimethyldiacrylylmethane. The route proposed in this study involves a series of simple and standard reactions which were expected to lead to the synthesis and isolation of the monomer, to its characterization, and to selecting the conditions and types of initiators that would result in its cyclopolymerization.

II. INTERPRETATION AND DISCUSSION OF RESULTS

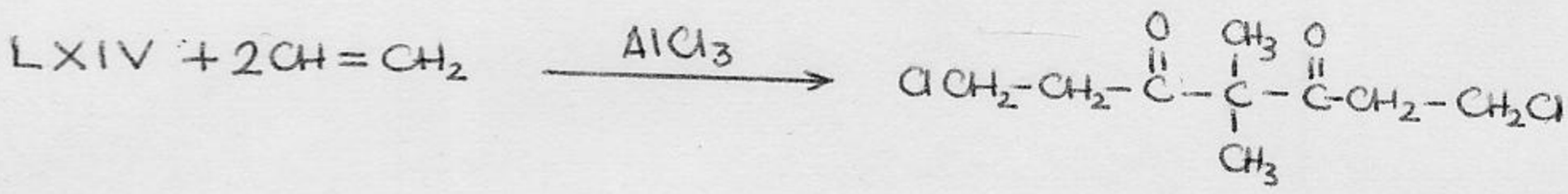
A conceivable route for the preparation of dimethyldiacrylylmethane from dimethyl malonic acid is through a Friedel-Crafts type reaction of the acyl chloride with ethylene in the presence of aluminium chloride followed by dehydrohalogenation of the product with potassium carbonate. The scheme involves the following sequence of reactions.

(A)



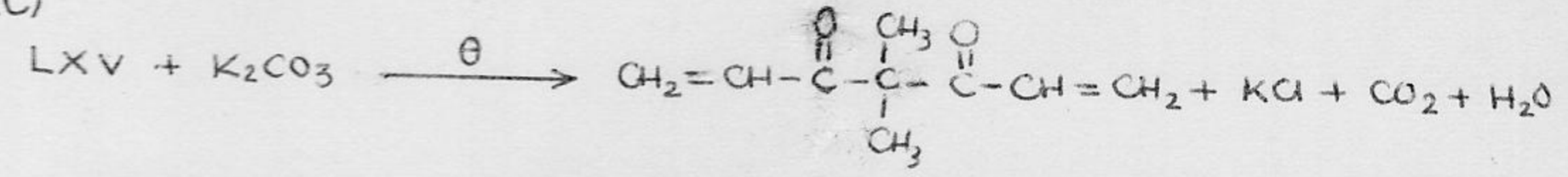
LXIII LXIV

(B)



LXV

(C)



LX

Attempts to prepare dimethyldiacrylylmethane by this route did not succeed. The product from reaction (B), LXV, when treated with

potassium carbonate yielded oily liquid fractions with a non-pleasant smell and showed no carbonyl absorption in the infrared region of the spectrum. Consequently reactions (A), (B) and (C) were investigated separately and the product from each studied and characterized.

Based on a procedure by C. Raha[51], it was found that reaction (A) proceeded as expected and produced dimethylmalonyl dichloride, LXIV, in yields up to 90%. The increase in the yield from that reported by Raha (70%) was due to doubling the amount of thionyl chloride used by the latter. The structure of the product was verified by boiling point determination (164°C/760 mm) which agreed with the value cited in the literature, and by infrared analysis which showed no absorption band typical of the carboxyl group (1710 cm^{-1}) and a shift of the absorption band of the carboxyl group from 1710 to 1780 cm^{-1} typical of a carbonyl group of an acyl chloride. The difference between the infrared spectra of dimethylmalonic acid and dimethylmalonyl dichloride is clearly demonstrated in figures III and IV.

It is well established that Friedel-Crafts acylation reactions in the presence of excess aluminium chloride proceed to give chloro-ketones.[52] In this laboratory, as mentioned earlier, Saliby[48] was able to prepare vinylisopropyl ketone by the reaction of isobutyryl chloride with ethylene followed by dehydrohalogenation with potassium carbonate. Hence, reaction (B) seemed to be quite feasible. However, the product, which was expected to be a high boiling liquid, was found to be a solid that melted at 59 - 60°C and failed, upon

dehydrohalogenation with potassium carbonate, to produce the expected monomer. Dehydrohalogenation from a heterogenious system and at high temperature was thought to be the cause of this failure. So dehydrohalogenation from a homogeneous solution was attempted using methanolic potassium hydroxide at different concentrations and different temperatures. The mixture was then acidified with hydrochloric acid to neutralize the base and avoid the possible polymerization of the monomer. It was found that when the mixture was extracted in ether, and the latter stripped off, the original product melting at 59 - 60°C was obtained.

In trying to explain these unexpected results, the addition of ethylene to one acyl chloride instead of two was thought to be a possibility. If this assumption were true, the product of reaction (B) should after hydrolysis, be 2,2-dimethyl-3-keto-5-chloropentanoic acid, LXVII, instead of 1,7-dichloro-4,4-dimethylheptane-3,5-dione, LXV.

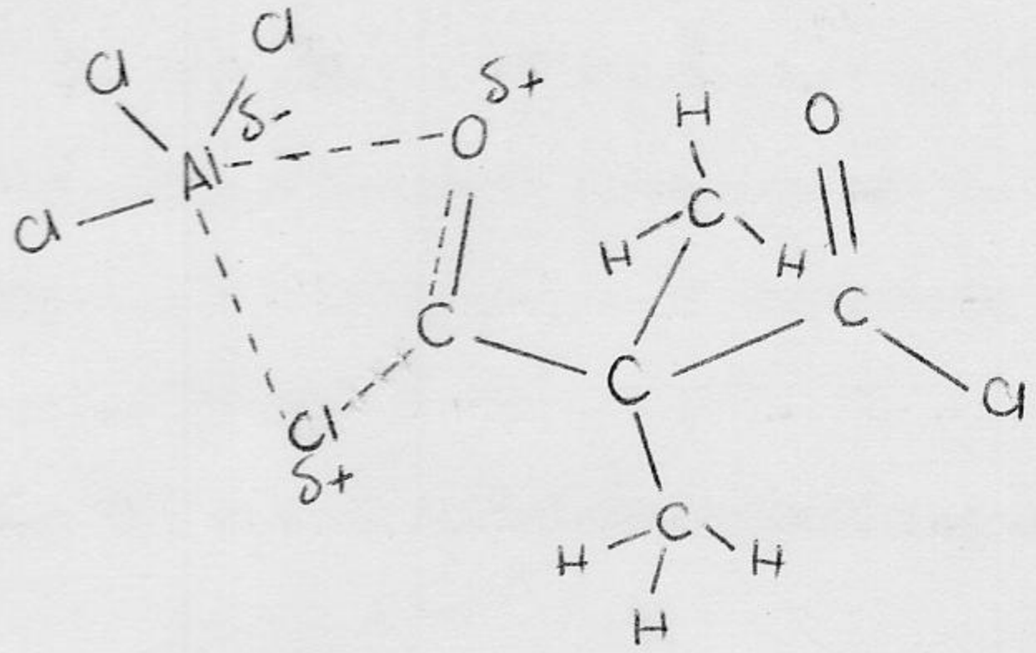
The formation of this chloroketo acid as the main product of reaction (B), in about 70% yield, was ascertained by the presence of chloride in the product, its solubility in aqueous sodium hydroxide, its infrared analysis and the determination of its neutralization equivalent which gave a molecular weight not differing by more than 3% from that of the stipulated acid, LXVII.

This acid which was found to melt at 59 - 60°C as mentioned earlier, was difficult to recrystallize. It was hence purified by dissolving in benzene, filtering the solution, allowing the solvent

to evaporate and drying in a desiccator. It was also found that LXVII could be purified by distillation at 86 - 88°C /0.3 - 0.4 mm, but this was avoided since a good part of the yield was lost in the process.

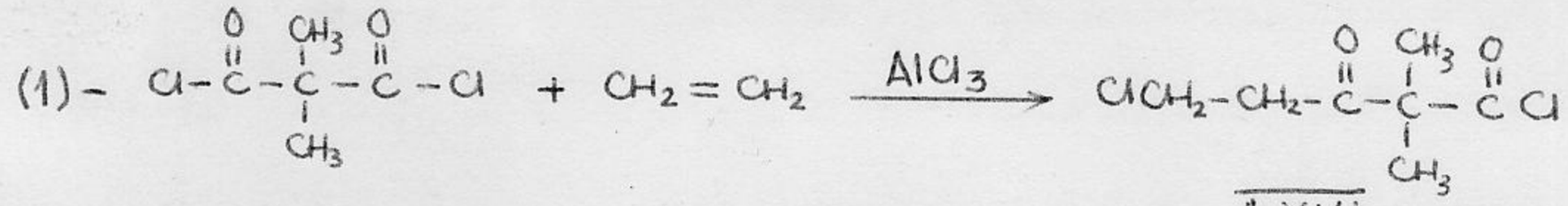
It is worth mentioning that besides the product LXVII in reaction (B), tarry materials were obtained, which after isolation indicated no relation to the main reaction investigated as evidenced by their lack of carbonyl absorption in the infrared region of the spectrum. These side reactions may be due to impurities in the reactants including the ethylene used which is of technical grade.

We believe that the formation of the chloroketo acid, LXVII, rather than the dichlorodiketone, LXV, is due to steric and charge effects. Dimethylmalonyldichloride, LXIV, is symmetrical with respect to both acyl chlorides and the attack of ethylene was expected to be feasible at both groups. As shown below, the formation of a bulky complex between aluminium chloride and the acyl chloride at one site, which is a prerequisite for the addition of ethylene, may sterically prevent the formation of another complex at the other site. Also the formation of a partial positive charge at one oxygen probably prevents the formation of a similar charge at the second one.

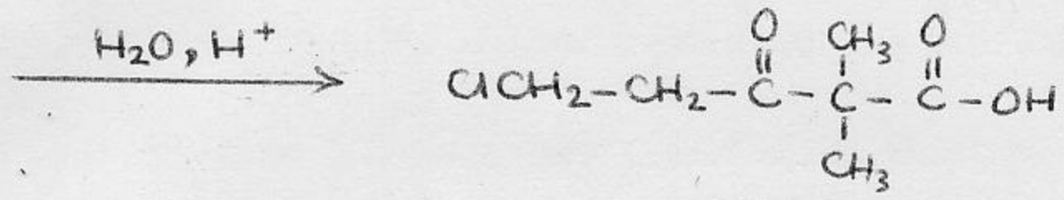


Based on the above results, reaction (B) leading to the preparation of LXV, as had been conceived, was modified to the following series of reactions:

(B)

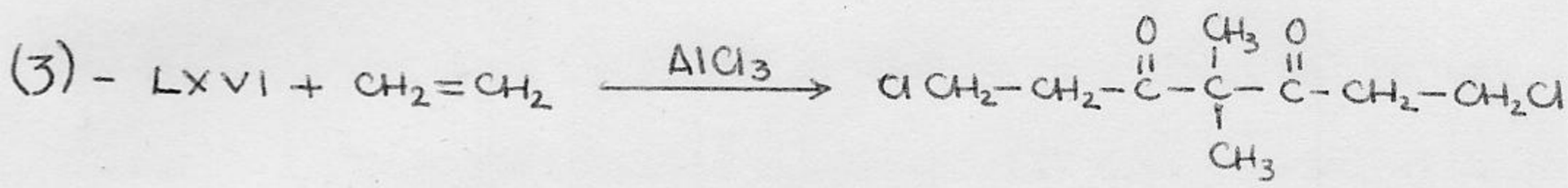
(1)- 

LXVI



LXVII

(2)- LXVII + $SOCl_2$ ⟶ LXVI + SO_2 + HCl

(3)- 

LXV

Reaction (B) as modified was feasible and the addition of ethylene to the second acyl chloride, LXVI, was possible, as evidenced by the preparation of the monomer and its subsequent polymerization. The successful formation of the dichlorodiketone, LXV, substantiates the explanation of the steric and charge effects mentioned earlier.

Reaction (2) yielded a fluffy crystalline product, LXVI, that

sublimed in the reflux condenser. It was found to be very sensitive to moisture as demonstrated by its infrared analysis which showed two carbonyl absorption bands typical of a carboxyl and of an acyl chloride. In order to avoid hydrolysis of the new acyl chloride, it was found necessary to prepare LXVI in the same reaction flask where reaction (3) was to be conducted. This was done by replacing the Claisen head in figure I with a reflux condenser capped with a calcium chloride drying tube. When reaction (2) was over and the flask cooled, the condenser was replaced by the Claisen head, as shown in figure I, and dry ethylene was passed through, followed by the addition of n- hexane and aluminium chloride.

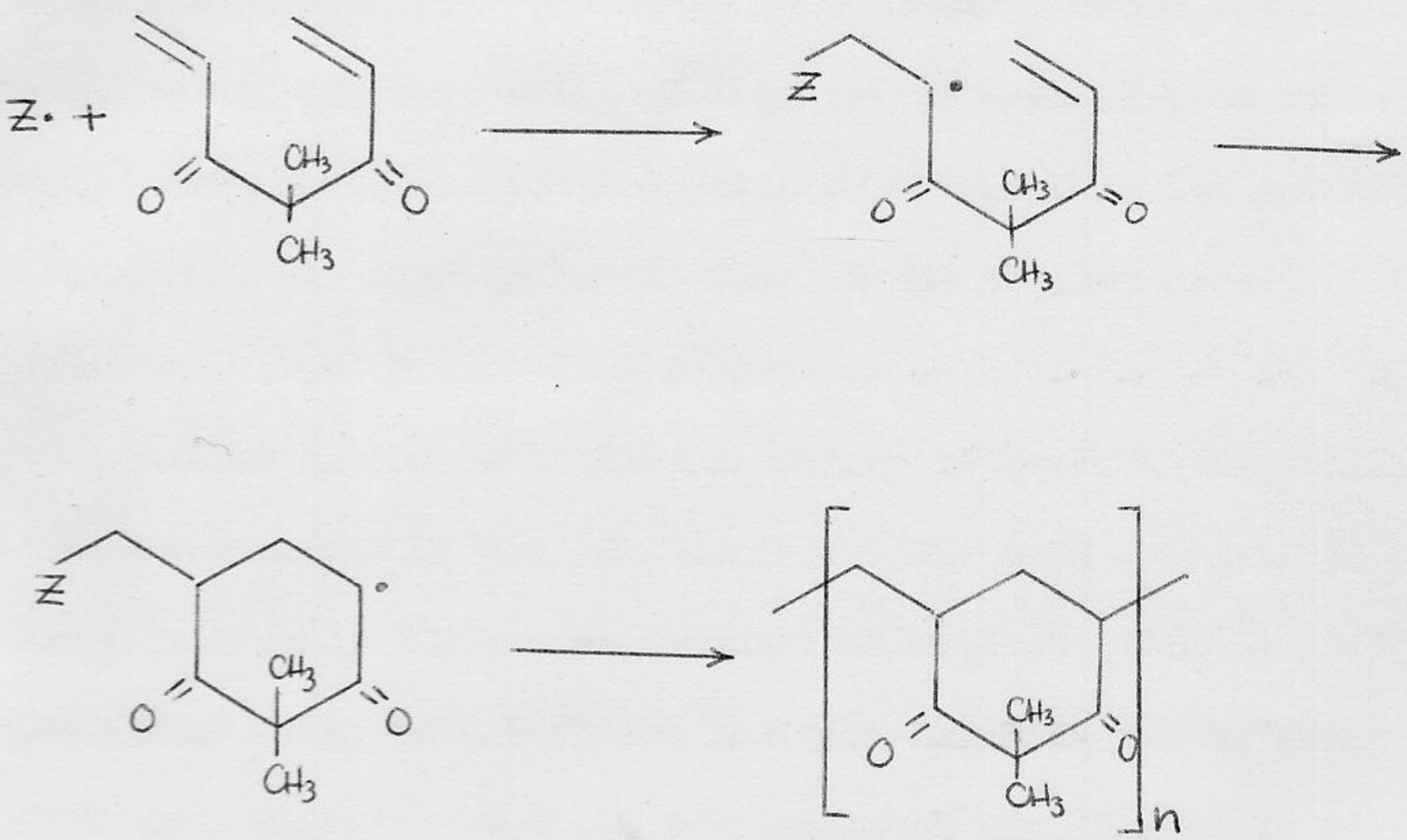
The dichlorodiketone, LXV, was separated from the reaction mixture as a pale yellow liquid that distilled at 94 - 96°C./2 mm. The presence of chloride was ascertained by sodium fusion test, and by the compound turning brownish violet upon standing in the deep-freeze. A freshly distilled sample of LXV was treated with potassium carbonate, in the presence of hydroquinone, and the mixture distilled under vacuum. The fraction distilling at 50 - 52°C./0.3 - 0.4 mm., is a pale yellow liquid with a lachrimatory garlic-like odor and its structure was characterized by infrared analysis which showed strong absorption bands typical of a conjugated carbonyl (1690 cm^{-1}) and a carbon-carbon double bond (1610 cm^{-1}). This liquid, dimethyl-diacrylylmethane, LX was found to polymerize slowly at room temperature.

The monomer, LX, was also obtained by dehydrohalogenation of

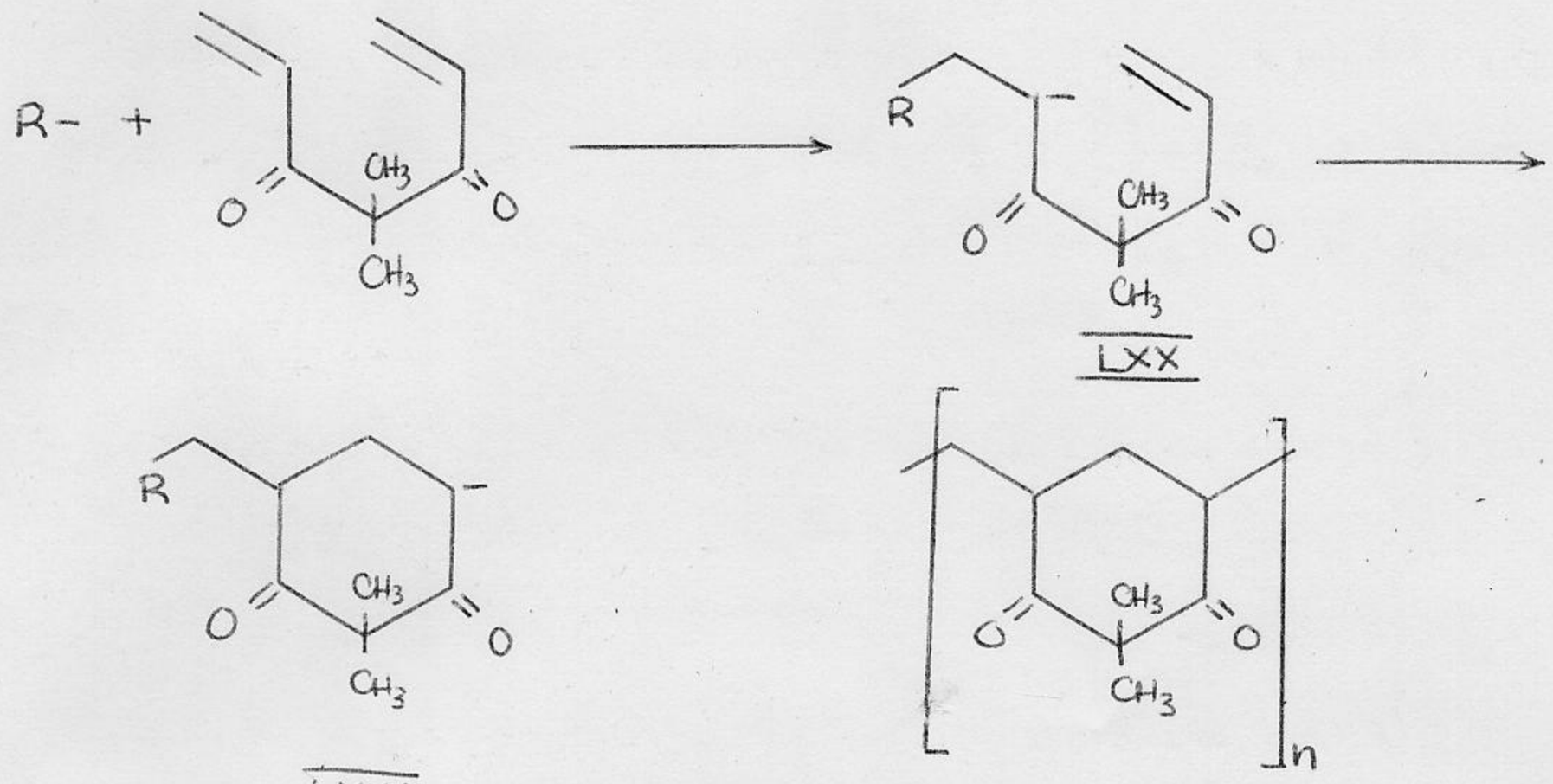
the dichlorodiketone, LXV, at room temperature using aqueous sodium hydroxide. However, this procedure was avoided due to the possibility of uncontrolled polymerization of the monomer in the presence of a strong base.

Polymerization of the purified monomer was undertaken using free radical and anionic initiation. The product formed was a white powdery polymer, soluble in most organic solvents and showed no absorption in the carbon-carbon double bond region of the infrared spectrum. Consequently a cyclic structure was assigned to the polymer, which resulted from an intramolecular-intermolecular mechanism as shown:

I- Free Radical Polymerization :

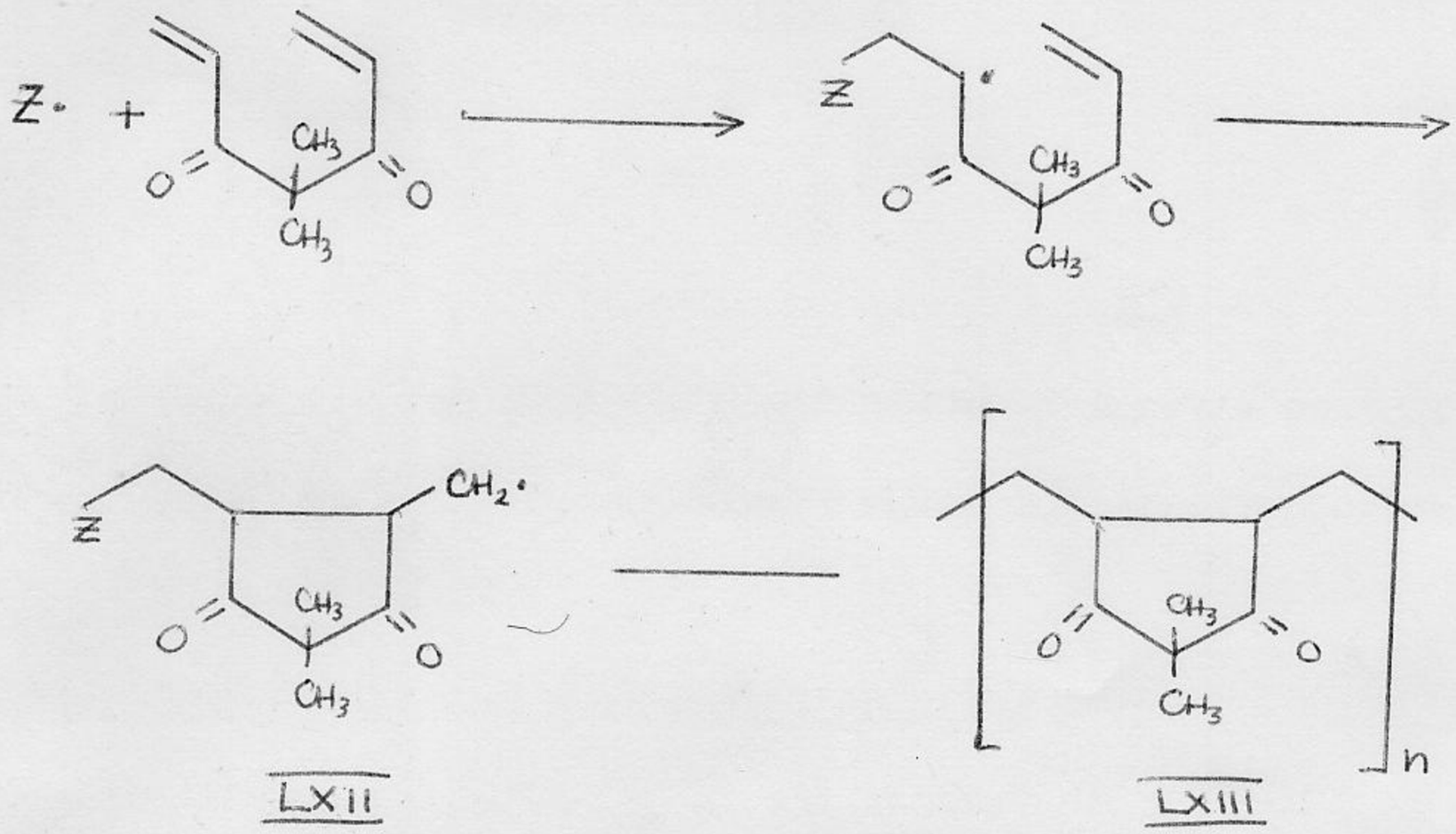


II- Anionic Polymerization :



LXXI

Polymerization of LX by free radical initiation was based on a procedure by Marvel and DeWinter[50] for the preparation of the same polymer. Marvel and DeWinter reported that the polymer formed showed two peaks in the carbonyl region of the infrared spectrum, one at 1750 cm^{-1} the other at 1720 cm^{-1}. From the structure of the polymer, which is symmetrical with respect to both carbonyls, only one carbonyl absorption should show in the infrared spectrum. This was seen to be the case in the polymer produced in this laboratory, which showed an absorption at 1710 cm^{-1}. The results obtained here were further confirmed by the polymer obtained by anionic initiation of the same monomer. The best explanation for the formation of the second carbonyl absorption (1750 cm^{-1}) in the polymer reported by Marvel and DeWinter could be due to the formation of a slightly strained five-membered ring structure in addition to the expected six-membered cyclic polymer, as shown:



LXII

LXIII

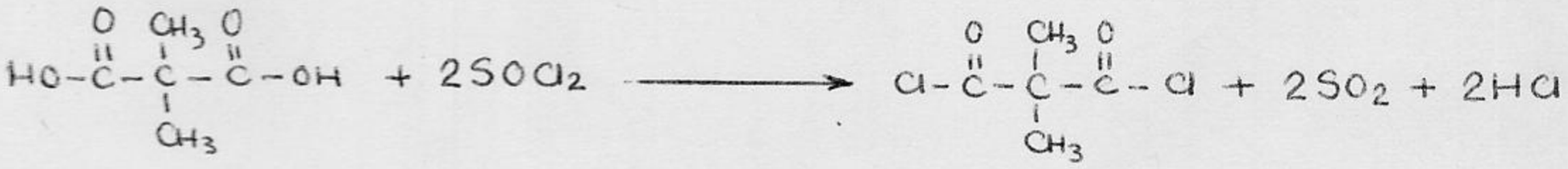
Polymerization of this monomer, LX, by anionic initiation was tried for the first time and the polymer obtained was very similar to that produced by free radical initiation.

III. EXPERIMENTAL

Unless otherwise specified, all infrared spectra were determined neat on an IR recording Perkin-Elmer, Model 137 spectrophotometer.

I.- Preparation of Dimethylmalonyl dichloride

Dimethylmalonic acid (33 g) and thionyl chloride (120 ml) were placed in a 250 ml round bottomed flask. The flask was fitted with a ground glass reflux condenser capped with a calcium chloride drying tube. The reaction mixture was allowed to stand in a bath maintained at 45 - 50°C for three days with occasional shaking. The temperature of the bath was then raised to 60°C and maintained at this temperature for six hours, afterwhich the mixture, which had turned reddish brown, was cooled to room temperature. Removal of thionyl chloride under reduced pressure (water suction) followed by distillation gave a pale yellow liquid boiling at 55°C./12 mm.



The infrared spectrum: 2940(s), 1780(s), 1460(m), 1385(w), 1370(w), 1200(w), 1160(w), 1130(m), 980(s), 915(s), 875(m), 845(s), 725(s) cm^{-1}.

II.- Preparation of 2,2-Dimethyl-3-keto-5-chloropentanoic acid

The apparatus used is shown in figure I. Ethylene was passed through concentrated sulfuric acid (A), then through a calcium chloride drying tube (B), and finally through the reaction mixture (D), and the excess was let out through liquid paraffin. The ethylene flow was discontinued when no further absorption was observed. This was clearly indicated by the liquid paraffin not sucking back in the delivery tube when the ethylene flow was shut off.

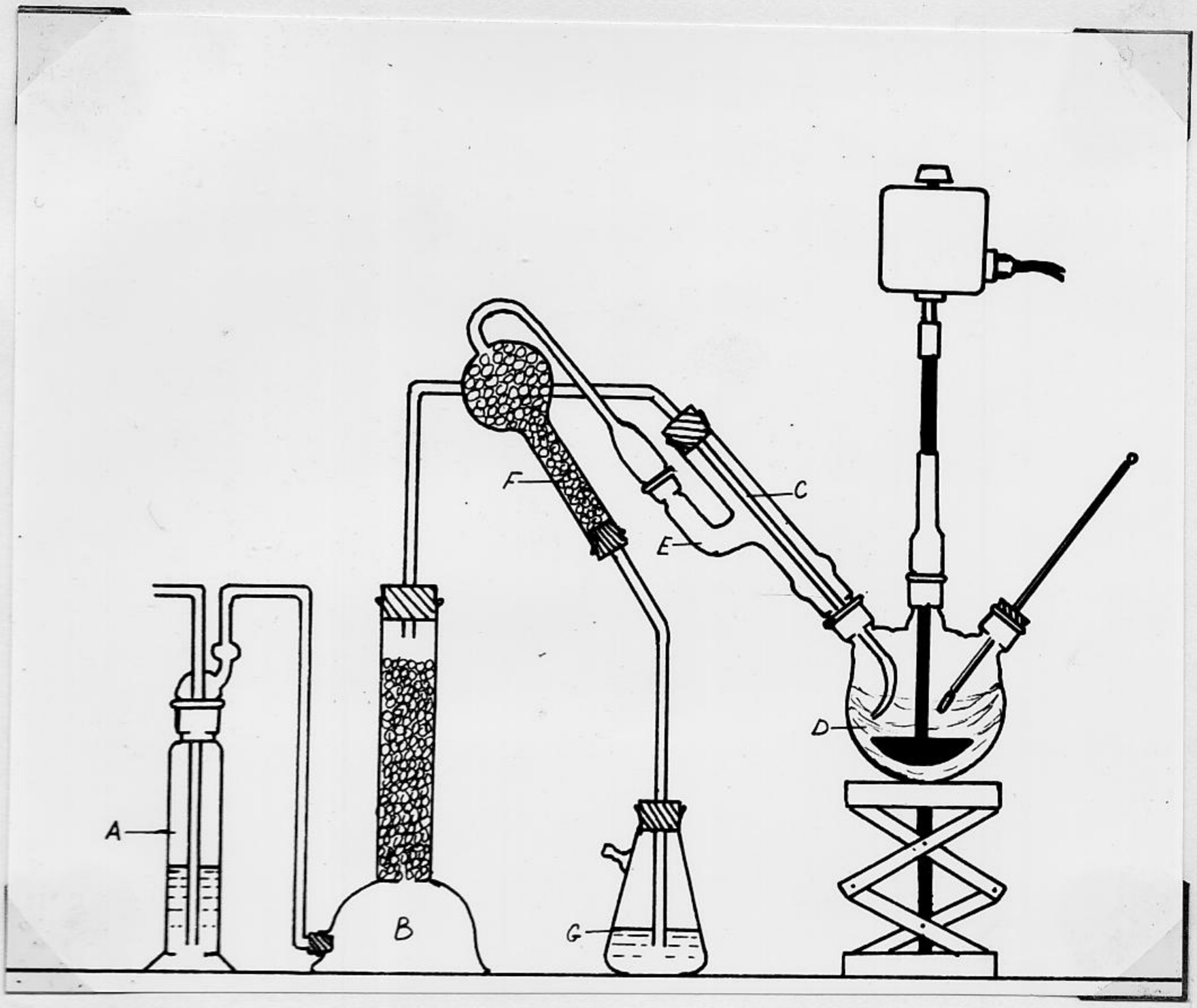


Figure I. Apparatus for the reaction of ethylene with dimethylmalonyl dichloride.

A - Sulfuric acid

B - Calcium chloride drying tower

C - Ethylene delivery tube (inlet)

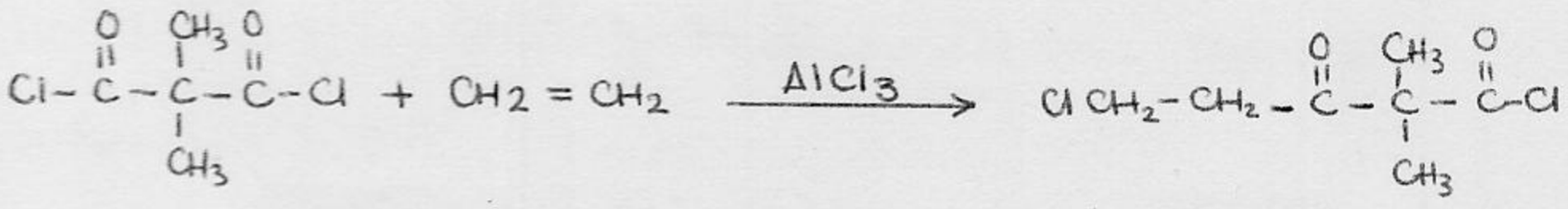
D - Reaction mixture

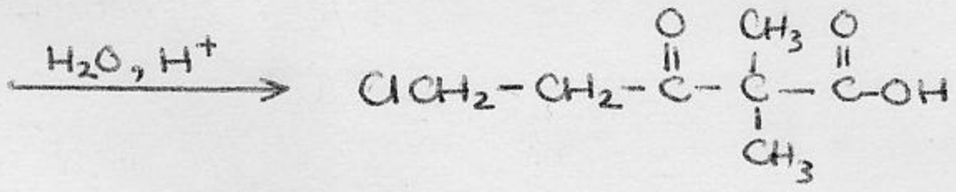
E - Ethylene delivery (outlet)

F - Calcium chloride drying tube

G - Liquid paraffin.

Powdered aluminium chloride (60 g) was added to a cold solution of dimethylmalonyl dichloride (25 g) in n-hexane (100 ml) in a 250 ml three-necked round bottomed flask. See figure I. The reaction mixture was stirred and cooled in an ice bath and ethylene was bubbled through at 0 - 10°C till no further absorption was observed. The ethylene was shut off and the ethylene delivery head was replaced by a stopper. Stirring was continued overnight at room temperature, after-which the mixture was poured slowly, with stirring, into 300 ml of crushed ice and 50 ml of concentrated hydrochloric acid. The mixture was extracted repeatedly with ether, and the combined ether extracts were extracted with 10% sodium hydroxide solution. The combined aqueous extracts were acidified with dilute hydrochloric acid and extracted with ether. Finally the solvent was stripped off using water suction, and the acid dried in a desiccator. It was found that this acid melted at 59 - 60°C, and distilled at 86 - 88°C /0.4 mm.

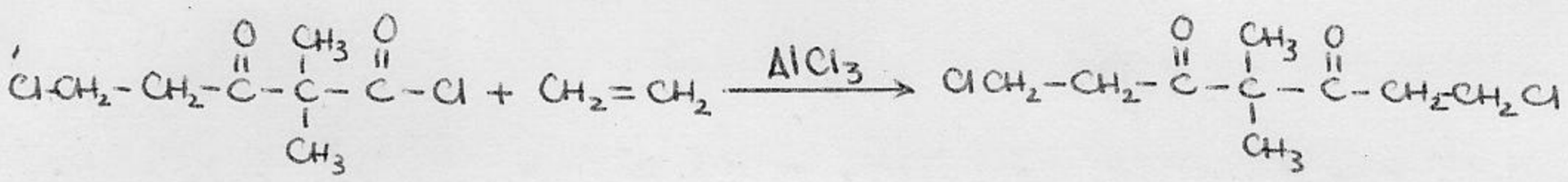




The infrared spectrum (nujol mull): 2850 (s), 1710(s), 1460(s), 1390(w), 1370(m), 1295(m) cm^{-1}.

III.- Preparation of 1,7-Dichloro-4,4-dimethylheptane-3,5-dione

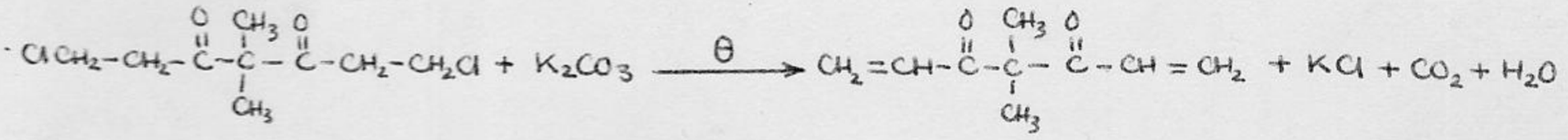
2,2-Dimethyl-3-keto-5-chlorpentanoic acid (20 g), thionyl chloride (25 ml) and dimethyl formamide (1 ml) were placed in a 250 ml three-necked round bottomed flask fitted with a mechanical stirrer and a condenser protected with a calcium chloride drying tube. The mixture was heated for 24 hours at 60°C. and was then cooled to room temperature. The condenser was replaced with a Claisen head equipped with a delivery tube and a calcium chloride drying tube connected to liquid paraffin. See figure I. n-Hexane (100 ml) was added and the flask was cooled in a salt-ice-bath. Aluminium chloride (25 g) was then added and ethylene was bubbled through at 0 - 10°C with stirring. The ethylene flow was stopped when no further absorption was observed, and the Claisen head was replaced with a stopper. The reaction mixture was allowed to stir overnight and was then poured into 300 ml of crushed ice and 50 ml of concentrated hydrochloric acid. The mixture was extracted several times with ether and the organic layer was separated. The solvent was stripped off using water suction, and the remaining mixture was distilled under vacuum using a fractionating column. The fraction distilling between 94 - 96°C /2 mm was collected.



The infrared spectrum: 2930(s), 1720(s), 1475(s), 1370(m), 1300(w), 1075(w), 865(w), 770(s) cm^{-1}.

IV.- <u>Preparation of Dimethyldiacrylylmethane</u>

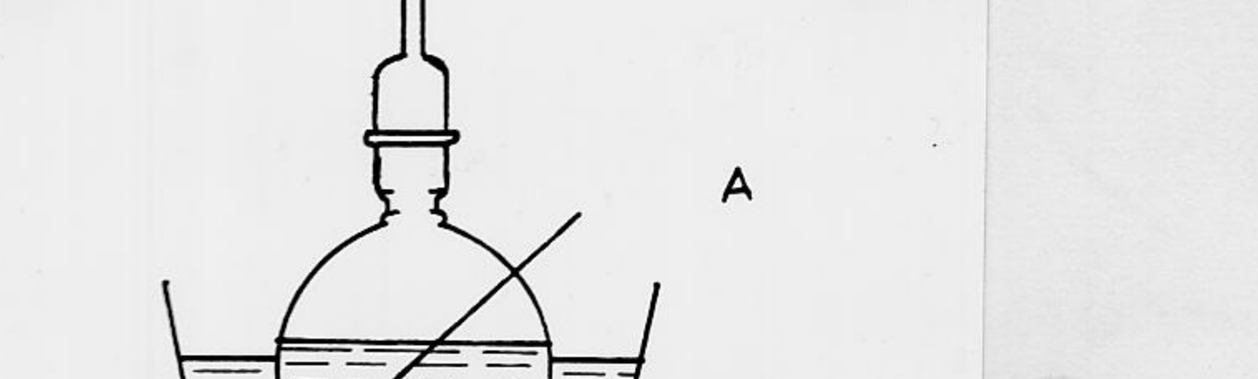
1,7-Dichloro-4,4-dimethylheptane-3,5-dione (6 g), potassium carbonate (6 g) and dihydroquinone (0.1 g) were placed in a 10 ml round bottomed flask fitted with a fractionating column connected to a distilling apparatus. The system was evacuated and the mixture heated gently, gave a pale yellow liquid, with acrylic odor, that distilled at 50 - 52°C /0.3 - 0.4 mm.



Infrared spectrum: 2920(s), 1690(s), 1610(s), 1460(s), 1400(m), 1050(s), 985(m), 865(m), 800(m), 760(s) cm^{-1}.

V.- Free Radical Polymerization of Dimethyldiacrylylmethane

To a solution of freshly distilled dimethyldiacrylylmethane (1.5 g) in 10 ml of benzene was added 15 - 20 mg of α, α'-azobis-isobutyronitrile as an initiator, and the whole was frozen in a 50 ml reaction flask. The flask was evacuated and flushed with nitrogen several times and finally evacuated to 2 mm pressure and sealed. See figure II. The flask and contents were then slowly heated in a silicone-fluid bath to a temperature of 65°C. and maintained at 60 - 65° C for 24 hours. The flask was then cooled to room temperature and the contents poured into methanol. A white powdery polymer was precipitated, separated, and purified by recrystallization several times from benzene and methanol.

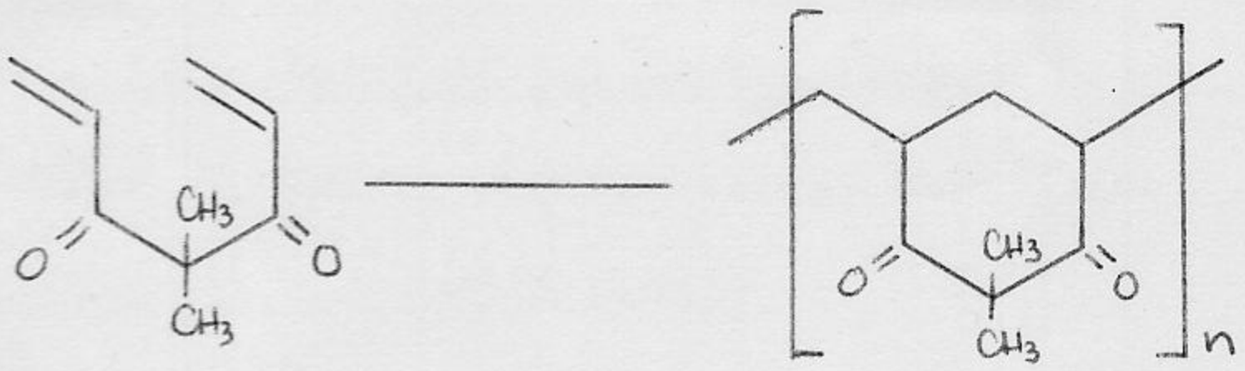


Infrared spectrum (nujol mull): 2950(s), 1710 (s), 1450 (s), 1370(s), 1230(w), 1000(m), 865(m), 785(m) cm^{-1}.

Figure II

VI.- Anionic Polymerization of Dimethyldiacrylylmethane

A solution of dry thiophene-free benzene (30 ml), toluene (30 ml), and pure dimethyldiacrylylmethane monomer (1 g) were placed in a 100 ml suction flask. The flask, protected with a calcium chloride drying tube at its outlet, was fitted with a magnetic stirrer and a two-hole rubber stopper equipped with a nitrogen inlet and a glass tubing connected to a small bottle containing sodium methoxide (0.45 g) by a clamped rubber tube. The flask was cooled to -75°C and the sodium methoxide was introduced through the clamp. The mixture was stirred for six hours at -70°C and was then allowed to warm up to room temperature within a period of two hours. The yellow precipitate which was filtered gave a white powdery polymer after washing several times with water and methanol and drying in a desiccator. The mother liquor was reduced to about 10 ml by evaporating the solvent under reduced pressure and the contents poured over methanol. A white powdery polymer precipitated which was purified by recrystallization from benzene and methanol. Both fractions of the polymer had identical infra red spectra.



Infrared spectrum (nujol mull): 2950(s), 1710(s), 1450(s), 1370(s), 1230(w), 1000(m), 865(m), 785(m) cm^{-1}.

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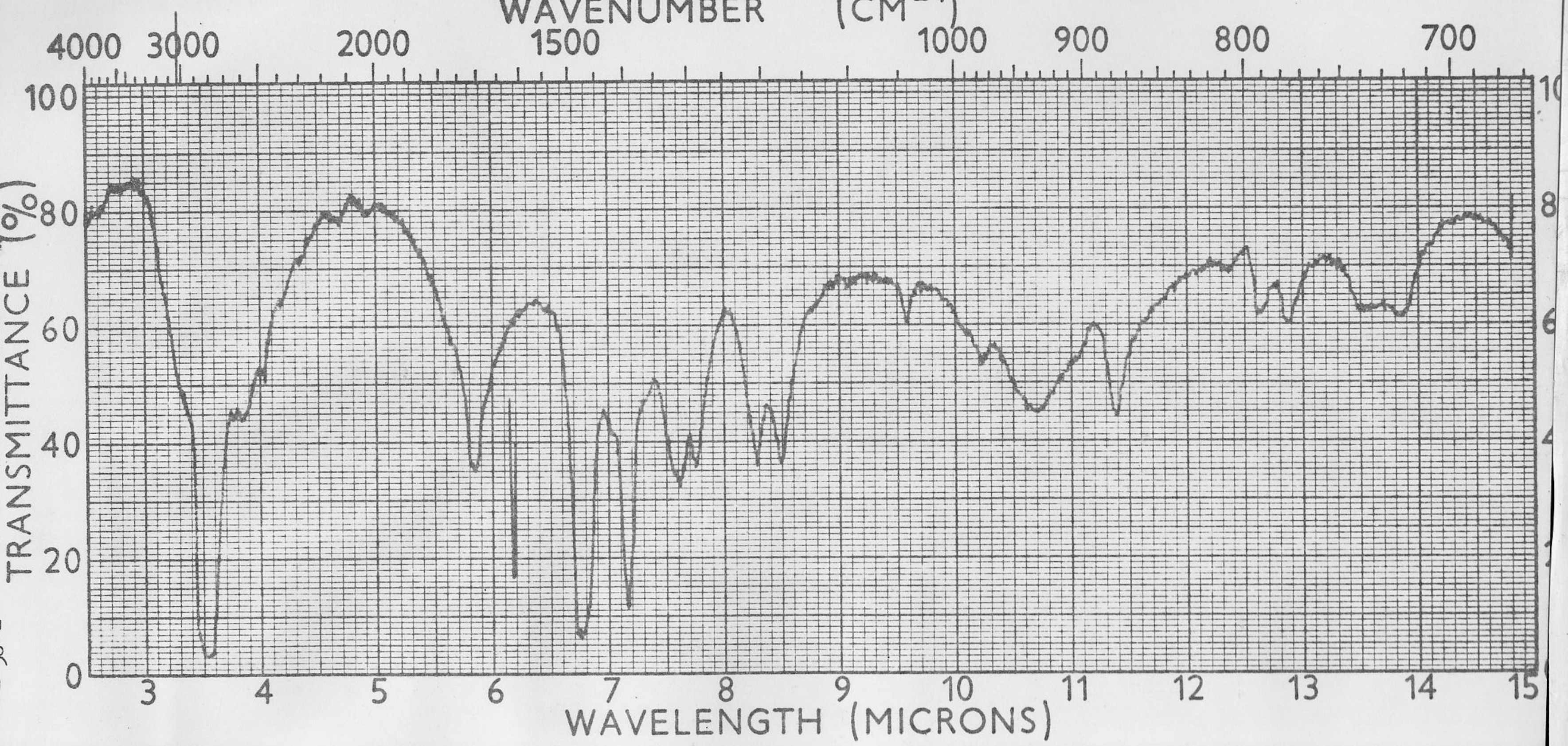
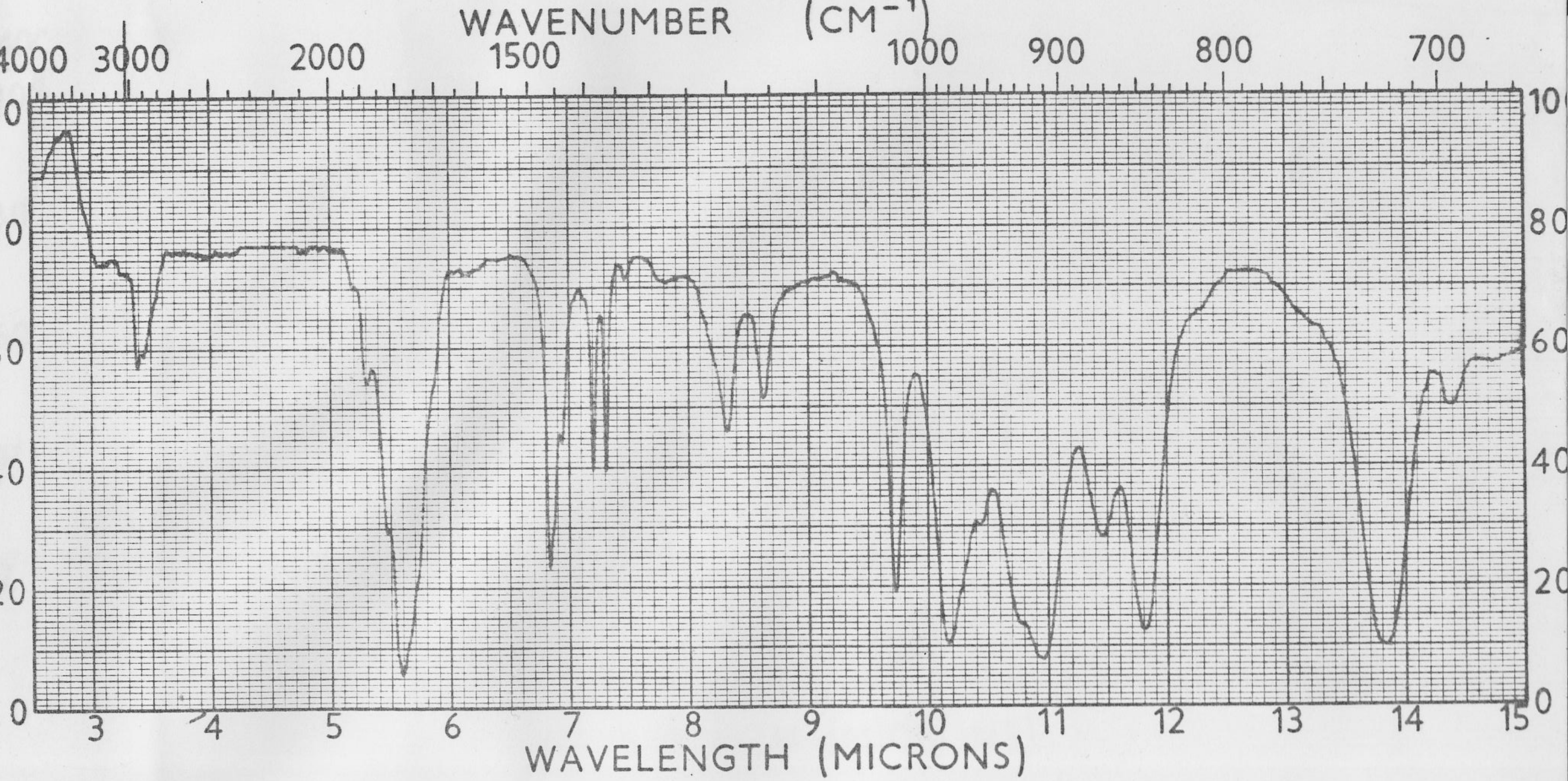


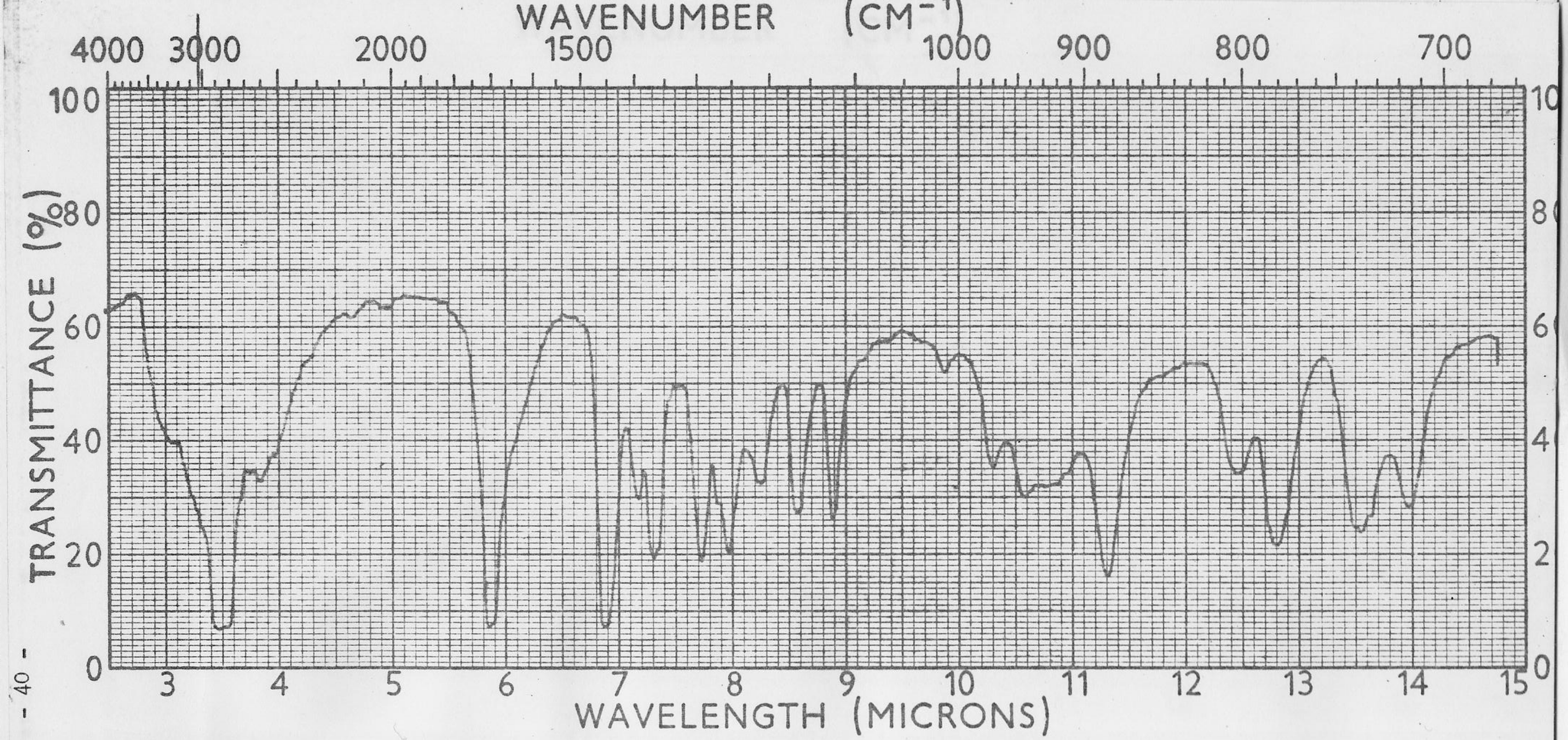
I- Infra Red Spectrum of Dimethylmalonic acid

Figure III



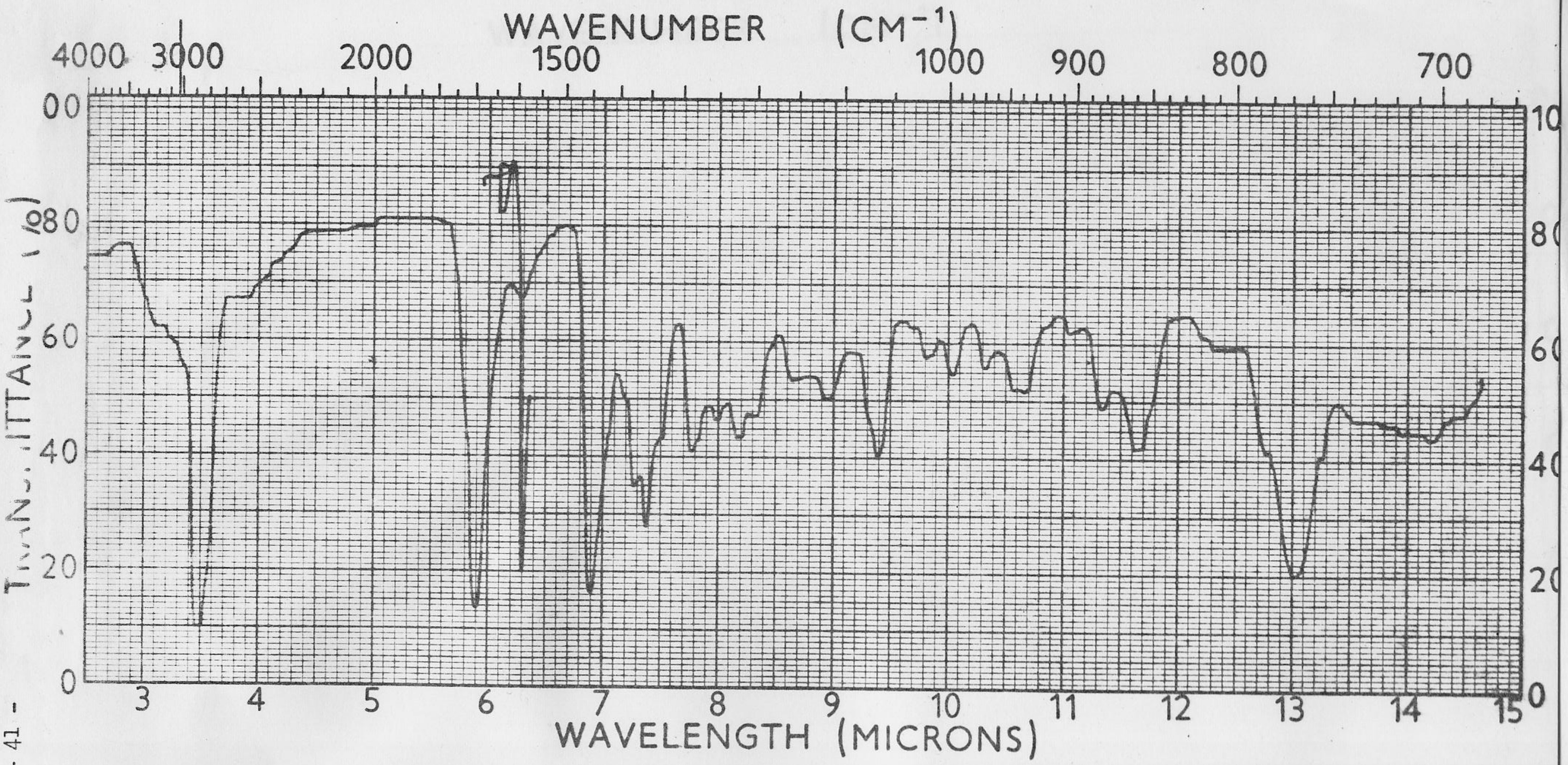
II- Infra Red Spectrum of Dimethylmalonyl dichloride

Figure IV



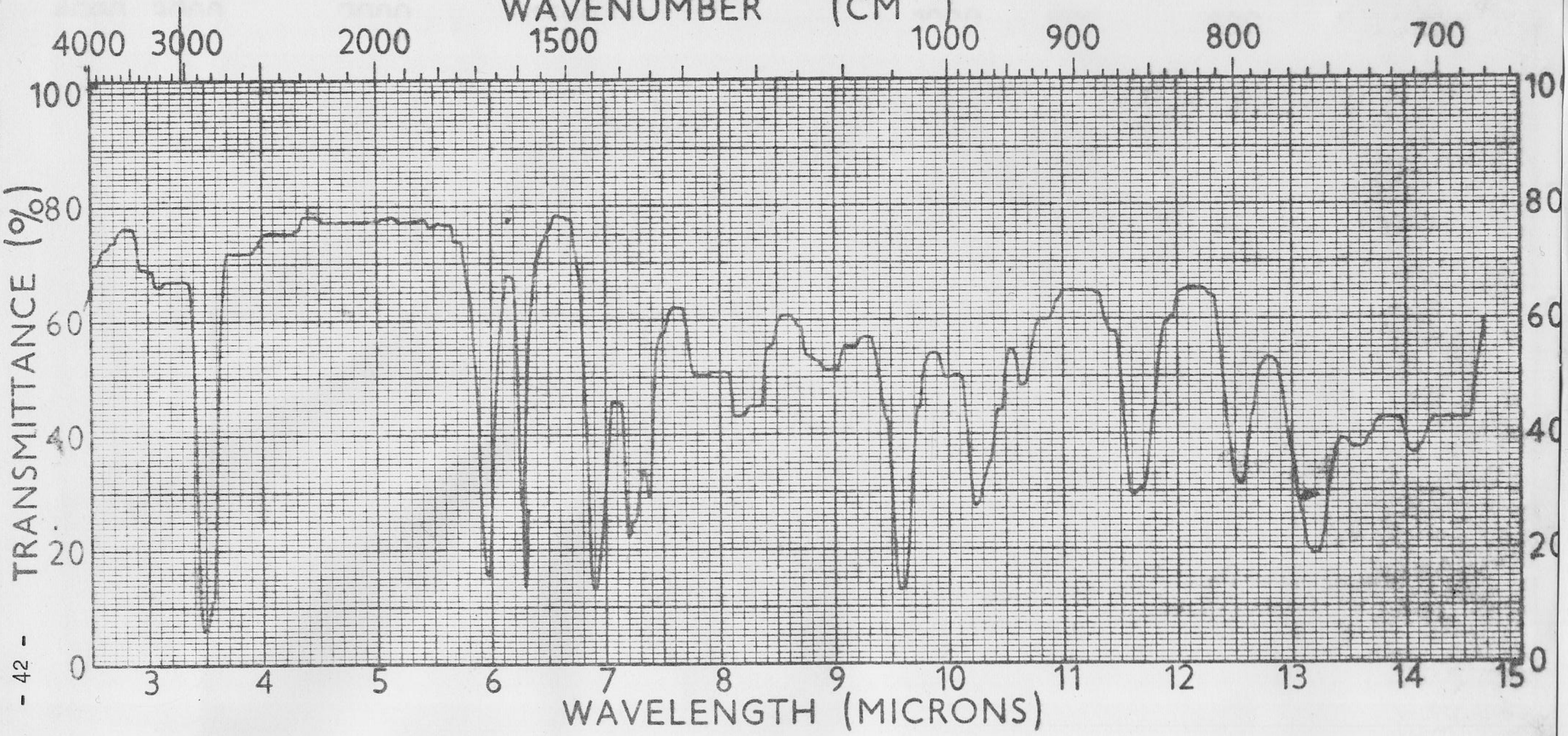
III- Infra Red Spectrum of 2,2-Dimethyl-3-keto-5-chloropentanoic acid

Figure V



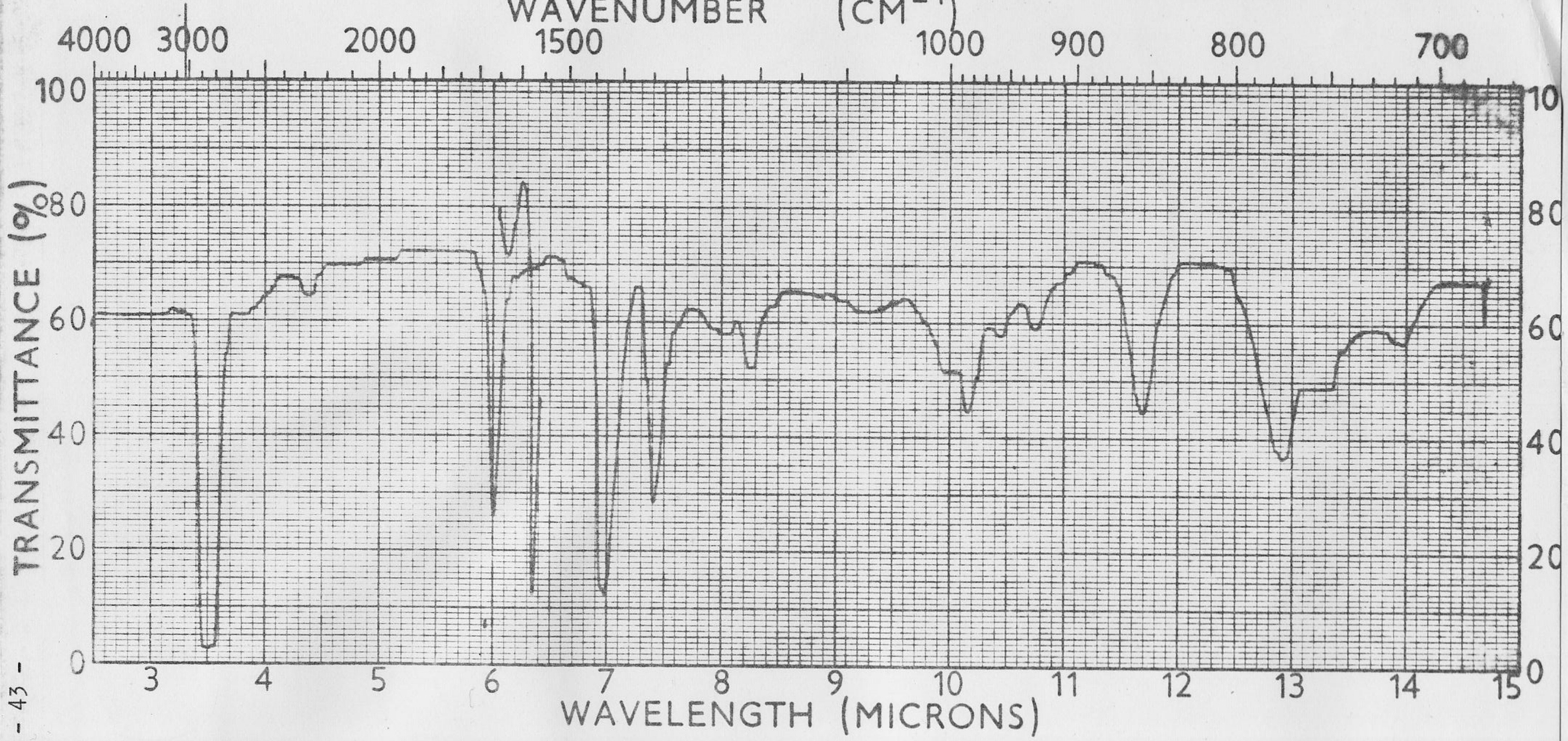
IV- Infra Red Spectrum of 1,7-Dichloro-4,4-dimethylheptane-3,5-dione

Figure VI



V- Infra Red Spectrum of Dimethyldiacrylylmethane

Figure VII



VI- Infra Red Spectrum of Poly-dimethyldiacrylylmethane

Figure VIII