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## Preparation and polymerization of 3-methylenecyclobutene and of 1-methyl-3-methylenecyclobutene.

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PREPARATION AND POLYMERIZATION OF 3-METHYLENECYCLOBUTENE AND  
OF 1-METHYL-3-METHYLENECYCLOBUTENE

A Dissertation Presented

By

CHESTER CHERNG-CHIOU WU

Submitted to the Graduate School of the  
University of Massachusetts in  
partial fulfillment of the requirements for the degree of

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April, 1971

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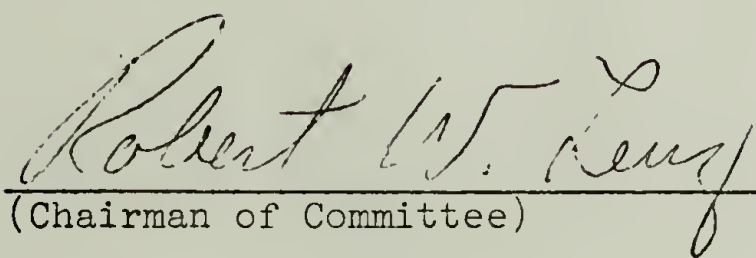
PREPARATION AND POLYMERIZATION OF 3-METHYLENECYCLOBUTENE AND  
OF 1-METHYL-3-METHYLENECYCLOBUTENE

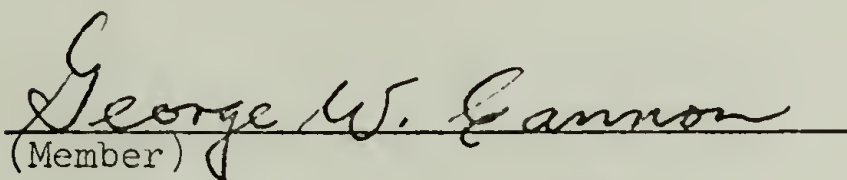
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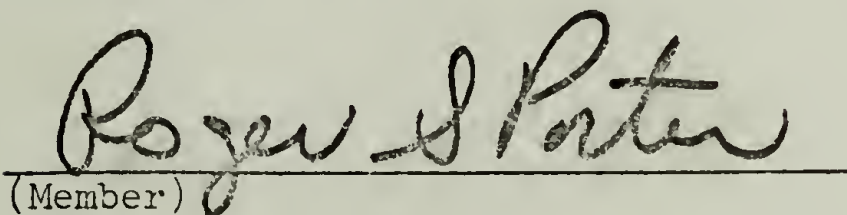
By

Chester Cherng-Chiou Wu

Approved as to style and content by:

  
(Chairman of Committee)

  
(Member)

  
(Member)

April, 1971

To  
My Parents  
and  
Johanna

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## ABSTRACT

In this study 3-methylenecyclobutene was prepared by way of 3-methylenecyclobutylcarbonitrile and 3-bromomethylcyclobutyl bromide. This synthetic route seems to be simpler than the method previously used by Roberts and co-workers. Analysis of the polymers obtained by IR and NMR spectroscopy indicated that cationic polymerization of 3-methylenecyclobutene proceeded entirely by a 1,5-propagation mechanism to give low conversions of low molecular weight polymers. Anionic polymerization, on the other hand, proceeded primarily through a 1,2-propagation path, again giving low molecular weight product in low yield. Poly-3-methylenecyclobutene prepared ionically is very susceptible to autoxidation, and a mechanism is proposed to account for this behavior. Another characteristic property of this polymer is its thermal crosslinking reaction, which presumably proceeds by a ring-opening reaction upon heating at moderate temperature.

In contrast to 3-methylenecyclobutene, 1-methyl-3-methylenecyclobutene polymerized readily with cationic initiators to produce unusually high molecular weight polymers in high conversions. On the basis of both IR and NMR spectroscopic analyses, it was concluded that the polymers also contain essentially 1,5-addition repeating units. Poly-1-methyl-3-methylenecyclobutene was observed to be more stable than poly-3-methylenecyclobutene to hydrogenation, autoxidation and crosslinking reactions. Anionic initiators such as n-BuLi were unable to induce

polymerization of 1-methyl-3-methylenecyclobutene. Polymerization by Ziegler-Natta catalysts proceeded readily to yield polymers virtually identical to those obtained from cationic initiators.

## List of Abbreviations

TMS = Tetramethylsilane

NMR = Nuclear Magnetic Resonance (multiplicities are:)

s = singlet

d = doublet

t = triplet

q = quartet

qn = quintet

m = multiplet

IR = Infrared (absorptions are:)

s = strong

m = medium

w = weak

DSC = Differential Scanning Calorimeter

AIBN = Azobisisobutyronitrile

AlEt<sub>2</sub>Cl = Diethyl aluminum chloride

Al(i-Bu)<sub>3</sub> = Triisobutyl aluminum

BF<sub>3</sub> = Boron trifluoride

n-BuLi = normal Butyllithium

i-Bu = isobutyl

t-Bu = tertiary butyl

Co(acac)<sub>3</sub> = Cobalt triacetylacetonate

I<sup>⊕</sup> = cationic initiator

I<sup>⊖</sup> = anionic initiator

NBS = N-Bromosuccinimide

P = polymer chain

Pd = Palladium

MW = molecular weight

$\bar{M}_n$  = number average molecular weight

THF = tetrahydrofuran

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## INTRODUCTION

In 1956 Roberts and co-workers synthesized 3-methylenecyclobutene and prepared three polymers by cationic, anionic and free radical methods. Based on IR spectra of the polymers, they concluded that the bulk cationic polymerization of 3-methylenecyclobutene gave predominantly the 1,5-structure, while anionic polymerization by  $\text{KNH}_2$  in liquid ammonia produced primarily 1,2-addition repeating units. In the free radical homopolymerization of this cyclic diene, they proposed that all types of 1,2-addition, 3,5-addition and 1,5-addition mechanisms were operative. Since this initial brief study, no further investigation of the polymerization of 3-methylenecyclobutene has been reported to date in the literature. It is, therefore, the objective of this project to examine in greater detail the polymer structures obtained by different types of initiators and thus to help elucidate the polymerization mechanisms involved, through the use of high resolution NMR and IR spectroscopy. In the course of this study, it was observed that poly-3-methylenecyclobutene prepared cationically was susceptible to very rapid autoxidation and crosslinking reactions, which complicated the polymer characterization.

Partly with the goal of preparing a polymer more resistant to autoxidation inherent to poly-3-methylenecyclobutene, 1-methyl-3-methylenecyclobutene monomer was also synthesized and its polymerizability was studied. Significant results were obtained in the cationic polymerizations of this monomer and the reactions of poly-1-methyl-3-methylenecyclobutene.

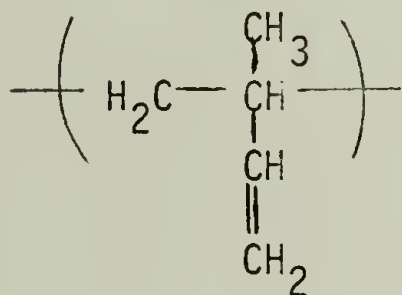
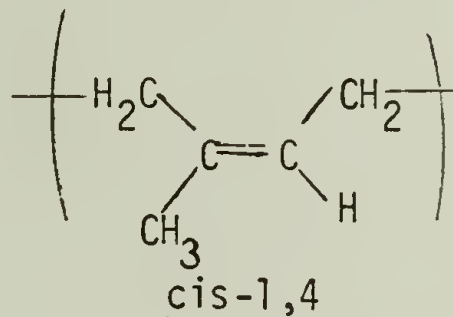
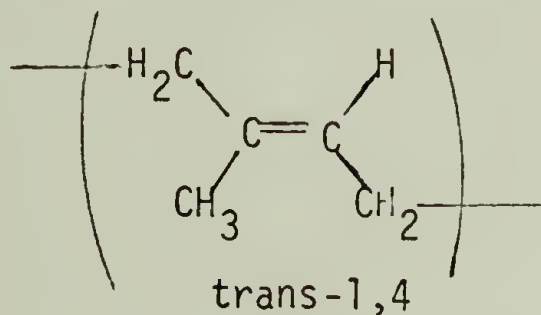
## LITERATURE REVIEW

I. Aliphatic Conjugated Diolefins

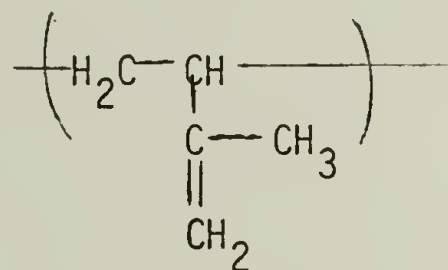
Isoprene and piperylene are two important diolefins which are the acyclic analogues of 3-methylenecyclobutene. It is simply impossible to completely review within the limited space available the great amount of work done on these monomers. For this reason, only their polymerizability and polymer microstructures will be briefly discussed so that effects of the cyclic structure of 3-methylenecyclobutene on these variables can be compared.

(A) Isoprene (2-Methylbutadiene)

Six types of stereoregular polyisoprenes are possible. They are trans-1,4, cis-1,4, isotactic-1,2, syndiotactic-1,2, isotactic-3,4, and syndiotactic-3,4 as shown by the following structures.



1,2



3,4

1. Free Radical Polymerizations [1]

Free radical polymerizations of isoprene have been of little importance because this monomer does not polymerize readily in bulk or solution with free radical initiators. The rate is slow and the polymers are characterized by low molecular weights or by cross-

linking reactions. Extensive dimerization of isoprene monomer by the Diels-Alder reaction and fast mutual termination of propagating radicals occur, which limit both the rate and degree of polymerization.

In order to localize the growing radicals and thus to minimize termination reaction, emulsion polymerization has been found satisfactory to produce high molecular weight polyisoprene containing high trans-1,4 structure.

## 2. Anionic Polymerizations [2,3]

In 1954, Firestone chemists succeeded in using lithium metal to synthesize 94% cis-1,4-polyisoprene which was identical to commercially important natural rubber [4]. This successful effort was followed by extensive studies of anionic polymerization of isoprene with alkali metals and organo-alkali metals as catalysts. Some of the significant results are tabulated as follows:

### Stereochemistry of Polyisoprene Formation [5]

Anionic initiator	Repeating Units, %				Total found, %
	<u>cis</u> -1,4	<u>trans</u> -1,4	1,2	3,4	
Li	94	0	0	6	95
<u>n</u> -BuLi	93	0	0	7	92
Na	0	48	10	42	94
<u>n</u> -BuNa	4	35	7	54	101
K	0	58	7	35	99
<u>n</u> -BuK	20	41	6	33	94
Rb	5	47	8	39	-
Cs	4	51	8	37	-
<u>n</u> -BuLi/THF*	63		1	36	98

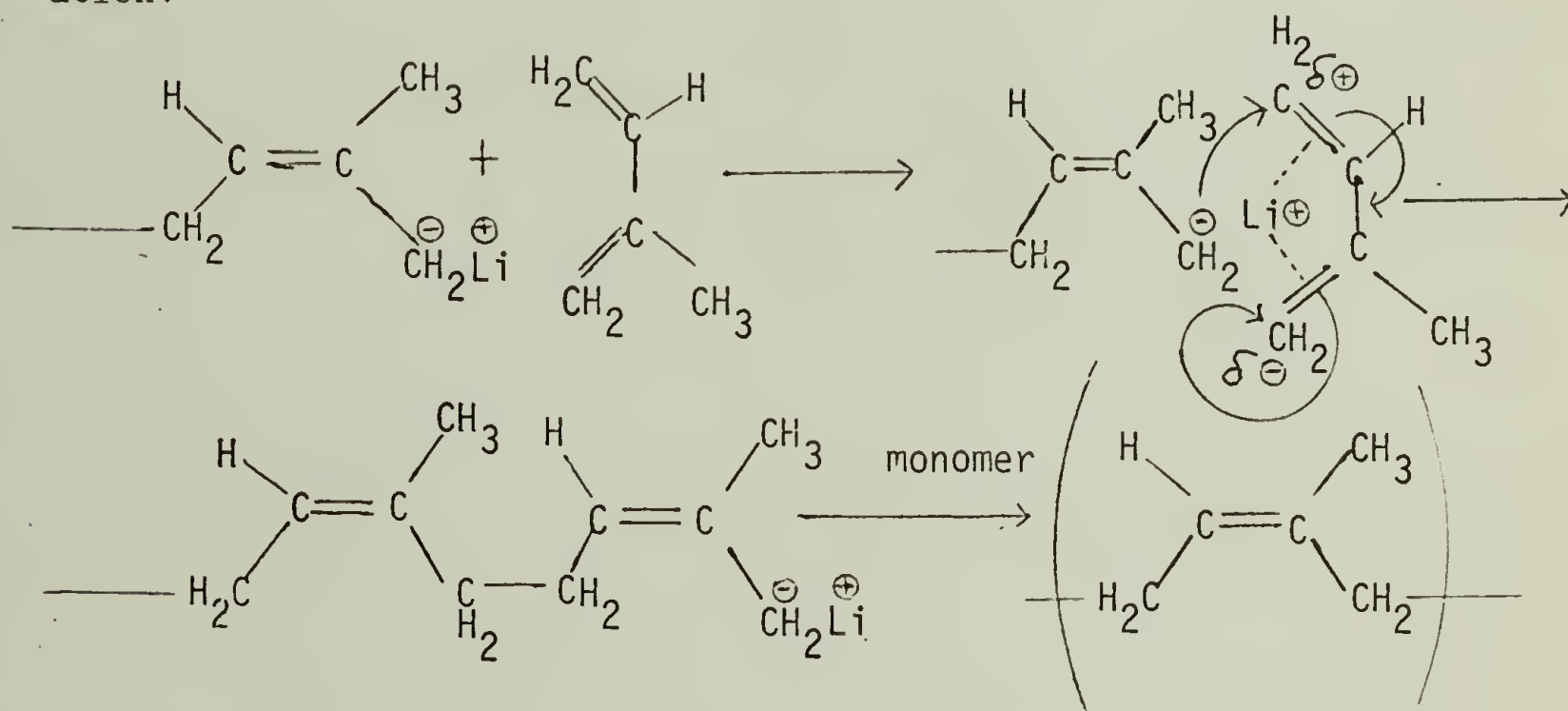
\*THF - tetrahydrofuran

From the above results, some generalizations can be made:

(i) Lithium or organolithium compounds initiate the formation of predominantly cis-1,4 polyisoprenes, whereas those alkali metals or organoalkali compounds other than lithium product polymers having approximately equal amounts of trans-1,4 and 3,4 units.

(ii) The use of polar solvents such as THF causes an increase in trans-1,4 and 3,4 components at the expense of cis-1,4 unit. Polymerization temperature is also important in determining the stereochemistry although to a much smaller extent.

The anionic polymerization by lithium catalysts to yield cis-1,4-polyisoprenes has been attributed to the bidentate coordination complex between unsolvated small lithium counterion and isoprene in cis conformation:



As depicted above, the coordination complex holds each incoming isoprene monomer in the cis conformation during the course of propagation, thus leading to the favorable cis-1,4 placement. Addition of THF brings

about competition for lithium counterion, thereby disrupts the stereoregulating interaction, leading to more random polymerization. Consequently, the formation of 3,4 structure is increased with concomitant decrease of cis-1,4 unit.

### 3. Cationic Polymerizations [1]

Cationic polymerizations of isoprene yield only low molecular weight polymers consisting of mainly trans-1,4 structure together with insoluble products containing cyclized structure. For example, polymerization of isoprene in ethyl chloride by stannic chloride gave molecular weights in the range of 900 to 3800. The complicated reactions which yield these products probably result from the different possible ionic intermediates and extensive chain transfer.

### 4. Coordinated Polymerizations [3]

A wealth and variety of Ziegler-Natta catalysts applied to this type of polymerization have produced various stereoregular polyisoprenes. No polymerization mechanism will be reviewed; only general outlines will be given in the following presentations.

#### 4.a. Cis-1,4-Polyisoprene [3]

Goodrich Co. revealed in its 1954 patent the use of  $\text{AlR}_3\text{-TiCl}_4$  system at an Al/Ti molar ratio of about one in a hydrocarbon solvent to give about 95% cis-1,4, high molecular weight polyisoprene. The catalyst activity for high yield and stereospecificity was obtained only over a narrow Al/Ti ratio range close to one, corresponding to the formation of the active  $\beta\text{-TiCl}_3$ . The microstructure was not influenced by changes in polymerization temperature, monomer or catalyst concentration.

However, higher rates and better yields were realized by the use of catalyst from  $\text{AlR}_3$  complexed with equal amount of ethers.

Largely cis-1,4-polyisoprenes were also obtained with the following catalyst systems:  $\text{TiCl}_4\text{-ZnEt}_2$ ,  $\text{TiCl}_4\text{-CdEt}_2\text{-(CaH}_2)_x\text{-(CaEt}_2)_y\text{-ZnEt}_2$ ,  $\text{TiCl}_4\text{-various alanes (e.g., AlHCl}_2, \text{OEt}_2, \text{AlHCl}_2\cdot\text{N(CH}_3)_3, \text{AlH}_2\text{Cl}\cdot\text{N(CH}_3)_3, \text{AlH}_3\cdot\text{N(CH}_3)_3, \text{and AlH}_2\cdot\text{N(CH}_3)_2\text{))}$ .

#### 4.b. Trans-1,4-Polyisoprenes [3]

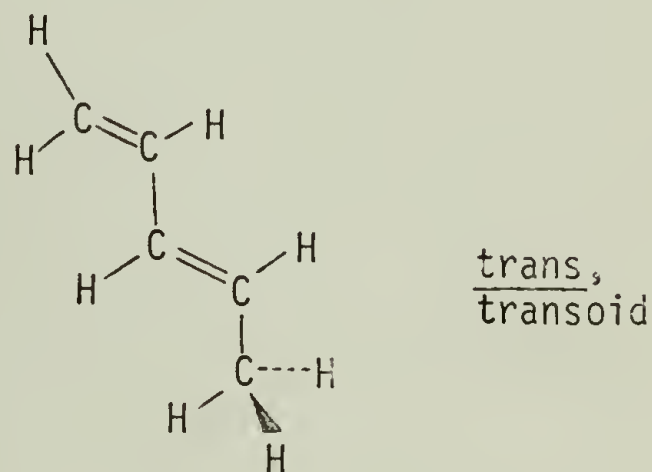
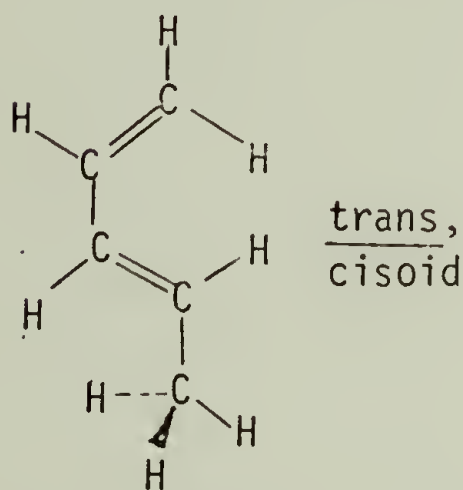
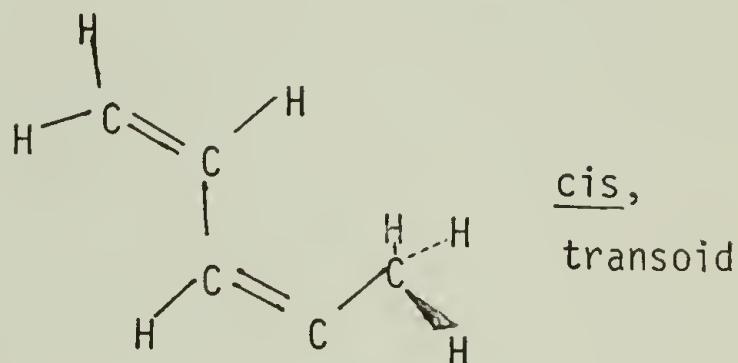
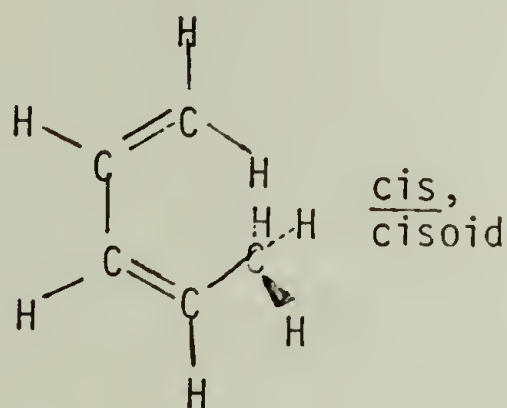
G. Natta was the first one to prepare trans-1,4-polyisoprene in 1955 by use of a heterogeneous catalyst of  $\text{AlEt}_3\text{-}\alpha\text{TiCl}_3$ , but the best catalyst system was found to be  $\text{AlR}_3\text{-supported VCl}_3$  which gave polymer of 99-100% trans-1,4 unit at higher rate. A homogeneous three component system of  $\text{AlR}_3\text{-VCl}_3\text{-Ti(OR)}_4$  ( $\text{Al/V/Ti} = 20/2/1$ ) yielded the same microstructure at much higher polymerization rate and with greater catalyst efficiency. Trans-1,4-polyisoprene was also obtained with several other catalysts; e.g.,  $\text{AlEt}_2\text{Cl-V(acac)}_3$  or  $\text{VCl}_3\cdot 3\text{THF}$ ,  $\text{LiAlH}_4$  (ether suspension)- $\text{TiI}_4$ .

#### 4.c. 3,4 Polyisoprenes [3]

A homogeneous catalyst consisting of  $\text{AlEt}_3$  and  $\text{Ti(OR)}_4$  (optimum  $\text{Al/Ti} = 6\text{-}7$ ) in aromatic or aliphatic solvents was developed simultaneously by G. Wilke and Natta for the preparation of 3,4-polyisoprene around 1955. Low polymerization temperatures tended to favor the 3,4 content.  $\text{AlEt}_3\text{-VO(OR)}_3$  catalyst system was also suitable for the preparation of 3,4-polyisoprene.

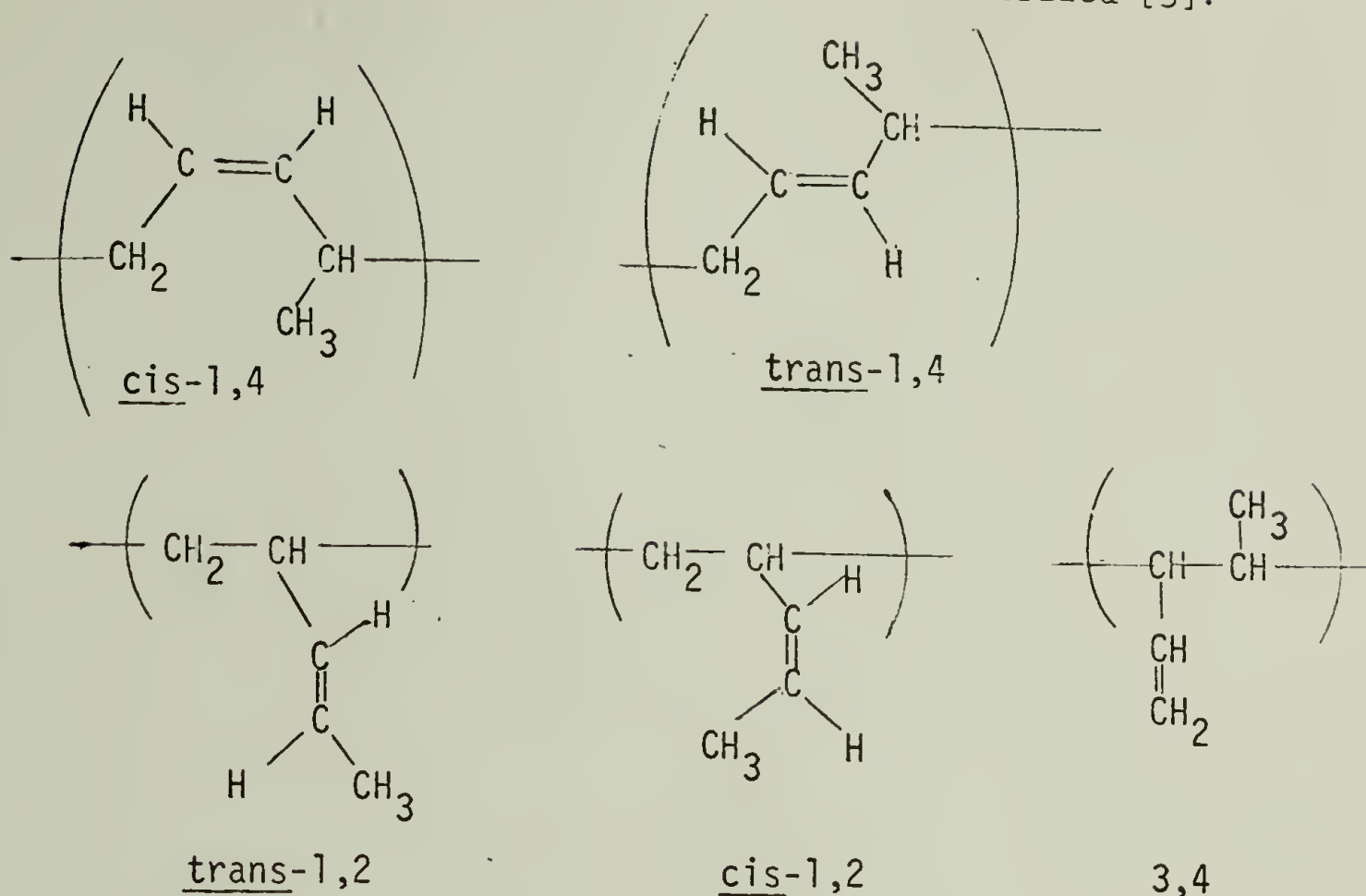
(B) 1,3-Pentadiene (Piperylene)

This compound exists in cis and trans isomers which can further assume transoid and cisoid conformations (2). The cis and trans forms do not always exhibit identical polymerization behavior.



The stereochemistry of poly-1,3-pentadiene is of particular interest because of the numerous geometric and steric isomers possible. From theoretical viewpoints, eleven stereoregular poly 1,3-pentadienes can be visualized. 1,4-polymerization gives four stereoregular polymers, i.e., isotactic and syndiotactic cis-1,4, and isotactic and syndiotactic trans-1,4. 3,4-Polymerization gives rise to two asymmetric centers per repeating unit and hence results in three stereoisomers, i.e., threodiisotactic, erythrodiisotactic, and disyndiotactic. The polymerization involving 1,2 unit yields four stereoregular polymers, i.e., isotactic cis- and trans-1,2, and syndiotactic cis- and trans-1,2. So far only isotactic trans-1,4, isotactic cis-1,4, syndiotactic cis-1,4, and

syndiotactic 1,2 have been prepared and characterized [3].



### 1. Free radical polymerizations [1]

Polypiperylene from free radical initiators has not been fully characterized but are probably of mixed micro-structure. The available data indicated that cis monomer was found to polymerize more rapidly than trans monomer.

### 2. Anionic polymerization [2]

Trans monomer polymerizes more rapidly than cis monomer when lithium or organolithium initiators are used. Predominantly trans-1,4-poly-1,3-pentadiene was obtained with lithium compounds in hydrocarbon solvents. The results of anionic polymerization of 1,3-pentadiene by alkali metals and organoalkalis are given in the following table.

### Stereochemistry of Poly-1,3-Pentadiene [2]

catalyst	solvent	monomer <u>cis/trans</u>	<u>Repeating unit, %</u>		
			<u>cis-trans</u> 1,4	<u>cis-trans</u> 1,2	3,4
Li	Pentane	-	85	15	0
Li	THF	-	60	30	10
Li or BuLi	Pentane	10/90	78	22	0
	Pentane	99/0	73	27	0
	THF		61	39	0
Na	Pentane		63	40	0
Na	HMPA*		58	32	5
K	Pentane		81	15	<5
K	HMPA		57	31	
Rb	HMPA		31	42	0
Cs	HMPA		37	37	0

\*Hexamethylphosphoramide

The generalizations made for anionic polymerizations of isoprene by alkali metals catalysts are also applicable here except that the more important vinyl-type addition for 1,3-pentadiene is 1,2 in contrast to 3,4 for isoprene.

### 3. Cationic Polymerizations [1]

Because of many possible ionic intermediates and extensive chain transfer reactions, the cationic polymerizations of piperylene are rather complicated, generally resulting in low molecular weight polymers. Polypiperylene obtained with  $\text{AlEtCl}_2$  consists mainly of 1,2 units.

### 4. Coordinated Polymerizations [3]

#### 4.a. Iostactic Trans-1,4

This stereoregular polymer of isoprene was first synthesized from a mixture of cis and trans monomers by Natta in 1955 using heterogeneous

$\text{AlEt}_3\text{-}\alpha\text{TiCl}_3$  catalyst system in heptane at about  $60^\circ\text{C}$ . Far better results were obtained with  $\text{AlEt}_3\text{-VCl}_3$  catalyst in heptane at room temperature which produced practically identical polymer microstructure from either cis or trans monomer.

#### 4.b. Cis-1,4

Isotactic Cis-1,4: With a homogeneous catalyst system of  $\text{AlR}_3\text{-Ti(OR)}_4$  ( $\text{Al/Ti}=7$ ), crystalline isotactic cis-1,4 polypiperylene was obtained from both trans and cis monomers. Trans monomer, however, was found to give better results with regard to polymerization yield and stereoregularity. Heterogeneous catalyst of  $\text{AlEt}_3\text{-TiCl}_4$  ( $\text{Al/Ti}=2$ ) also produced the same microstructure from trans monomer.

Syndiotactic Cis-1,4: Homogeneous catalyst from aluminum alkyl halides and  $\text{Co(acac)}_{2,3}^*$  in aromatic solvents was used by Natta, et al. to polymerize trans-1,3-pentadiene to the syndiotactic cis-1,4 polymer, and addition of a Lewis base such as thiophene or pyridine to  $\text{AlEt}_2\text{Cl}$  was found to increase the cis-1,4 yield.

#### 4.c. 1,2 Syndiotactic

When the solvent was changed to n-heptane or other aliphatic solvents, the same catalyst combination of  $\text{AlEt}_2\text{Cl-Co(acac)}_3$ , which produced syndiotactic cis-1,4-polypiperylene, yielded polymer of predominantly 1,2 structure from trans monomer.

---

\*A list of abbreviations is given on page vii, Preliminary Section.

(C) 2,4-Hexadiene

Murahasi and co-workers [5] found that 2,4-hexadiene was polymerized by Friedel-Crafts catalysts such as  $\text{TiCl}_4$  and  $\text{AlEt}_2\text{Cl}$  to give an amorphous high molecular weight polymer containing predominantly trans-1,4 structure. An anionic initiator such as  $\text{BuLi}$  only slightly polymerized this diene monomer. A high polymer of 2,4-hexadiene was again obtained by Ziegler-Natta type catalysts, and the polymers initiated by  $\text{TiCl}_4$ - $\text{AlEt}_3$ ,  $\text{Ti}(\text{acac})_3$ - $\text{AlEt}_2\text{Cl}$ , and  $\text{Co}(\text{acac})_3$ - $\text{AlEt}_2\text{Cl}$  were found by x-ray analysis to be crystalline.

(D) 2,5-Dimethyl-2,4-Hexadiene

2,5-dimethyl-2,4-hexadiene was readily polymerized by  $\text{BF}_3$  to a high molecular weight polymer [6]. The polymer structure, however, was not reported.

## II. Alicyclic Olefins and Diolefins

### A. Three-member Ring Compounds

#### 1. Cyclopropene [6]

Cyclopropene is stable indefinitely as a solid at liquid nitrogen temperature, but undergoes a spontaneous polymerization at temperature above its boiling point of  $-36^{\circ}\text{C}$ . On the basis of NMR analysis of the polymer, the chain repeating units so formed have been determined to contain only cyclopropane rings. Wiberg and co-workers proposed a free radical propagation mechanism which accounted for the stable cyclopropenyl radical and restricted chain transfer reaction to carbon 3. Cyclopropene possesses a large ring strain of 52.6 kcal/mole, and about 27.6 kcal/mole strain is relieved in the polymerization reaction. A number of cyclopropene derivatives have been synthesized, but their polymerization behaviors have not been reported in the literature [8].

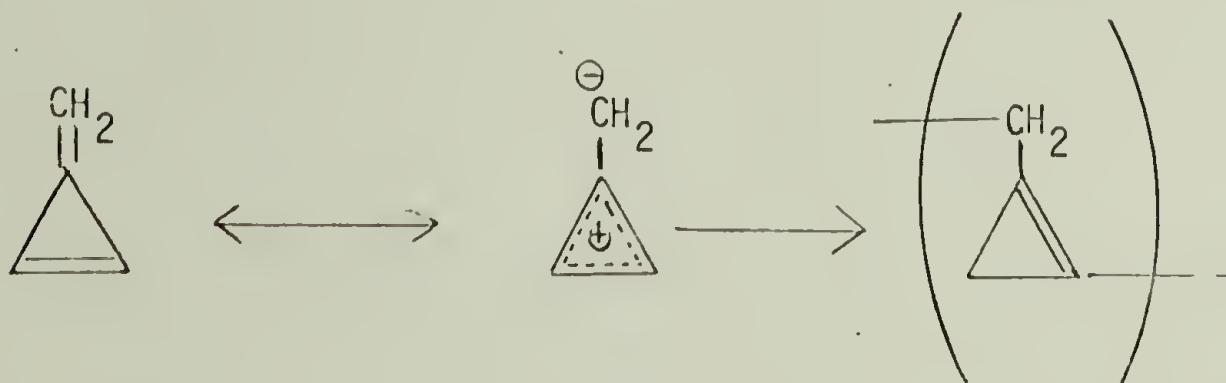
#### 2. Vinylcyclopropane

Overberger and co-workers prepared and polymerized vinylcyclopropane by a Ziegler-Natta catalyst to yield a crystalline isotactic polymer. By using a catalyst of diethylaluminum chloride and titanium trichloride, vinylcyclopropane was polymerized to give mixtures of isotactic, atactic and stereoblock polymers. Hydrogenation of the atactic polyvinylcyclopropane fraction from this polymerization with Raney nickel yielded poly-3-methylbutene-1 quantitatively, demonstrating that ring-opening occurred only between the two methylene groups.

#### 3. Methylenecyclopropene [10]

Methylenecyclopropene is a highly strained, resonance-stabilized, lower member of the fulvene homologues. This compound has been the

subject of several molecular orbital calculations, and its preparation and isolation was predicted to be difficult, if not impossible, because of the low activation energy required for polymerization to proceed as a result of release of the large ring strain energy.



Several stable substituted methylenecyclopropenes have been synthesized, but so far no polymerization study has been reported in the literature.

## B. Four-member Ring Compounds

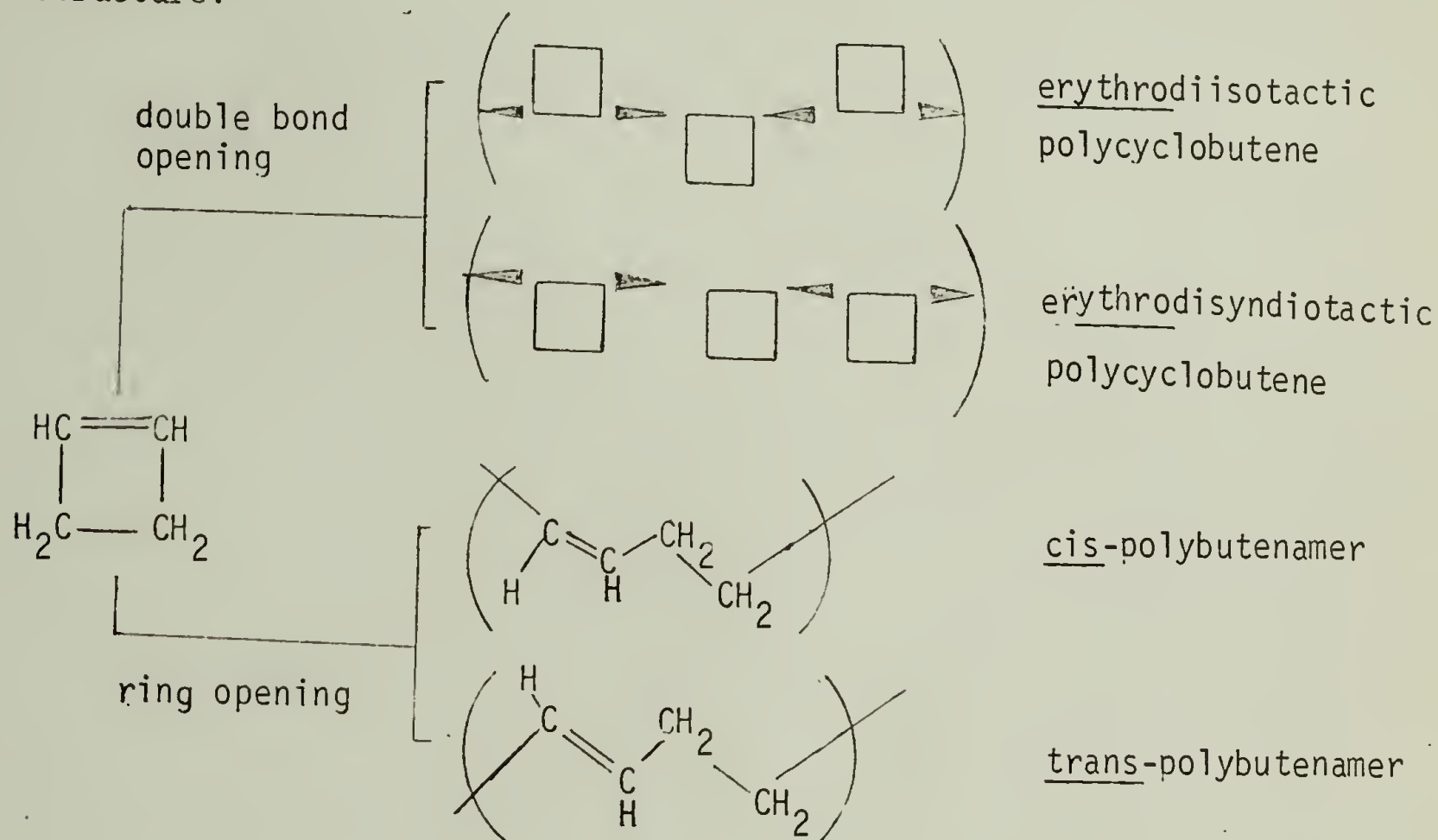
### 1. Methylenecyclobutane

Cationic polymerizations of methylenecyclobutane with  $\text{AlCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$  and  $\text{BF}_3$  as catalysts gave only low conversions of low molecular weight polymers, possibly because of the high steric effect of the cyclobutane [11, 12]. In contrast, cationic polymerizations of isobutene proceed readily because the propagating carbonium intermediate is stabilized by the two electron-donating methyl groups. By IR and NMR analyses, the polymethylenecyclobutane were shown to have a regular polymethylene structure with lateral cyclobutane groups.

No polymerization was observed for methylenecyclobutane initiated by AIBN in benzene solution at  $70^\circ\text{C}$  for thirty hours [13]. Neither  $\text{BF}_3$ -etherate nor  $n\text{-BuLi}$  could induce the homopolymerization of this monomer for a period of 99 hours. However, methylenecyclobutane could be copolymerized readily with several vinyl monomers by a free radical initiator [13].

## 2. Cyclobutenes [14]

Natta and co-workers studied the stereospecific polymerizations of cyclobutene and found that it can be polymerized by four different groups of catalysts to stereoregular polymers having four different types of structure:



The two types of polycyclobutenes were determined by marked differences in some physical properties, and in particular by the use of X-ray spectra. The stereospecific polymerization of cyclobutene depends first of all on the nature of the transition metals. The catalyst systems can be classified according to relative electronegativity of the transition and noble metals as follows:

- (a) Catalysts containing more electronegative metals such as Cr, V, Ni, and Rh polymerize cyclobutene exclusively by double-bond opening.

- (b) Catalysts containing more electropositive metals such as Ti, Mo, W, and Ru polymerize cyclobutene exclusively by ring opening.

For example, 3-methylcyclobutene can be converted exclusively to trans-polypentadiene by the catalyst system of  $\text{RuCl}_3/\text{C}_2\text{H}_5\text{OH}$ .

### 3. Methylenecyclobutene

Polymethylenecyclobutene was first made by Roberts and co-workers in 1956 [26]. The bulk polymerization initiated by  $\text{BF}_3$  gave an insoluble polymer containing mainly the 1,5-structure. An anionic polymerization of methylenecyclobutene yielded predominantly the 1,2-addition type repeating unit. Combination of 1,2-addition, 3,5-addition and 1,5-addition were believed to occur in the free radical polymerization. The polymer structure in each case was determined by IR spectroscopy.

The du Pont Company in a patent in 1958 [16] utilized 3-methylenecyclobutene in preparing thermally-crosslinkable copolymers with a number of vinyl monomers.

### 4. 1-methy-3-methylenecyclobutene

In a patent issued in 1961, the du Pont Company made soluble copolymers of 1-methyl-3-methylenecyclobutene and other substituted 3-methylenecyclobutenes with a number of vinyl monomers. These copolymers could be converted to insoluble crosslinked products on heating to temperatures between 100°C and 325°C [17].

## C. Five-Member Ring Compounds

### 1. Cyclopentene [14]

Organometallic catalysts containing titanium, zirconium, molybdenum and tungsten polymerize cyclopentene exclusively by a ring-opening

reaction. The Ti or Zr containing catalysts form almost exclusively trans-polypentanamer in low yields while those based on  $\text{WCl}_5$  and  $\text{MoCl}_5$  produce all cis-polypentenamer in higher yields.  $\text{RuCl}_3$  in protic solvents does not polymerize cyclopentene.

## 2. 3-methylenecyclopentene

No study on the polymerizations of this cyclic diene has been found in the literature. Its polymerizability is expected to be good because of the highly strained conjugated double bonds.

## 3. 1,3-Cyclopentadienes

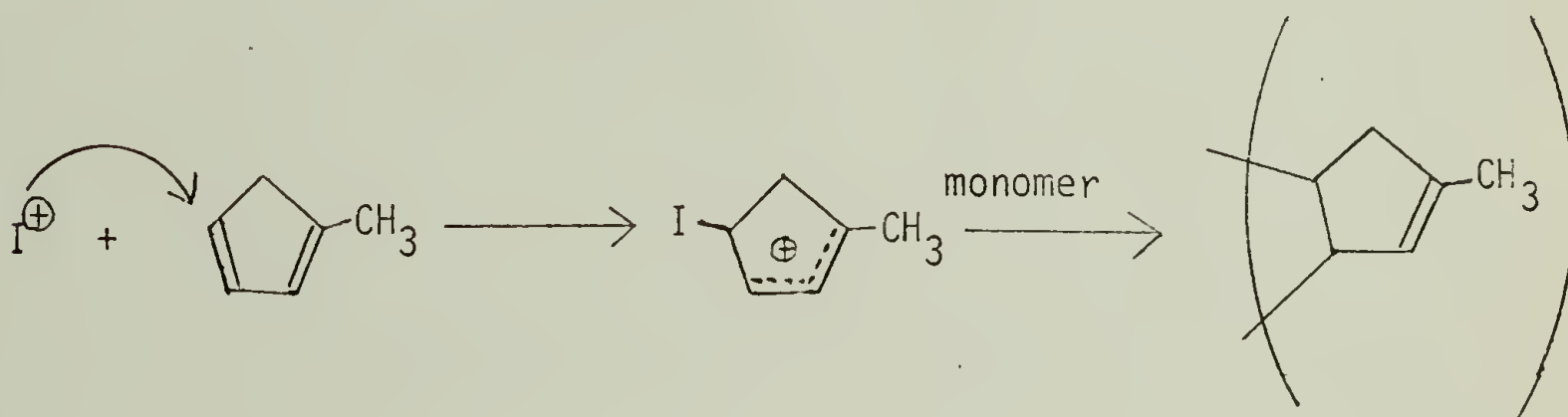
3.a. 1,3-Cyclopentadiene: Cyclopentadiene does not polymerize with anionic initiators and it produces only low molecular weight polymers by free radical initiators [18]. Okamura's group reported that cyclopentadiene polymerized rapidly with  $\text{TiCl}_4\text{-CCl}_3\text{CO}_2\text{H}$ ,  $\text{SnCl}_4\text{-CCl}_3\text{CO}_2\text{H}$  and  $\text{BF}_3$ -etherate in toluene at  $-78^\circ\text{C}$  [19]. A stationary and non-stationary polymerization mechanism was proposed to account for the interesting but complicated kinetic features observed in these polymerization systems.

Based on the characteristic NMR spectra of the model compounds, Aso and co-workers developed two methods of estimating the polymer structure from the relative peak area of the methine-methylene and olefinic protons [20]. Polycyclopentadiene obtained with Friedel-Crafts catalysts at low temperatures had predominantly 1,4- and 1,2-structures. The content of 1,2-structure varies with catalyst in the order of  $\text{TiCl}_4 > \text{AlBr}_3 > \text{SnCl}_4 > \text{BF}_3\text{-etherate}$  [21]. The structural variation of polycyclopentadiene was explained in terms of the tightness of the growing ion-pairs. A more acidic catalyst is considered to give a loose ion pair

with delocalization of the positive charge, resulting in less selective attack by another monomer.

Polycyclopentadienes prepared with cationic initiators undergo rapid autoxidation reactions apparently because there exists labile allylic tertiary hydrogen atoms in the polymer repeating units [22]. The activation energy of the abstraction of these tertiary hydrogen atoms by molecular oxygen was found to be as low as 14.9 kcal/mole.

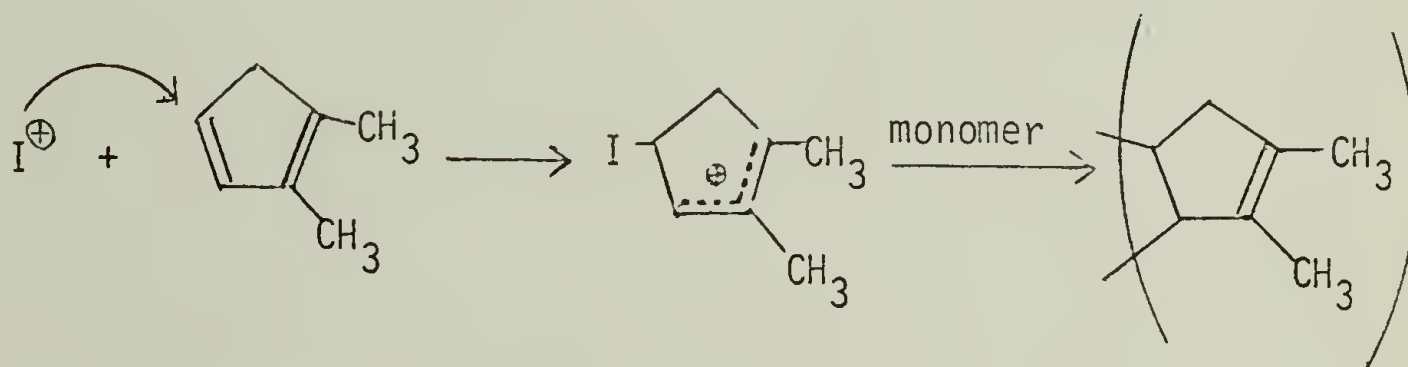
3.b. 1-Methylcyclopentadiene [22,23,24]: The 3,4-structure seems to be predominantly produced by the cationic polymerization of this monomer. The suggested mechanism is that cation adds mainly at carbon 4 of 1-methylcyclopentadiene to yield an allylic cation stabilized at the methyl group and propagation takes place at the secondary cation. The 1,4-structure is not favored in this case presumably because of the steric effect of the methyl group.



3.c. 2-Methylcyclopentadiene [22,23]: This monomer is more reactive than 1-methylcyclopentadiene apparently because there are two reactive sites for attack by the growing cation at carbons 1 and 4. Polymers with predominantly 1,4-structure are obtained, but some 3,4-structure is also found.

3.d. Allyl-substituted cyclopentadienes [25]: The cationic polymerizations of allylcyclopentadiene, methallylcyclopentadiene and allylmethylcyclopentadiene occur almost entirely through the double bonds in the cyclopentadiene ring. The amount of 1,4-structure increases with increasing steric hindrance around the conjugated double bond system. The 1,4-addition is readily achieved in the polymerizations of 2-substituted cyclopentadiene while 3,4-addition occurs primarily in 1-substituted cyclopentadienes.

3.e. 1,2-Dimethylcyclopentadiene [22,23]: A propagating cation adds predominantly to carbon 4 of this monomer and the chain grows from the secondary carbonium ion. Consequently, the polymer has an almost pure 3,4 structure.



3.f. 2,3-Dimethylcyclopentadiene [22,23]: The situation is similar to that of the 1,2-dimethylcyclopentadiene, and the polymer again has essentially the 1,4-structure.

3.g. 1,3-Dimethylcyclopentadiene [22,23]: The propagating cation preferentially attacks carbon 4 of this monomer because this position has more partial negative charge than carbon 1 and a more highly resonance stabilized cation is formed. The amounts of 1,4- and 3,4-structures vary with the tightness of the ion pair, and the propagation takes place through the tertiary cation. If the ion pair is tight,

the monomer attacks preferentially at 1-position giving more 1,4-structure. If the ion pair is loose, the monomer attacks both 1- and 3-positions resulting in about equal amounts 1,4- and 3,4-placements.

After a series of studies on polymers from cyclic dienes, Aso and co-workers proposed the following common rules which determine the modes of monomer addition in cationic polymerizations of cyclopentadiene and substituted cyclopentadienes [22,23]:

(i) A propagating cation reacts with monomer so as to form an allylic cation.

(ii) A propagating cation adds predominantly to the unsubstituted position of a substituted monomer, thus avoiding the formation of a quaternary carbon.

(iii) When there are two possible reaction sites, such as the secondary and the tertiary carbonium ions in a propagating allylic cation formed for a substituted cyclopentadiene, propagation from the secondary carbonium ion is predominant because it is more reactive and sterically less hindered.

(iv) When polymerization conditions favor a tight ion pair, the anion hinders the approach of monomer to the cation from the side at which the anion is located.

## EXPERIMENTAL

### General.

Elemental analyses were performed by Mr. Charles Meade of the University of Massachusetts Office of Research Services, Chemical Analysis Laboratory, Amherst, Massachusetts. Molecular weight determinations were run at 50°C in benzene solution on a Mechrolab Model No. 302 Vapor Pressure Osmometer.

Proton NMR spectra were recorded on a Varian Associates A-60 spectrometer. An internal tetramethylsilane reference was employed for all NMR spectra. Infrared spectra were run on a Perkin Elmer 257 and a Beckman IR-10 spectrophotometer.

Thermal analyses were run on a Perkin Elmer Model DSC 1-B Differential Scanning Calorimeter. All scanning speeds were 10°C per minute unless otherwise noted. Polymer birefringence was examined on a Carl Zeiss Polarizing Microscope equipped with a hot stage.

The prepurified nitrogen gas used in the polymerization reaction was further purified by passing it through a 30 cm-long glass column packed with pulverized BASF's BTS copper catalyst and 20 cm-long glass column packed with Linde 3A molecular sieves which was immersed in a dry ice-propanol cold bath. A stainless steel needle was attached to a Tygon tubing at the end of nitrogen scrubbing system so as to insert it through one of the self-sealing septum caps of a polymerization flask.

Polymerization flasks and Trubore stirring unit were soaked in dichromate cleaning solution overnight, and thoroughly washed with water and finally rinsed with distilled water. All glassware was dried

in an oven maintained at 150°C for several hours. When ready for use, they were taken out of the oven and, while still hot, quickly assembled and the flask was capped with rubber septum(s) which was further tightened by copper wire around the neck.

The polymerization flask equipped with Trubore stirrer and septum caps was evacuated under flame and then filled with pure nitrogen by the use of a needle attached to nitrogen scrubbing and vacuum pumping systems. The successive procedure of evacuation and nitrogen-filling was repeated several times. Finally a slight positive nitrogen pressure in the polymerization flask was maintained before charging reactants into the flask. No more nitrogen was passed through the flask during the course of polymerization.

Hypodermic syringes were washed with dichromate cleaning solution and thoroughly rinsed with water and with distilled water before being dried in an oven. The syringes were cooled in a nitrogen stream by inserting the needle into a tubing through which prepurified nitrogen was passing.

Polymer precipitation and filtration were carried out in a large dry bag filled with nitrogen. The polymerization mixtures after termination were added dropwise to an excess of magnetically-stirred methanol containing a small amount of 2,2'-methylene-bis(4-methyl-6-tert-butyl phenol) antioxidant. The precipitant was filtered with a glass filter. The wet polymer was transferred to a flask which was wrapped with aluminum foil to exclude light and dried in vacuo overnight. Polymer characterization was carried out soon after the drying process to avoid possible antoxidation reaction.

Polymerization grade solvents such as n-hexane, benzene, toluene and methylene chloride were purified before use by washing with concentrated sulfuric acid with vigorous stirring for two days, then washing twice with water, dilute sodium carbonate solution, and water again. With the exception of methylene chloride, they were dried, refluxed and distilled over calcium chloride under purified nitrogen through a 30 cm column packed with small glass helices. Phosphorous pentoxide was used for methylene chloride.

$\text{BF}_3$  and anhydrous HBr gas (Matheson Co.) were used as received.  $\text{BF}_3$ -etherate was purified before use by distillation under reduced pressure and the center cut was collected. Diethylaluminum chloride (4.7 ml, 4.5 g; Texas Alkyl Inc.) was diluted as received with 16.5 ml purified benzene under nitrogen to make a 1.86 mmole per ml  $\text{AlEt}_2\text{Cl}$  solution.

Triisobutylaluminum (8.5 ml, 6.67 g; Texas Alkyl Inc.) was diluted as received with 20 ml purified n-hexane under nitrogen to make a 1.18 mmole per ml  $\text{Al}(\text{i-Bu})_3$  solution.

Vanadium trichloride was washed with purified n-hexane and dried in vacuo. Cobalt triacetylacetonate was recrystallized from absolute ethanol and dried in vacuo.

## EXPERIMENTAL

PART I. Poly-3-methylenecyclobutene1. Monomer preparation

1.a. 3-Methylenecyclobutanecarbonitrile. The procedure of Roberts and co-workers [26] was used except that the reaction was run for ten and half hours in a 2-liter stainless steel Parr bomb. The maximum yield was 60%. The purified sample had b.p. 66-67° (23 mm) and  $n_D^{25}$  1.4586.

Anal. Calcd. for  $C_6H_7N$ : C, 77.38; H, 7.58; N, 15.04

Found: C, 77.30; H, 6.73; N, 15.90

IR spectrum neat,  $cm^{-1}$  (intensity, assignment): 1689(m,  $CH_2=C$ )  
1422 (m, ring methylene); 2258 (s,  $C\equiv N$ );

NMR spectrum in  $CCl_4$ ,  $\tau$  (relative intensity, multiplicity, assignment): 5.10 (2H, q,  $CH_2=$ ); 6.9 (5H, m, cyclobutane ring).

Appendix, page 10, NMR Spectra No. 1.

1.b. 3-Methylenecyclobutanecarboxylic acid. The method of Roberts and co-workers [26] was followed. The compound had b.p. 82-83°C (2.5 mm) and  $n_D^{25}$  1.4658.

Anal. Calcd. for  $C_6H_8O_2$ : C, 64.27; H, 7.18; O, 28.54.

Found: C, 64.40; H, 7.36; O, 28.50.

IR spectrum neat,  $cm^{-1}$  (intensity, assignment): 880 (3,  $CH_2=$ ).

1419 (m, ring methylene); 1705 (s,  $C=O$ ); 2644, 2560, 1245,  
935 (m, COOH).

NMR spectrum in  $CCl_4$ ,  $\tau$  (relative intensity, multiplicity, assignment);  
-1.00 (1H, s, COOH); 7.64 (2H, m,  $CH_2=$ ); 8.55 (5H, m, cyclobutane ring). Appendix, page 10, NMR Spectra No. 2.

1.c. 3-Bromomethycyclobutanecarboxylic Acid. The method of Wiberg and co-workers [27] was used except that carbon tetrachloride was removed by a rotary evaporator after completion of the reaction. The maximum yield was 88%. The compound after distillation had b.p. 108-110°C (2.5 mm) and  $n_D^{25}$  1.4968.

Anal. Calcd. for  $C_6H_9O_2Br$ : C, 37.3; H, 4.7; Br, 41.4; O, 16.60

Found: C, 39.20; H, 4.34; Br, 40.50; O, 16.70

IR spectrum neat,  $cm^{-1}$  (intensity, assignment): 1422 (m, ring methylene); 1705 (s, C=O).

NMR spectrum in  $CCl_4$ ,  $\tau$  (relative intensity, multiplicity, assignment): 6.59 (1H, m, methine  $\alpha$  to COOH); 7.25 (2H, m,  $CH_2Br$ ); 7.30-9.21 (5H, m, cyclobutane ring).

1.d. 3-Bromomethylcyclobutyl Bromide. The procedure of Wiberg and co-workers [27] was followed. Most of the carbon tetrachloride was removed by use of a rotary evaporator before the reaction product was distilled under reduced pressure. The yield was 60-79%, b.p. 55-60° (0.4mm),  $n_D^{25}$  1.5342.

Anal. Calcd. for  $C_5H_8Br_2$ : C, 26.3; H, 3.5; Br, 70.1

Found: C, 27.55; H, 3.35; Br, 69.00

IR spectrum neat,  $cm^{-1}$  (intensity, assignment): 1421 (m, ring methylene).

NMR spectrum in  $CCl_4$ ,  $\tau$  (relative intensity, multiplicity, assignment): 5.55 (1H, q, methine  $\alpha$  to Br); 6.50 (2H, d,  $CH_2Br$ ); 6.70-8.50 (5H, m, cyclobutane ring).

1.e. 3-Methylenecyclobutene. Into a 500 ml round-bottom, three-neck flask fitted with a Trubore stirrer, a pressure-equalizing addition funnel, and a short upright condenser leading through a dry ice-

methanol cold trap to a vacuum line, were charged 220 ml of diethylene glycol and 16.0 g of sodium methoxide (0.296 mole). The mixture was stirred and heated to 170°C in a silicone oil bath, and the pressure was reduced to about 300 mm as 15.0 g (0.066 mole) of 3-bromomethylcyclobutyl bromide was added dropwise from the addition funnel during 1.5 hours. Crude diene was collected in the cold trap. Heating was continued for an additional 40 minutes after all of the dibromide had been added. The material in the cold trap was warmed to about 0°C and washed four times with 10 ml of precooled distilled water. The washed diene was then transferred to a 10 ml two-neck pear-shaped flask which was immersed in a dry ice cold bath, and residual water was frozen out and removed. After the diene was warmed to 0°C, 0.12 ml of *n*-BuLi solution (1,6 mole in hexane) was injected into the flask through a self-sealing cap while the flask was being shaken. The monomer was quickly distilled, under reduced pressure in nitrogen through a 15 cm long Vigreux column cooled by ice water, into a dry ice - methanol cold trap. A yield of 1.305 g of pure monomer (about 30% yield) was obtained.

IR spectrum in  $\text{CCl}_4$ ,  $\text{cm}^{-1}$  (intensity, assignment): 873 (s,  $\text{CH}_2=$ ); 1431 (m, ring methylene); 1666 (s, conjugated double bonds); 3096 (m,  $\text{CH}_2=$ ). See Appendix, page 1, IR Spectra No. 1.

NMR spectrum in  $\text{CCl}_4$ ,  $\tau$  (relative intensity, multiplicity, assignment): 3.51 (1H, m,  $\text{H}_b$ ); 3.84 (1H, s,  $\text{H}_a$ ); 5.47 (1H, s,  $\text{H}_c$ ); 5.67 (1H, s,  $\text{H}_d$ ); 7.21 (2H, s, ring methylene). Appendix, page 12, NMR Spectra No. 5.

Attempted synthesis of 3-Methylenecyclobutyl Bromide. 90.0 g of allene, 690 g (6.90 mole) of vinyl bromide, 5 g of hydroquinone and 35

ml of toluene were placed in a 2000 ml stainless steel Parr bomb. The bomb was heated at 260-270°C with stirring for 14 hours. After cooling to room temperature, the bomb was opened to give 200 ml (300 g) of unreacted vinyl bromide, 125 ml of black oily product, and 30 ml of liquid compound having b.p. 58-60°C (15 mm).

Anal. Calcd. for  $C_7H_{10}Br_2$ : C, 30.3; H, 4.10; Br, 65.51

Found: C, 26.63; H, 3.43; Br, 69.83

NMR spectrum in  $CCl_4$ ,  $\tau$  (relative intensity, multiplicity, assignment):

4.38 (2H, d,  $CH_2=$ ); 6.45-8.70 (8H, m, cyclohexane ring). Appendix, page 11, NMR Spectra No. 4.

## 2. Cationic Polymerizations

2.a. Bulk polymerization by  $BF_3$  gas. A 25 ml one-neck flat-bottom flask was set up for the polymerization reaction in the usual manner. By use of a hypodermic syringe, about 0.51 g (7.73 mmole) of the freshly purified monomer was injected into the flask while it was maintained in a -78° cold bath. About 3 ml of  $BF_3$  gas was injected through the self-sealing cap; a layer of pale yellow polymer film was formed the moment  $BF_3$  contacted this monomer. Even with vigorous shaking, the monomer below this polymer layer remained as a liquid. Using a long needle syringe, more  $BF_3$  was injected into the liquid monomer at the flask bottom, and localized yellow polymer was produced again. The polymerization reaction was stopped in 30 minutes by adding methanol. The total monomer conversion to polymer was about 35%.

### 2.b. Solution Polymerization by $BF_3$ -etherate at Room Temperature.

A 25 ml one-neck, flat-bottom flask with a Teflon magnetic bar and self-sealing septum cap was evacuated and filled with purified nitrogen. About 12 ml of pure  $CH_2Cl_2$  was distilled under nitrogen direct into the

polymerization flask. About 0.68 g of the freshly purified monomer (10.3 mmole) was then added to the flask, which was immediately capped and immersed in a water bath maintained at 22°C. With stirring begun, 15  $\mu$ l (0.1 mmole) of  $\text{BF}_3$ -etherate was injected into the flask and a yellow color immediately appeared. The polymerization reaction was stopped in 14 hours by adding methanol. After precipitation and drying, about 0.14 g (20% conversion) polymer was obtained.  $\bar{M}_n$ :3,100.

Autoxidation - Gel Formation Time. About 0.1 g of the above polymer was dissolved in 6 ml of reagent grade benzene. The polymer solution was then transferred into three vials containing a small amount of 2,2-methylene-bis(4-methyl-6-tert-butylphenol) antioxidant and into another three vials without the antioxidant. Either with or without antioxidant, one vial was filled with prepurified nitrogen, one with air, and the third with air but excluded from light by wrapping it with aluminum foil. The time required for gel formation in each vial was observed and recorded.

Autoxidation - IR Spectrum. A KBr disk of the above polymer was prepared and IR spectra were taken from time to time. Thus any structural change due to autoxidation was recorded.

2.c. Solution Polymerization by  $\text{AlEt}_2\text{Cl}$ -HBr. A 50 ml three-neck round-bottom flask provided with a Trubore stirrer and two self-sealing rubber caps was evacuated and filled with purified nitrogen in accordance with the normal procedure. About 1.5 g (22.7 mmole) of freshly distilled monomer and 20 ml of freshly prepared methylene chloride were charged via syringes into the flask which was immersed in a dry ice-isopropanol cold bath. Into the monomer solution was injected with stirring 0.27 ml of  $\text{AlEt}_2\text{Cl}$  solution (0.5 mmole) in benzene followed by 1.0 ml anhydrous HBr. A pale yellow color developed. The polymerization

reaction was run for three days and terminated by adding methanol.

Yield of the white, rubbery polymer after reprecipitation and drying was 0.53 g (35.4% yield).  $\bar{M}_n$ : 3,100.

Hydrogenation. About 0.16 g of the above polymer was dissolved in 10 ml of reagent grade benzene in a 100 ml Parr pressure bottle. 5% palladium on calcium carbonate was used as a catalyst. The hydrogenation was run at 43 psi for 61 hours in a medium pressure Parr apparatus.

2.d. Solution polymerization by  $\text{BF}_3$ -etherate at  $-78^\circ\text{C}$ . A 50 ml round-bottom, three-neck flask equipped with a Trubore stirrer and two septum caps was made ready for polymerization reaction in the usual way. About 1.3 g of the freshly distilled monomer (19.7 mmole) and 20 ml of freshly prepared *n*-hexane were injected into the flask which was maintained with stirring at  $-78^\circ\text{C}$ . Then through a micro syringe, 0.025 ml (0.2 mmole) of  $\text{BF}_3$ -etherate initiator was injected. A yellow precipitation was observed at the flask bottom, which increased its size as the polymerization reaction proceeded. At the end of four days, the polymerization was terminated by adding methanol. After precipitation and drying according to the usual procedure, 0.3 g (23% yield) of tough, white polymer was obtained.

3. Anionic Polymerization. A 10 ml round-bottom one-neck flask capped with a rubber septum was evacuated and filled with purified nitrogen according to the normal procedure. An amount of 0.60 g (8.17 mmole) of freshly prepared monomer was injected into the flask which was maintained in an ice-water bath. Then 0.06 ml of *n*-BuLi solution in *n*-hexane (40.8 mg, 0.48 mmole) was injected. A yellow color appeared

after an induction period of a few minutes. The polymerization reaction was run for 12 hours and terminated by adding methanol. After precipitation and drying, 0.24 g (40% yield) of white, rubbery polymer was obtained.  $\bar{M}_n$ :3,200.

## Part II. Poly-1-methyl-3-methylenecyclobutene

### 1. Monomer preparation

1.a. 3-Methylelecyclobutylcarbinylamine. In the reduction of 3-methylenecyclobutanecarbonitrile, the procedure of Amundsen and Nelson [27] was used except that anhydrous ether was distilled over  $\text{LiAlH}_4$  directly into the reaction flask filled with nitrogen. The yield was 59%.

IR spectrum neat,  $\text{cm}^{-1}$  (intensity, assignment): 872 (s,  $\text{CH}_2=$ ); 1416 (m, ring methylene); 3352, 3280, 1600 (m,  $\text{NH}_2$ ).

NMR spectrum in  $\text{CCl}_4$ ,  $\tau$  (relative intensity, multiplicity, assignment): 5.30 (2H, q,  $\text{CH}_2=$ ); 7.00-8.00 (7H, m, cyclobutane ring plus  $-\text{CH}_2-$ ); 8.95 (2H, s,  $\text{NH}_2$ ). Appendix, page 11, NMR Spectra No. 3.

### 1.b. (3-Methylenecyclobutylcarbinyl)-trimethylammonium Iodide.

The procedure of Roberts and co-workers [27] was used except that absolute ethanol was used instead of absolute methanol. One preparation gave 83% yield.

### (3-Methylenecyclobutylcarinyl)-trimethylammonium Hydroxide

The method of Roberts and co-workers [26] was used. The filtered solution was used directly in the following step of syntheses.

1.c. 1-Methyl-3-Methylenecyclobutene. The above filtered solution was concentrated by distillation at atmospheric pressure to remove most of the water at  $100^\circ\text{C}$ . When the pot temperature reached  $120^\circ\text{C}$ , the distillate began to come over in two phases and these were collected in a dry ice - methanol cold trap. The decomposition was considered to be completed when no more material was distilled over. The contents of the trap were warmed to about  $0^\circ\text{C}$  in an ice water bath and transferred

to a graduated addition funnel to discard the lower aqueous layer. The upper organic layer was kept in an ice water bath and washed several times with pre-cooled distilled water to remove trimethylamine. The crude washed diene was transferred to a 50 ml pear-shaped flask and dried over calcium hydride at 0°C until bubbles ceased evolving. A semi-micro still equipped with heating jacket was used to distill the monomer in nitrogen atmosphere to give 29% yield of pure monomer, b.p. 69-70°C. The monomer purity was further checked by a gas chromatographic analysis using a Parapak Q column.

IR spectrum in  $\text{CCl}_4$ ,  $\text{cm}^{-1}$  (intensity, assignment): 852 (s,  $\text{CH}_2=$ ); 3080 (m,  $\text{CH}_2=$ ); 1666 (s, conjugated double bonds); 1592 (s, internal double bond); 1440 (m, ring methylene); 1371 (w, methyl). Appendix, page 1, IR Spectra No. 2.

NMR spectrum in  $\text{CCl}_2$ ,  $\tau$  (relative intensity, multiplicity, assignment): 3.83 (1H, s,  $\text{H}_b$ ); 5.42 (1H, s,  $\text{H}_c$ ); 5.62 (1H, s,  $\text{H}_d$ ); 7.18 (2H, s, ring methylene); 8.03 (3H, s,  $\text{CH}_3$ ). Appendix, page 12, NMR Spectra No. 6.

## 2. Cationic polymerizations

2.a. Bulk polymerization by  $\text{BF}_3$  gas. A ten ml round-bottom one-neck flask capped with a rubber septum was flamed-out under vacuum and filled with purified nitrogen according to the usual procedure. While the flask was immersed in a dry ice - propanol cold bath, 0.31 g (3.87 mmole) of monomer was injected into the flask from a syringe. One ml of  $\text{BF}_3$  gas was then injected into the flask, and a yellow polymer formed immediately when the  $\text{BF}_3$  gas contacted the liquid monomer. Polymerization was stopped in ten minutes by adding methanol containing a small amount of 2,2'-methylenebis(4-methyl-6-tert-butylphenol) antioxidant. The benzene-

soluble and insoluble portions of the polymer were precipitated and dried in the usual manner. The total polymer yield was 66%.

2.b. Solution polymerization by  $\text{BF}_3$ -etherate. A 50-ml round-bottom three-neck (14/20 ground joint) flask provided with Trubore stirrer, Teflon paddle, and two septum caps tightened with wire was evacuated and filled with purified nitrogen in the usual way. While the polymerization flask was kept in a  $-78^\circ\text{C}$  cold bath, 15 ml of freshly prepared *n*-hexane and one ml of monomer (0.89 g, 11.2 mmole) were injected into the flask. Six ml of  $\text{BF}_3$ -etherate (6.75 mg, 0.48 mmole), distilled before use, was injected into the flask with stirring. A bright yellow color developed instantaneously, the polymerization solution became viscous in 15 minutes. The polymerization was run for 5.5 hours, and terminated by adding methanol. After precipitation and drying according to the normal procedure, 0.502 g of white polymer (71%) was obtained.

Anal. Calcd. for  $-(\text{C}_6\text{H}_8)_n-$ : C, 89.94; H, 10.06

Found: C, 89.60; H, 9.87

$\bar{M}_n$ : 19,200

2.c. Solution Polymerization by  $\text{AlEt}_2\text{Cl}$ -HBr. A 50 ml round-bottom three-neck flask equipped with Trubore stirrer and two septum caps was filled with purified nitrogen in the usual manner. After the flask was immersed in a dry ice - propanol cold bath, 20 ml of freshly prepared toluene, 1.5 ml of monomer (1.4 g, 18.1 mmole) and 0.14 ml of  $\text{AlEt}_2\text{Cl}$  solution in benzene (31.1 mg, 0.26 mmole) were injected in that order into the polymerization flask from syringes. The solution so obtained immediately became and remained pale yellow with continued stirring for ten minutes, then 2.5 ml of anhydrous HBr gas was injected from a

syringe, and a bright yellow color formed instantaneously. The polymerization was run for 5.5 hours and stopped by adding methanol. After precipitation and drying, 1.1 g of white polymer (77.5%) was obtained.

Anal. Calcd. for  $-(C_6H_8)-$ : C, 89.94; H, 10.06

Found: C, 89.56; H, 9.89.

$\bar{M}_n$  : 16,200

Hydrogenation - Method A: 0.2 g of the above polymer was dissolved in about 20 ml of reagent grade benzene in a 100 ml Parr pressure bottle. Hydrogenation was run with the aid of about 0.02 g of 5% palladium of calcium carbonate at 50 psi hydrogen pressure for three days using the Parr medium apparatus. The catalyst was removed by filtration and the polymer was precipitated in methanol and dried.

Hydrogenation - Method B. Into a 50 ml round-bottom three-neck flask was placed 0.15 g of the polymer dissolved in 10 ml of o-xylene and 0.2 of toluenesulfonylhydrazide. The mixture was heated at reflux under the nitrogen for three hours. After removing the solid residue by precipitation, the polymer was reprecipitated and dried.

### 3. Anionic Polymerizations

3.a. Bulk Polymerization. A 10 ml pear-shaped flask capped with a rubber septum was evacuated and filled with nitrogen in the usual manner. With a syringe, 0.4 g of monomer (5.0 mmole) was charged into the flask, then 0.015 ml of n-BuLi in hexane (10.2 mg, 0.12 mmole) was injected while the flask was maintained at room temperature. A slight yellow color developed but soon faded away. Another 0.015 ml initiator was added in two hours. The pale yellow color formed again but the monomer remained a non-viscous liquid over the entire reaction period of twenty-four hours.

3.b. Solution Polymerization. A 50 ml round-bottom three-neck flask equipped with a Trubore stirrer and two septum caps was set up for polymerization in the usual manner. An amount of 20 ml freshly prepared n-hexane and 0.8 ml monomer were injected into the polymerization flask which was maintained in a cold bath at  $-78^{\circ}\text{C}$ . Then through a syringe about 0.03 ml of n-BuLi solution was injected, but no color change was observed. After two hours, another 0.05 ml of initiator solution was added. Because there seemed to be no polymerization after 24 hours, the mixture was warmed up to  $0^{\circ}\text{C}$  with injection of another 0.08 ml of n-BuLi solution. After 48 hours, no polymer was observed when the polymerization mixture was poured into an excess of methanol.

#### 4. Polymerizations by Ziegler Natta Catalysts

4.a. Heterogeneous Catalyst of  $\text{Al}(\text{i-Bu})_3\text{-VCl}_3$ . A 50 ml round-bottom three-neck flask provided with a Trubore stirrer and two septum caps was set up for polymerization in the usual manner. An amount of 0.15 g of  $\text{VCl}_3$  (0.96 mmole) was added to the flask under nitrogen stream through an opened neck, which was quickly recapped, and 9 ml of freshly prepared hexane and 2.0 ml of  $\text{Al}(\text{i-Bu})_3$  catalyst solution in hexane (0.47 g, 2.4 mmole) were injected into the flask kept at room temperature of  $22^{\circ}\text{C}$ . The catalysts were aged with stirring for 15 minutes, then 1.8 ml of monomer (1.52 g, 19.0 mmole) was injected from a syringe. A yellowish-violet color formed and intensified in the reaction mixture as the polymerization proceeded. Polymerization reaction run at room temperature was terminated by adding methanol in twenty-four hours. The precipitated and filtered polymer was continuously washed with methanol

for several hours, and 1.1 g of benzene-insoluble polymer (75% yield) in the form of a white powder was obtained after drying in vacuo.

4.b. Heterogeneous Catalyst of  $\text{Al}(\text{i-Bu})_3\text{-VCl}_3$ . The exact procedure described above was repeated but with the following amounts of reactants being changed:

$\text{VCl}_3$	0.03 g (0.19 mmole)
$\text{Al}(\text{i-Bu})_3$ solution	0.4 ml (0.94 g, 0.48 mmole)
<u>n</u> -hexane	12 ml
monomer	2.5 ml (2.02 g, 25.2 mmole)

The polymerization reaction was run for twenty-four hours, after which the products were precipitated, washed and dried as above to yield 1.0 g of a white, slightly tacky polymer (50% conversion).

Anal. Calcd. for  $(\text{C}_6\text{H}_8)_n$ :- C, 89.94; H, 10.06.

Found: C, 86.05, H, 8.24

$\bar{M}_n$  : 19,500

4.c. Homogeneous Catalyst of  $\text{AlEt}_2\text{Cl-Co(acac)}_3$ . A 50 ml round-bottom three-neck flask equipped with a Trubore stirrer and two septum caps was set up for the polymerization reaction in the usual manner. To the flask, 0.71 g of  $\text{Co(acac)}_3$  (0.002 mmole) was added through an open neck under a stream of nitrogen, then 12 ml of freshly-distilled benzene and 0.54 ml of  $\text{AlEt}_2\text{Cl}$  solution (1.0 mmole) were injected into the flask while it was immersed in an ice water bath. After the homogeneous catalyst was aged for ten minutes, 2 ml of monomer (1.66 g, 20.08 mmole) was added from a syringe. A yellow color formed immediately in the reaction mixture. The polymerization reaction was run at 0°C for twenty-two

hours and terminated by adding methanol. The precipitated polymer was thoroughly washed with methanol and dried under vacuum at room temperature; 0.8 g of a white polymer (48.2%) was obtained.

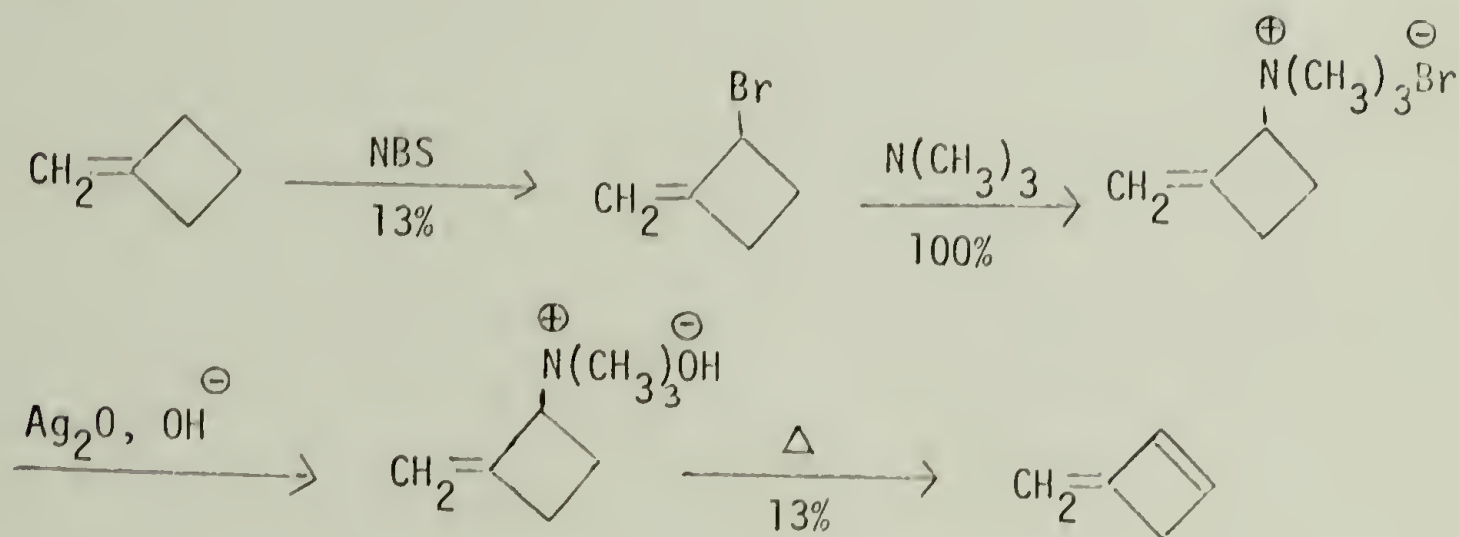
Anal. Calcd. for  $-(C_6H_8)_n-$ : C, 89.94; H, 10.06.

Found: C, 87.29; H, 9.65.

## RESULTS AND DISCUSSION

Part I. Poly-3-Methylenecyclobutene1. Monomer Synthesis and Purification

3-Methylenecyclobutene was first synthesized by Howton and Buchman [29,30] in 1956 from the pyrolysis of (2-methylenecyclobutyl)-trimethyl ammonium hydroxide. The sequence of preparation is shown in the following:

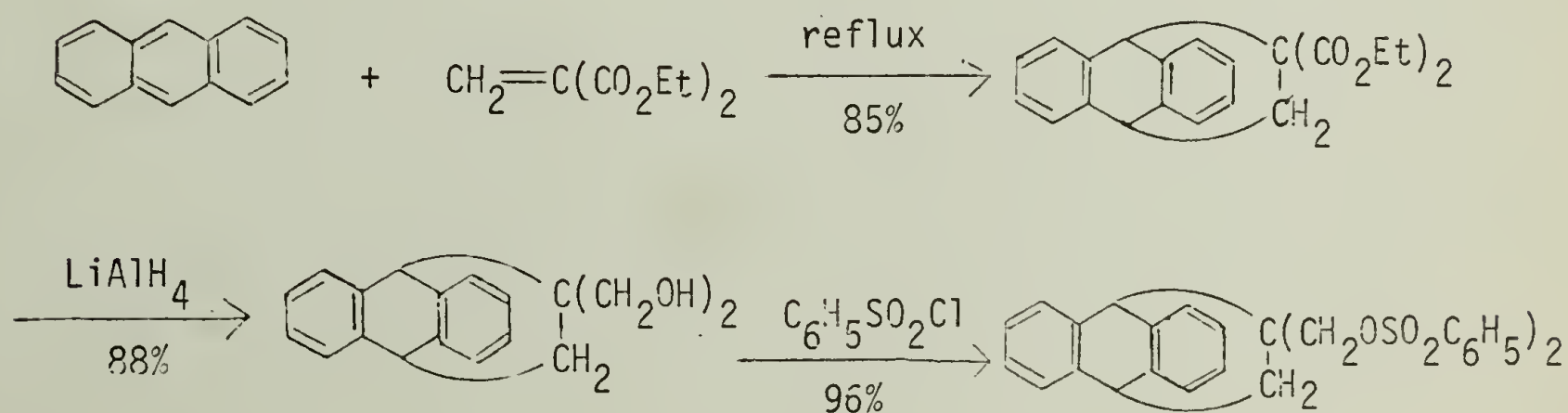


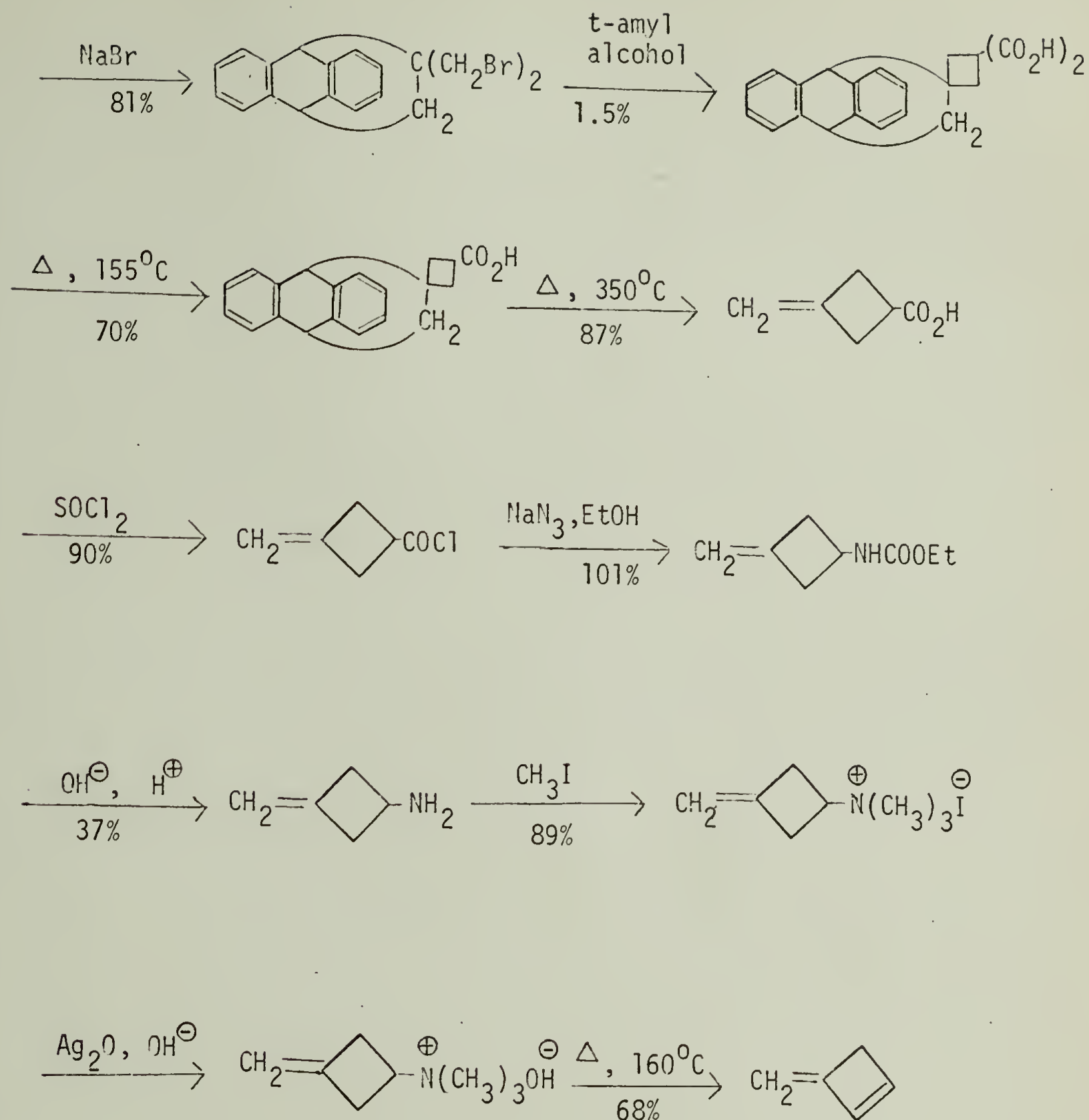
The Ziegler bromination of methylenecyclobutane by an equal molar amount of N-bromosuccinimide gave monobromide in 13% yield and dibromide in 56% yield. The overall yield was small. The structure of the diene was established by an infrared spectroscopic analysis.

Methylenecyclobutane is commercially available and it can also be made from pentaerythritol by the method of Roberts and co-workers [21]. It is expected that the formation of monobromide would be increased at the expense of dibromide if excess of methylenecyclobutane were used in the above Ziegler bromination. The unreacted methylenecyclobutane

could be recovered. Furthermore, it would be of interest to try dehydrobromination of 2-methylenecyclobutane bromide by such reagents as N-phenylmorpholine, silver oxide and trimethylphosphite to see if the compound could be produced.

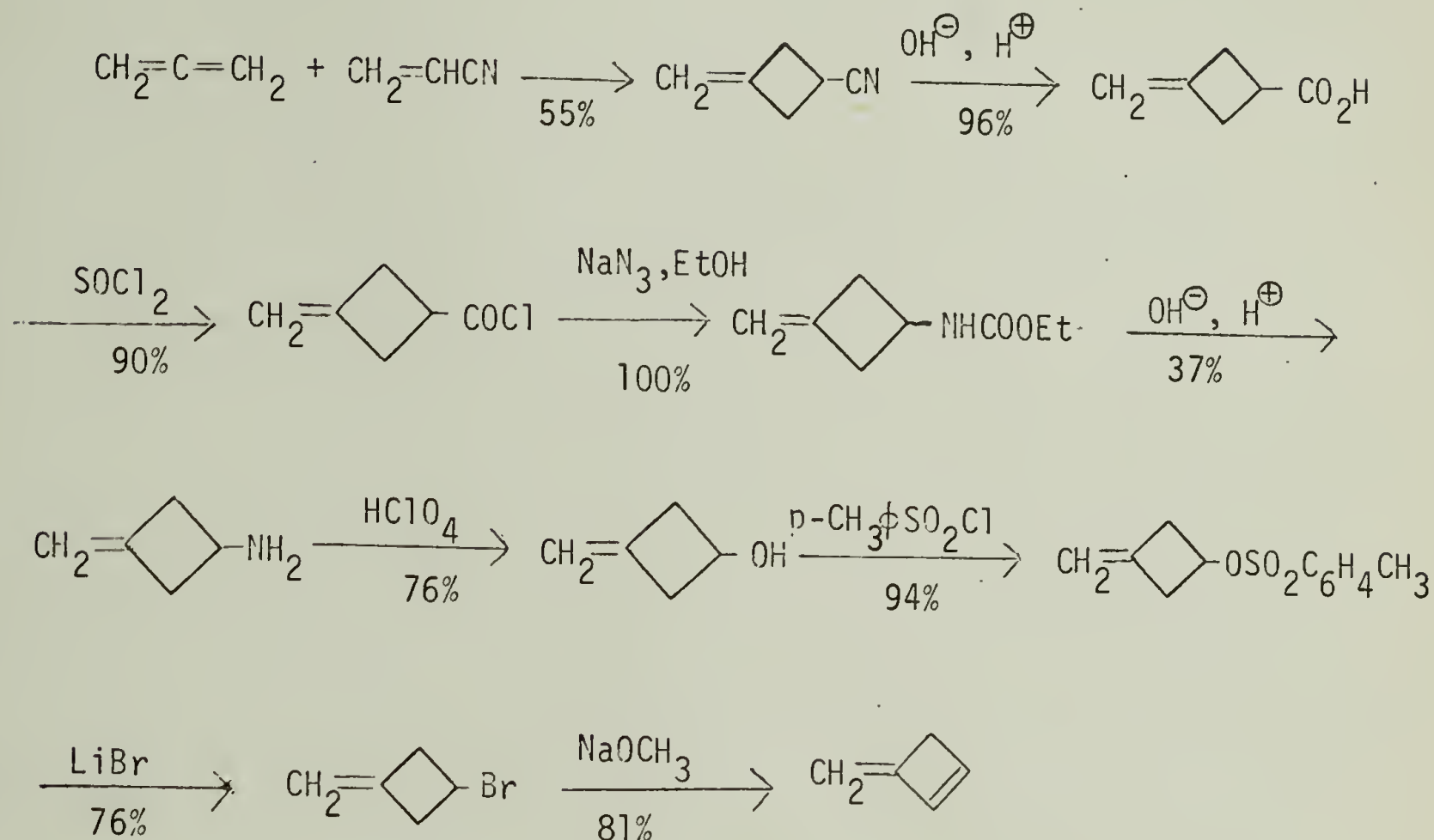
In the same year, Roberts and Applequist prepared 3-methylenecyclobutene [15] in order to study the stability of cyclobutadienyl-carbiny radical, cation and anion in relation to predictions of simple molecular orbital calculations. The compound was made from diethyl methylenemalonate by way of 3-methylenecyclobutylcarboxylic acid and 2-methylenecyclobutylamine. Their syntheses featured the use of anthracene as a blocking group for the exocyclic double bond during malonic ester closure of the cyclobutane ring. The total yield was negligibly small because conversion of 9,10-ethano-9,10-dihydro-11,11-bis(bromomethyl)anthracene to 2,3,5,6-dibenz-spiro(bicyclo[2.2.2]octane-7,1'-cyclobutane)-3',3'-dicarboxylic acid amounted to only 1.5%. The complicated synthetic steps are given in the following equation.





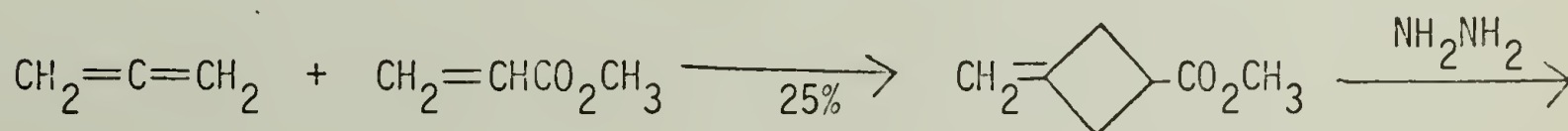
In the 1950's, high temperature, high pressure cycloaddition reactions were developed and found very useful to prepare four-membered ring compounds [32]. In 1961, Roberts and co-workers utilized the cycloaddition reaction to make 3-methylenecyclobutylcarbonitrile which was further

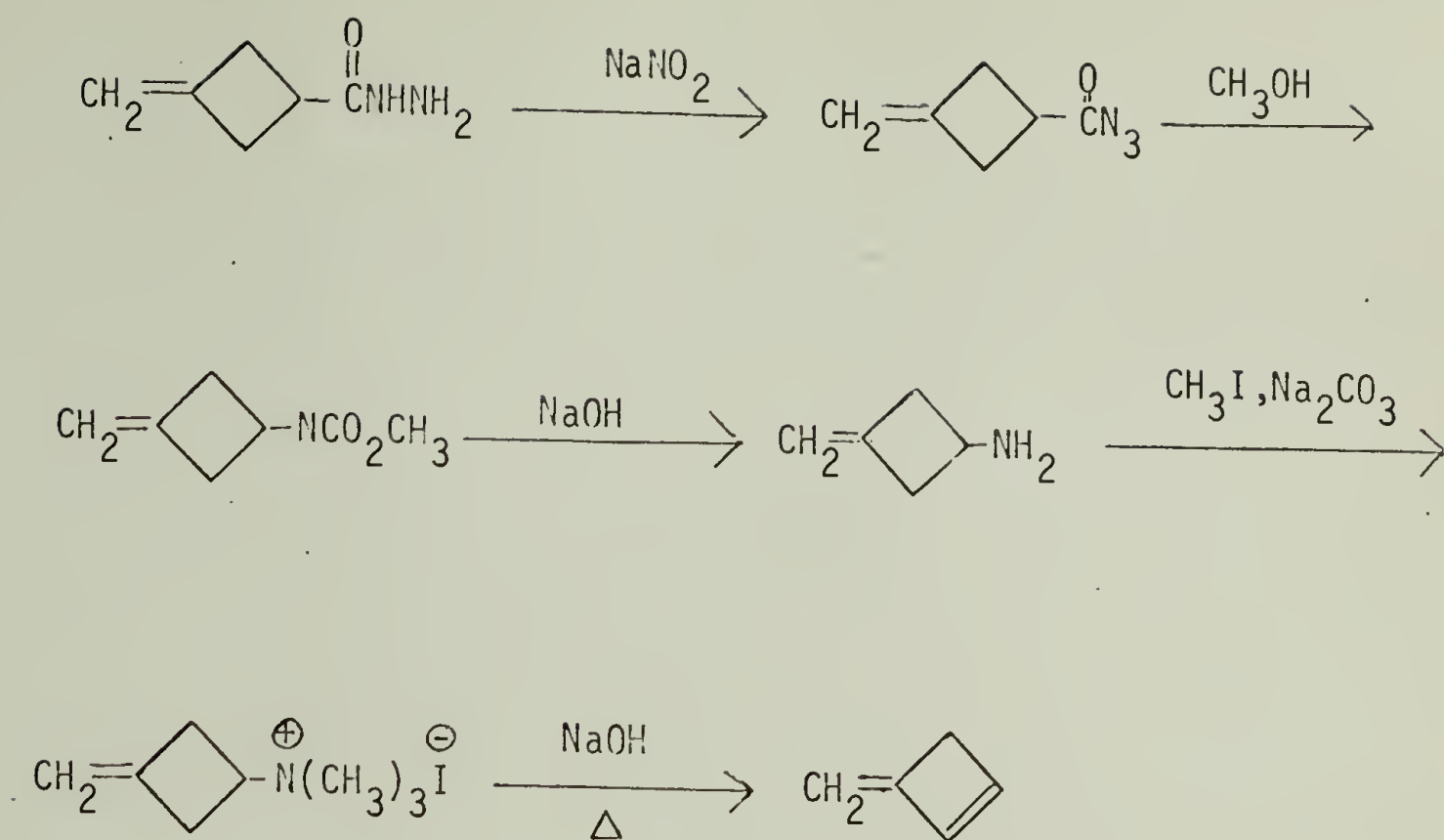
reacted under mild conditions to give 3-methylenecyclobutene [33]. This synthetic route is presented in the following sequence:



The above procedure showed improvement over the previous long tedious preparations. An overall yield of 8.1% was obtained. The IR spectrum of the diene sample was identical to that reported by Howton and Buchman. However, no NMR spectrum of the compound was given in that paper.

In a patent issued in 1958 [16], du Pont Company described roughly their method of preparing 3-methylenecyclobutene as follows:



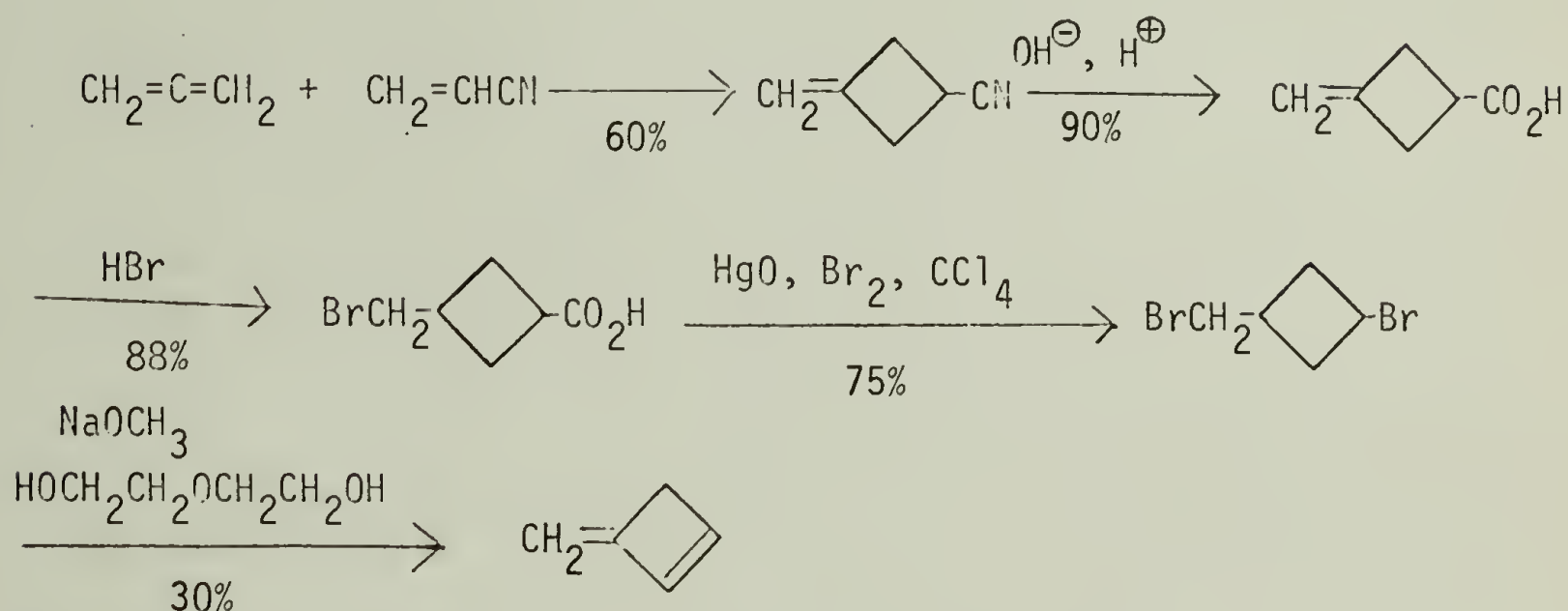


It is anticipated, not without reason, that a cycloaddition reaction between allene and acetylene might lead to a one-step synthesis of 3-methylenecyclobutene. However, Bensen and Lidsey [34] reported that the reaction of two moles of allene with one mole of acetylene gave 3,5-dimethylenecyclohexene in 45% yield and 3,5,7-trimethylenecyclooctene in 5% yield. It was an encouraging evidence that reaction between allene and phenylacetylene produce a 1% yield of 1-phenyl-3-methylenecyclobutene [31]. Hence, it might still be feasible to realize a direct synthesis of the monomer from allene and acetylene if right reaction conditions (such as employment of excess of acetylene and suitable catalysts) could be found.

In the present study, an attempt to make 3-methylenecyclobutyl bromide from 1.25 moles of allene with 6.45 moles of vinyl bromide was not successful. A small amount of a product was obtained which was identi-

fied as methylenecyclohexyl dibromide according to NMR and elemental analyses.

The monomer in this study was prepared in accordance with the steps and yields shown in the following equation:

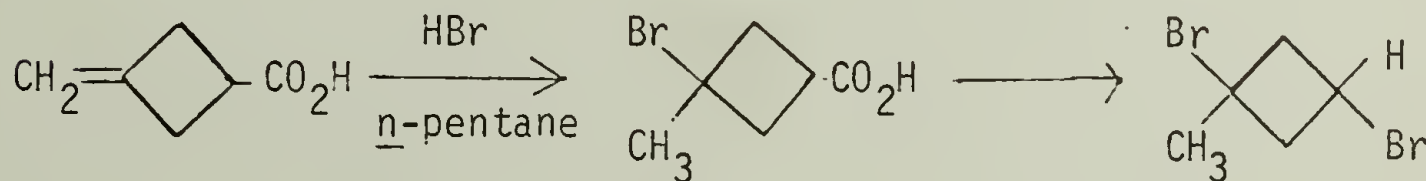


The procedures of Roberts and co-workers [15,33] were followed in the first two steps, and the methods of Wiberg and co-workers [27] were adopted in the HBr addition to 3-methylenecyclobutylcarboxylic acid and in the decarboxylation-bromination of the above bromoacid. The last step of double dehydrobromination was patterned after that of Roberts [33]. The total yield was about 10.7%, which is the same range as Roberts' second route, although the above scheme appears to be much simpler in terms of synthetic steps involved.

Because the monomer was unstable and readily polymerized on standing at room temperature and even at 0°C, it was found necessary to store bulk sample of (3-bromomethyl)cyclobutyl bromide in a refrigerator and to freshly prepare the monomer from 10 to 30 grams of dibromide each time a polymerization reaction was to be carried out.

Some difficulty was encountered in the double dehydrobromination reaction because the conversion was relatively low. The reason Roberts, et al. [33], could get 81% yield in the HBr elimination of 3-methylene-cyclobutyl bromide by sodium methoxide was apparently because abstraction of one of the four protons, at either the carbon 2 or carbon 4 position, was facilitated by the presence of the exocyclic double bond. The protons in the dibromide compound were less readily removed either because of the fully saturated structure or possibly because of steric effects operating in this compound, which presumably assumes a puckered ring conformation. In addition, the relatively low yield of HBr elimination of the dibromide could be explained on the basis that substitution as well as elimination might take place at the primary bromine. Secondly, the double dehydrobromination would lead to the formation of four trigonal carbon centers in the monomer resulting in a high ring strain. Thus an anionic reaction in cyclobutanes, involving  $C_{sp^3} \rightarrow C_{sp^2}$ , would be difficult according to I-strain theory of H. C. Brown [35]. One attempt to increase the efficiency of double dehydrobromination by using a much stronger base, potassium tert-butoxide in diglyme, did not bring about the desired result.

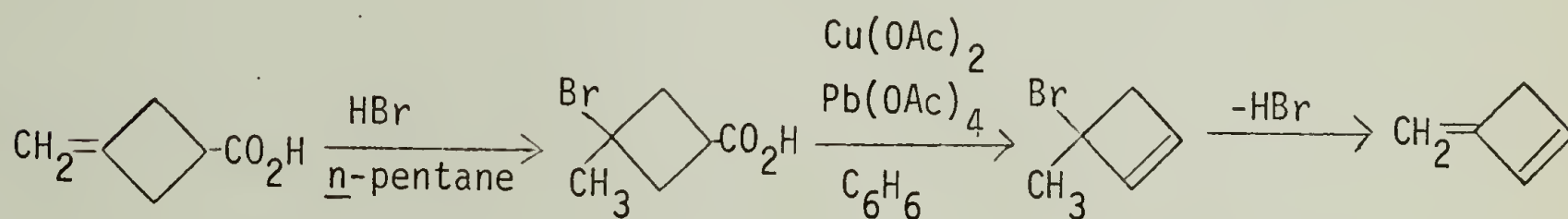
In order to minimize the difficulties mentioned above, 1,3-dibromo-3-methylcyclobutane could be prepared as presented in the following:



The above HBr addition across the exocyclic double bond is based

on the procedure employed by Wiberg, et al. who obtained 90% of yield in converting 3-methylenecyclobutane-1-methyl bromide to 3-bromo-3-methylcyclobutane-1-methyl bromide [27]. The modified Hunsdiecker reaction usually gives fairly high yield. Double HBr elimination from this compound would not produce 3-methylcyclobutadiene because this diene is known to be very unstable to the point of being non-existent in accordance with molecular orbital calculations [36]. Therefore, the major product should be 3-methylenecyclobutene. It is worthwhile to investigate the above modified synthetic routes aimed to increase the total yield.

Another possible way of modifying the present synthetic scheme is shown in the following equation:



Here, to avoid double dehydrobromination, the recently-developed method of preparing a cyclobutene from a cyclobutylcarboxylic acid by oxidative decarboxylation is utilized. The oxidative decarboxylation of cyclobutanecarboxylic acid has been found to produce 77% conversion [37]. No big problem would be expected in the base-catalyzed dehydrobromination of 3-bromo-3-methylcyclobutene.

In this study, several trials at carrying out an oxidative decarboxylation of 3-methylenecyclobutylcarboxylic acid by lead dioxide in temperature range of 150-170°C met with failure because this reaction was found to be explosive in nature.

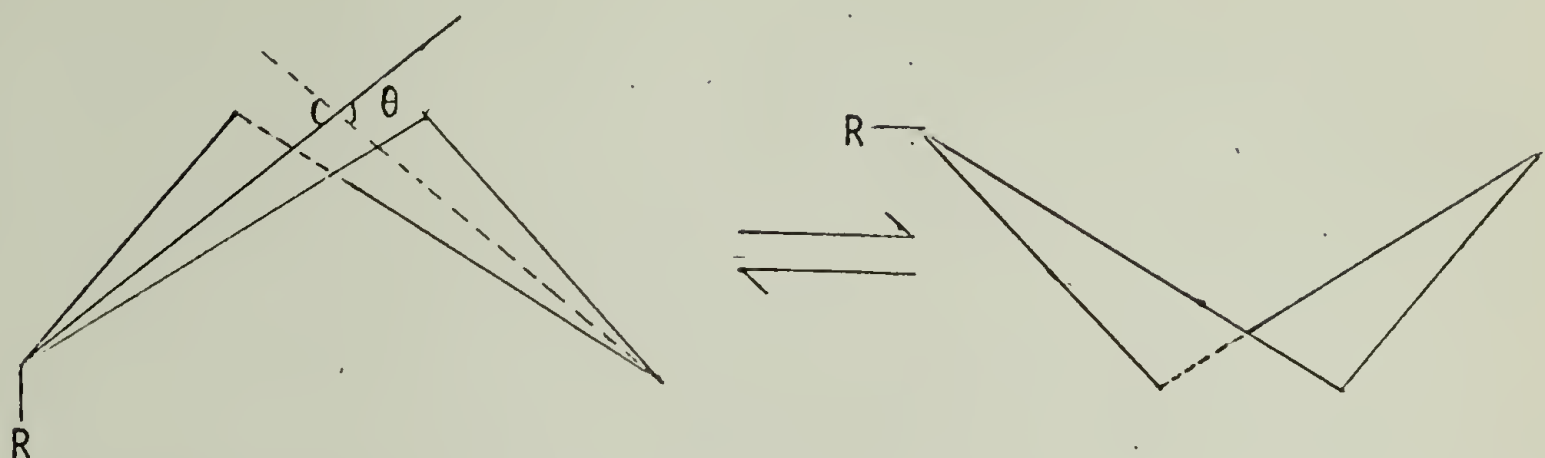
It is well-established that monomer of highest purity is essential for a successful polymerization reaction. The purification of 3-methylenecyclobutene, however, presented a problem. Small amounts of methanol and water impurities were always found in the washed monomer according to gas chromatographic analyses using a Porapak Q column. Because the monomer was capable of both cationic and anionic polymerization reactions, neutral drying agents such as Drierite, calcium chloride and calcium hydride were tried. These drying agents were found to be unsatisfactory because they could not remove methanol, which was a reactive terminating agent in ionic polymerizations. Moreover, the drying agents adsorbed the monomer causing its undesirable loss. Linde 4A molecular sieves seemed capable of removing both water and methanol, but complete removal of traces of water and methanol impurities could not be realized presumably because the adsorption was an equilibrium process.

The impurity problem was finally solved by use of a reactive initiator. A very small amount of n-butyllithium dissolved in n-hexane (1.6 M) was injected into the crude diene to rapidly destroy traces of water and methanol while the contents were shaken. The monomer was then quickly distilled under reduced pressure into a dry-ice cold trap. A minute amount of n-hexane was distilled over with the pure monomer, but it was not considered to be detrimental to subsequent polymerization reactions.

## 2. Monomer Structure

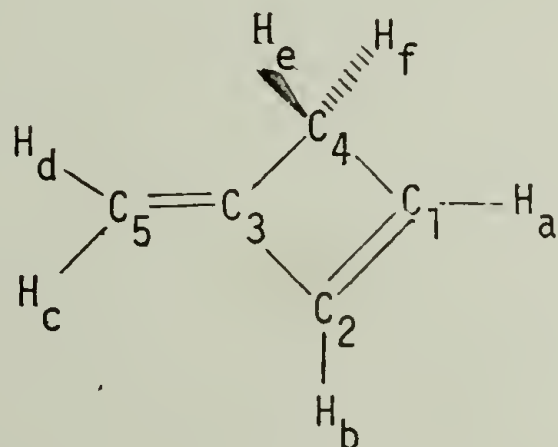
It is known that cyclobutane compounds assume a puckered ring conformation in order to relieve eclipsing interactions between adjacent hydrogens. Like a cyclohexane ring, it can then rapidly invert between

the two equivalent conformations [38] as depicted in the following figure:



The fold angle,  $\theta$ , is about  $20^\circ$  and can be as high as  $51^\circ$  depending upon the substituent(s) present [35]. If a double bond is introduced into a cyclobutane ring, the ring will be forced to assume a planar structure. Therefore, cyclobutene [39] and 3-methylenecyclobutene are planar in structure while (3-bromomethyl)cyclobutylcarboxylic acid and (3-bromomethyl)cyclobutyl bromide have puckered ring conformations.

The IR spectrum of the monomer (see Appendix, page 1, IR Spectra No. 1) was identical to that obtained by Roberts and co-workers [15]. The characteristic absorption bands of the exocyclic methylene appear at  $3090\text{ cm}^{-1}$ ,  $1667\text{ cm}^{-1}$  and  $873\text{ cm}^{-1}$ . The peak at  $3060\text{ cm}^{-1}$  is assigned to C-H stretching of the olefinic hydrogens of the endocyclic double bond. The ring methylene group shows characteristic peaks at  $3000\text{ cm}^{-1}$  and  $1436\text{ cm}^{-1}$ . The structure of the monomer with numbering of carbons and hydrogens is shown as follows:



The monomer presumably has a planar structure, and as a result,  $H_a$ ,  $H_b$ ,  $H_c$  and  $H_d$  should all lie in the same plane as the five carbons, while

$H_e$  and  $H_f$  should project above and below the plane. Since  $H_e$  and  $H_f$  are in identical chemical environments, they appear as a singlet at  $7.15\tau$  in the NMR spectrum of the monomer (see Appendix, page 12, NMR Spectra No. 5). Exocyclic methylene protons of methylenecyclobutene appear also as a singlet at  $5.30\tau$  because of the symmetrical structure [40]. Hence, the two singlets at  $5.47\tau$  and  $5.67\tau$  observed in the monomer spectrum can be assigned to the two exocyclic methylene protons. It is to be expected that  $H_c$  and  $H_d$  have different electronic surroundings and that the peak at  $5.47\tau$  can be assigned to  $H_c$  because this proton experiences the deshielding effect of the endocyclic double bond nearby. Coupling between  $H_c$  and  $H_d$  is negligibly small and the long range couplings are also not noticeable.

The chemical shift of the olefinic protons of cyclobutene is  $4.05\tau$  [41], thus the multiplets at  $3.51\tau$  and  $3.84\tau$  observed for the monomer can be assigned to the olefinic protons.  $H_b$  is close to the exocyclic double bond which will shift  $H_b$  downfield by the deshielding anisotropy, so the multiplet at  $3.51\tau$  is ascribed to  $H_b$  and the one at  $3.83\tau$  to  $H_a$ . Based on Roberts' analysis of cyclobutene proton spectrum [41] which shows  $J_{ab}$  to be 2.7 Hz and  $J_{ae,af}$  to be -0.80 Hz,  $H_a$  peak should be mainly split into a doublet with small shoulders. As for  $H_b$ , it is expected to couple with  $H_a$  by  $J_{ab}=2.7\text{Hz}$ , with  $H_e$  and  $H_f$  by  $J_{ae,af}=1.55\text{Hz}$ . It is therefore, reasonable that  $H_b$  appears as a multiplet at  $3.51\tau$ .

Simple molecular orbital calculations of the monomer [15,42] indicate that it should contain a partial negative charge at carbon 5 and

a partial positive charge at carbon 1. The NMR spectrum seems to support this theoretical finding. That is, because the electrons of the endocyclic double bond are polarized toward carbon 5, the olefinic protons show a downfield shift of about  $0.38\tau$  from those of cyclobutene at  $4.05\tau$ . On the other hand, the exocyclic methylene protons, being in an area of higher electron density, are shifted upfield by about  $0.27\tau$  from those found for methylenecyclobutane at  $5.30\tau$ .

## II. Cationic Polymerization

The data of cationic polymerizations of 3-methylenecyclobutene prepared with various initiators are collected in Table 1. In general, rather low yields of low molecular weight polymer were obtained.

It is interesting to note that a small amount of monomer contained in the discarded distilled water which was used to remove methanol from the crude monomer, polymerized itself in a few hours at room temperature in the presence of air and water. However, no attempt was made to characterize these polymers.

In addition to the successful polymerizations listed in Table 1, more than twenty runs of cationic polymerizations of 3-methylenecyclobutene met with failure. In three instances of bulk polymerization by  $\text{BF}_3$  at  $-78^\circ\text{C}$ , little excess of  $\text{BF}_3$  was injected into monomer in an attempt to increase initiation and propagation reactions. But when the reaction mixture was removed from the cold bath and allowed to warm up, the whole mixture quickly turned black apparently due to the consequent large exothermic reaction.

Solution polymerizations with  $\text{BF}_3$ -etherate in benzene and  $\text{CH}_2\text{Cl}_2$  at room temperature in the air atmosphere proceeded readily. No characterization was made of these polymers because they soon turned yellow after preparations.

In the early stage of this study, several attempted low temperature polymerizations by  $\text{BF}_3 \cdot \text{OEt}_2$  in heptane, hexane, toluene,  $\text{CH}_2\text{Cl}_2$ , by  $\text{AlEt}_2\text{Cl-HBr}$  in pentane,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  all failed because stringent requirements for the highest purity of polymerization glassware, nitrogen and especially monomer were not realized.

Table 1. Cationic polymerizations of 3-methylenecyclobutene

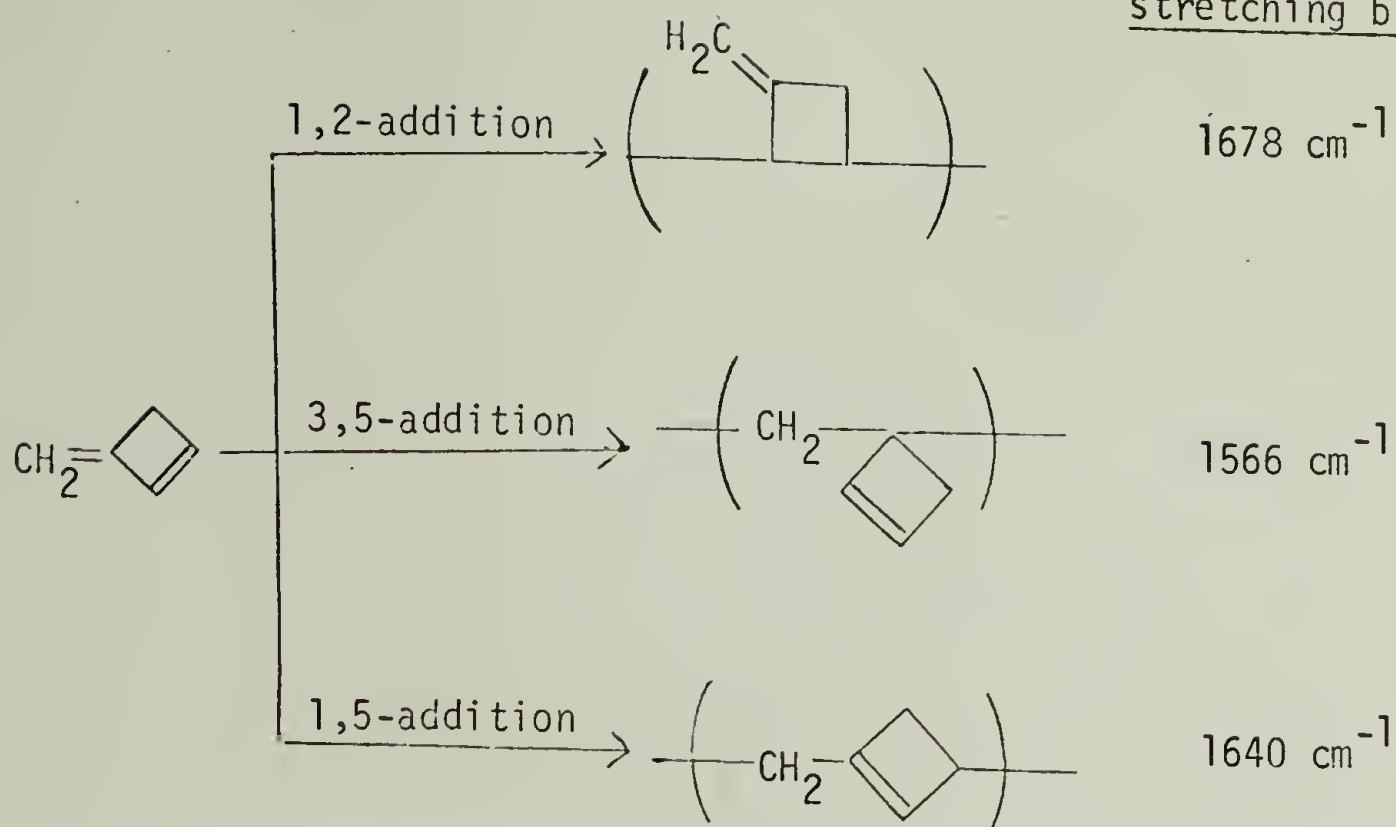
polymer	monomer (mmole)	initiator (mmole)	solvent (ml)	temperature, °C	time	yield, %	$\bar{M}_n$
A	7.7	BF <sub>3</sub> , 0.2	--	-78	30 minutes	35	--
B	10.3	BF <sub>3</sub> -etherate 0.1	CH <sub>2</sub> Cl <sub>2</sub> 11	22	14 hours	20	3,500
C	22.7	AlEt <sub>2</sub> Cl, 0.5	CH <sub>2</sub> Cl <sub>2</sub> 20	-78	3 days	35	3,100
D	19.7	BF <sub>3</sub> -etherate 0.2	hexane 20	-78	4 days	25	--

Polymerization of 3-methylenecyclobutene by  $\text{BF}_3$ -etherate in  $\text{CH}_2\text{Cl}_2$  at  $22^\circ\text{C}$  for 5 hours, by  $\text{AlEt}_2\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$  for 12 hours, and by  $\text{AlEt}_2\text{Cl}$  in benzene at  $22^\circ\text{C}$  for fourteen days produced 1.5-addition polymers which were already oxidized as shown by their IR spectra (see Appendix, page 2, IR Spectra Nos. 3 and 4).

### 1. Determination of Polymer Structure

1.a. Infrared Spectra: When an infrared spectrum was to be taken, polymers A, B and D (see Table 1) were found to be insoluble in common organic solvents after vacuum drying, apparently because rigorous precautions to prevent autoxidation were not carefully carried out. Consequently, IR spectra were taken on these samples in the form of KBr disks. Only the IR spectrum of the polymer initiated by  $\text{AlEt}_2\text{Cl}$  with HBr was obtained on a solution of the polymer in benzene.

Regardless of polymerization condition or the state of the sample, the IR spectra of cationally-prepared poly-3-methylenecyclobutene all exhibited essentially the same features (see Appendix, pages 2, 3, and 4, IR Spectra Nos. 3, 4, 5, 6, and 7). The three possible modes of chain propagation reactions, which would be expected to give polymers with the respective double bonds of these units, are shown in the following:



The IR band at  $1678 \text{ cm}^{-1}$  was absent in the polymer spectra; the possibility of 1,2-addition was ruled out, and this point was further confirmed by the absence of a band at  $3090 \text{ cm}^{-1}$  generally observed for the C-H stretching mode of an exocyclic methylene group. The weak band seen at  $855 \text{ cm}^{-1}$  is perhaps caused not by the exocyclic methylene but by the ring deformation.

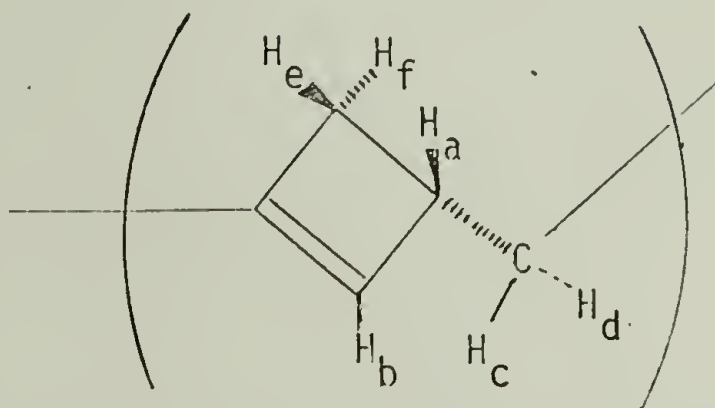
In view of the absence of a band around  $1566 \text{ cm}^{-1}$ , it was also reasonable to assume that propagation did not proceed by 3,5-addition. In the C=C stretching region, only a single band at  $1635 \text{ cm}^{-1}$  was observed which was close to that reported for the double bond stretching frequency of 1-methylcyclobutene at  $1640 \text{ cm}^{-1}$  [15,43]. Further evidence of 1,5-addition was provided by the appearance of a band at  $3030 \text{ cm}^{-1}$  attributable to the C-H stretching of an olefinic proton attached to the endocyclic double bond, and the appearance of a band at  $810 \text{ cm}^{-1}$  generally found for the C-H out-of-plane bending vibration of a tri-substituted double bond. On the basis of above analyses, it was

concluded that the cationic polymerizations of 3-methylenecyclobutene proceeded mainly by a 1,5-addition mechanism. Furthermore, the band at  $1435\text{ cm}^{-1}$  clearly indicated the presence of a four-membered ring in the polymer, so that ring-opening reactions do not make a significant contribution to this polymerization.

1.b. NMR Spectrum: Because of some difficulty encountered in polymer solubility, only one NMR spectrum with relatively good resolution could be obtained, that for polymer C which was initiated by  $\text{AlEt}_2\text{Cl-HBr}$ . This spectrum was taken in deuterated benzene at room temperature (see Appendix, page 13, NMR Spectra No. 7). The small peak at  $3.10\tau$  is ascribed to benzene impurity in the solvent. The 1,2-addition mechanism was again ruled out because there was no peak in the region of  $5.3\tau$  as would be found with the existence of an exocyclic methylene group. In view of the fact that the olefinic protons of cyclobutene appear at  $4.05\tau$  [41], the peak at  $4.40\tau$  is probably attributable to the olefinic protons attached to the endocyclic double bond. Both 3,5- and 1,5-chain propagation would lead to the formation of a repeating unit composed of a substituted-cyclobutene ring, but the integration of the spectrum revealed that this peak was about one fifth in area that of the rest of the peaks at  $7.20 - 8.40\tau$ . This area ratio would eliminate the possibility of 3,5-addition because the structure demanded for this placement would have a peak area ratio of 2 to 4. Accordingly, 1,5-addition again appears to be confirmed as the mechanism for the cationic polymerizations of 3-methylenecyclobutene. The area ratio between the olefinic protons and the remaining protons was about 1 to 5.6, which was close to the theoretical value of 1 to 5 calculated from the structure

of the repeating unit resulting from complete 1,5-propagation without any branching or crosslinking reaction.

The repeating unit of the polymers in Table 1 is, therefore, presented by the following structure:



The cyclobutene ring is believed to assume a planar structure. The singlet at  $4.40\tau$  then is assigned to  $H_b$  because it should experience a very small interaction from  $H_a$  along with negligible long range coupling constants. The doublet of two doublets at  $7.61\tau$  which contains two protons is assigned to  $H_c$  and  $H_d$ . The geminal coupling between  $H_c$  and  $H_d$  should be about 12-15 Hz whereas the vicinal coupling constant between  $H_a$  and  $H_c$  (or  $H_d$ ) should be about 2-9 Hz [44]. From the NMR spectra No. 7 on page A-13,  $J_{cd}$  is calculated to be 13 Hz and  $J_{ac,ad}=4\text{Hz}$ , which shows good agreement with the prediction. Hence  $H_c$  and  $H_d$  are split into a doublet by a coupling constant  $J_{c,d}=13\text{ Hz}$ , which is split again by coupling with  $H_a$ ,  $J_{ac,ad} = 4\text{ Hz}$ .

The doublet at  $8.07\tau$  contains three protons, and  $H_a$ ,  $H_e$  and  $H_f$  are expected to appear at about that position in the spectrum. There are complicated coupling constants among these three protons and with the other protons. At present, no reasonable explanation can be forwarded for the unsymmetrical doublet.

The shoulder at  $8.31\tau$  is probably due to a saturated cyclobutane

ring impurity which could possibly be formed by a crosslinking reaction through the endocyclic double bond. If this shoulder peak is excluded, the area ratio of the olefinic proton to the other protons becomes close to the value of 1:5 calculated from the linear polymer composed of 1,5-addition repeating unit.

Thus, the IR and NMR spectroscopic analyses clearly show that cationic polymerization of 3-methylenecyclobutene proceeds predominantly by 1,5-propagation mechanism.

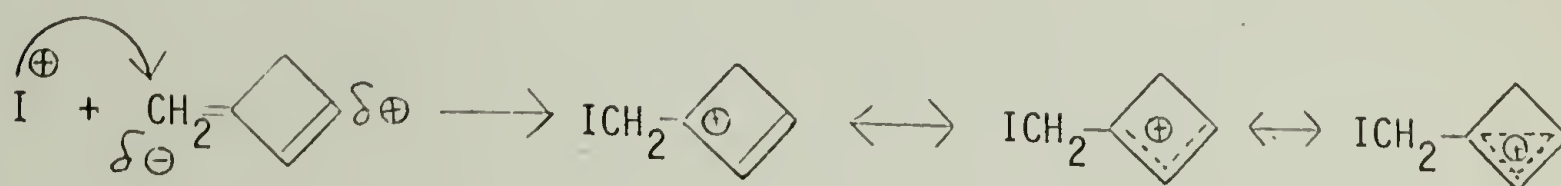
There is an asymmetric center in the polymer repeating unit and a pseudotacticity is expected. However, the analysis of the tacticity is difficult if not impossible because resolution of 60 MHz spectrum is not good enough to allow undisputable assignment, and more importantly because only sparse NMR data on four-membered ring compounds are available to be used as the basis for analysis.

## 2. Polymerization Mechanism

2.a. Initiation and Propagation: Roberts, et al. performed a bulk polymerization of 3-methylenecyclobutene at room temperature initiated by  $\text{BF}_3$  gas [15]. A brownish, translucent filmy polymer was found to deposit immediately when  $\text{BF}_3$  contacted the monomer. The polymer was insoluble in carbon tetrachloride and chloroform. From the presence of the band at  $1631\text{ cm}^{-1}$  and the absence of the band at  $1678\text{ cm}^{-1}$  which was due to exocyclic methylene group in the IR spectrum, he also concluded that polymerization proceeded by 1,5-addition path. Bromination of the monomer in  $\text{CCl}_4$  at  $0^\circ\text{C}$  produced only 3-bromo-1-bromomethylcyclobutene, which supported the mechanism of 1,5-propagation [15].

A simple molecular orbital calculation suggested that the monomer was polarized with a small negative charge at carbon 5 and a small

positive charge centered at carbon 1 [15,42]. The initiator therefore attacked the carbon 5 which bears a partial negative charge and formed an intermediate having an allylic carbonium which could be stabilized by delocalization in the ring as shown in the following equation:



The above intermediate may be homoaromatic in character because this structure fits Hückel's  $(4n+2)$  rule for a conjugated ring molecule. The propagation then took place at carbon 1 position because there was less steric hindrance to attack at this position compared to carbon 3.

This monomer being a conjugated small ring diene possesses a very large ring strain. The actual ring strain of the monomer has not been experimentally measured, but its value can be estimated from the heat of hydrogenation of methylenecyclobutane and cyclobutene. According to Turner [45], the heat of hydrogenation of methylenecyclobutane is 29.4 kcal/mole, whereas that of cyclobutene is 31.1 kcal/mole based on Kaarsemaker's experiment [46]. To a first approximation therefore, the ring strain of the monomer should be about 57.5 kcal/mole, which is the sum of 29.4 kcal/mole and 31.1 kcal/mole minus about 3 kcal/mole of stabilization due to the two double bonds being conjugated. This large ring strain undoubtedly provides the driving force for the polymerization reaction. About half of the total strain should be released in the process.

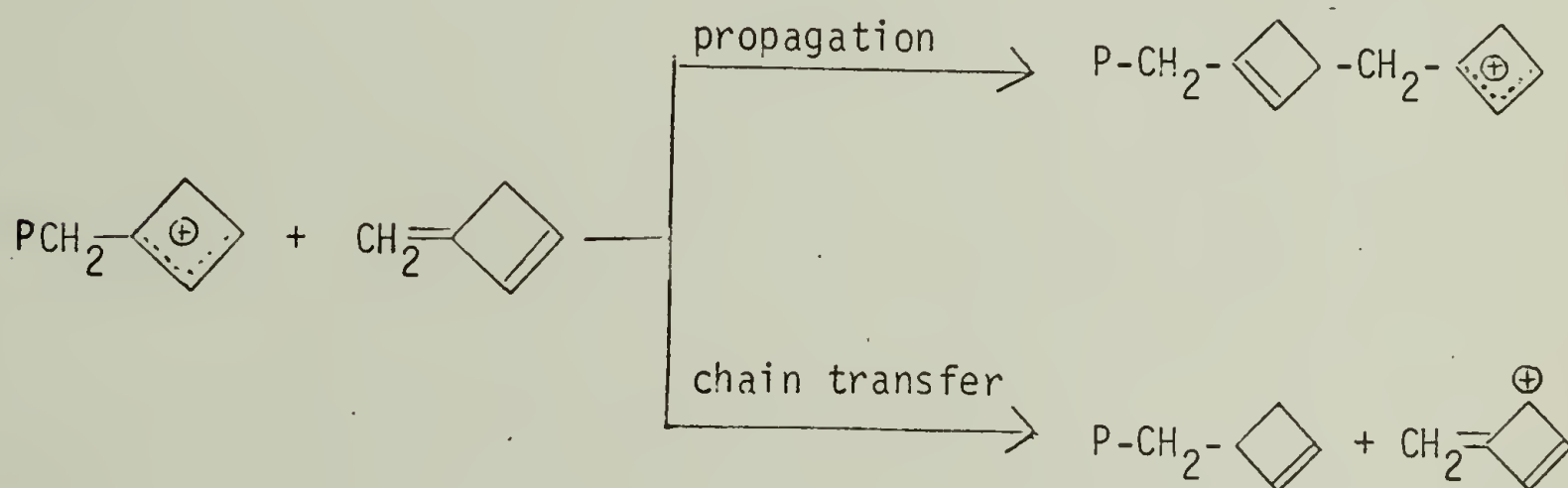
Roberts and co-workers observed that  $\text{BF}_3$ -initiated polymer turned brown soon after preparation. No explanation was offered. The phenomenon was probably caused by autoxidation of the polymer, which will be discussed in the next section.

The du Pont Company in a patent issued in 1958 [16] described a series of copolymers of 3-methylenecyclobutene with a number of ethylenically-unsaturated monomers. The copolymers usually contained 1 to 45 weight percent of polymerized 3-methylenecyclobutene, and it was found that these products could easily be crosslinked by heat treatment. However, no information on the molecular weights, polymer structure and modes of propagation was given in the patent literature.

2.b. Chain Transfer: Termination via chain transfer probably occurs to a substantial degree in the cationic polymerizations of 3-methylenecyclobutene, and accounts for the low molecular weights observed. It has been observed in this work that when  $\text{BF}_3$  contacted monomer liquid maintained at  $-78^\circ\text{C}$  in a cold bath, a layer of polymer film formed immediately at the surface while most of the monomer remained as a liquid beneath this film layer. Vigorous shaking of the reaction mixture failed to promote the propagation. Further injection of the initiator directly into the liquid monomer again produced only localized polymer. Hence, there seemed to be a sluggishness in the propagation reaction because most of the monomer remained unreacted in the reaction.

In the solution polymerizations of the monomer, only low number average molecular weights of 3,500 and 3,100 were obtained, corresponding to degree of polymerization of 53 and 47, respectively. The results of low molecular weight polymer and localized polymer film formation

lead one to speculate that termination through chain transfer takes place to a considerable extent in the cationic polymerizations of 3-methylenecyclobutene. As discussed in the section 2.a, the propagating intermediate for this reaction is  $\text{ICH}_2\text{-}\text{Cyclobutadienyl}^{\oplus} \leftrightarrow \text{ICH}_2\text{-}\text{Cyclobutadienyl}^{\oplus}$  which is expected to be rather stable, particularly if it behaves as a homoaromatic molecule in accord with Hückel's  $(4n+2)$  rule. On the other hand, simple molecular orbital calculations indicate the cyclobutadienylcarbinyl cation should also be very stable [15,42]. Consequently, carbon 4 in the monomer is a reactive chain transfer site because a hydride ion can be readily removed by either an initiator or a propagating cation to give this stable cyclobutadienylcarbinyl cation, which is resonance-stabilized by both endo and exo double bonds. The competing reactions for a growing cation between chain transfer and propagation, therefore, are presented in the following:



This highly possible chain transfer mechanism could account for the lack of prolonged propagation and for the consequent formation of low molecular weight polymers obtained in the cationic polymerizations of 3-methylenecyclobutene. In contrast, the  $\text{BF}_3$ -initiated polymer obtained

by Roberts and co-workers was insoluble in  $\text{CCl}_4$  and  $\text{CHCl}_3$ , and because of this they suggested that the polymer had a very high molecular weight and that chain transfer was absent [15]. However, their IR spectrum clearly showed the presence of a broad band at  $3100 - 3600 \text{ cm}^{-1}$  and a band at  $1725 \text{ cm}^{-1}$ , and the polymer soon turned brown after preparation. From this evidence and the characteristic bands in their IR spectrum of the polymer, it can be concluded that autoxidation occurred to their polymer to cause the insolubility.

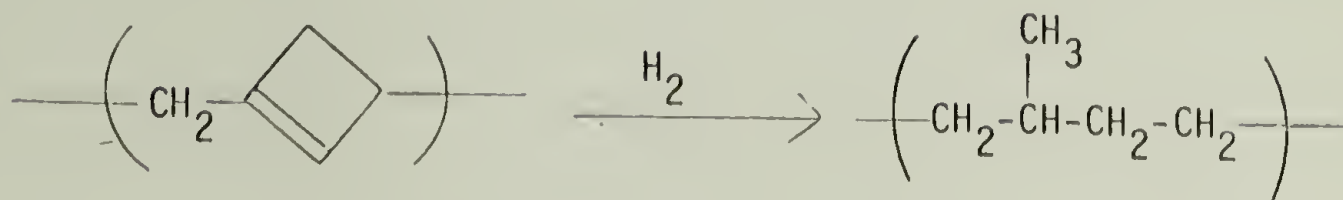
The broad band at  $3100-3600 \text{ cm}^{-1}$  can be assigned to hydroperoxide OH group, while the band  $1725 \text{ cm}^{-1}$  can be due to carbonyl group in the polymer formed by autoxidation. This autoxidation reaction could cause structural changes in the polymer such as crosslinking or decomposition which can account for the insolubility problem rather than crosslinking directly in the polymerization as suggested by Roberts and co-workers.

Moreover, Roberts and co-workers did not observe the lack of propagation in the polymerization of 3-methylenecyclobutene initiated by  $\text{BF}_3$  probably because the amount of monomer they used in the experiment was only 0.1 ml [15].

### 3. Polymer Reactions

3.a. Hydrogenation: Hydrogenation of the soluble polymer prepared by  $\text{AlEt}_2\text{Cl-HBr}$  was carried out in 10 ml benzene solution in a Parr medium apparatus with the aid of about 5% Pd on calcium carbonate as catalyst. The reaction was run for three days at 43 psi of hydrogen pressure. At the end of the reaction, an IR spectrum was taken, which showed the disappearance of the band at  $1435 \text{ cm}^{-1}$  due to ring methylene. Moreover, there appeared extra bands at  $1465 \text{ cm}^{-1}$  due to acyclic methylene and at  $1378 \text{ cm}^{-1}$  due to methyl group. From the IR spectroscopic

analysis, therefore, it was concluded that the cyclobutene ring was opened, and hydrogenolysis took place instead of the desired hydrogenation.

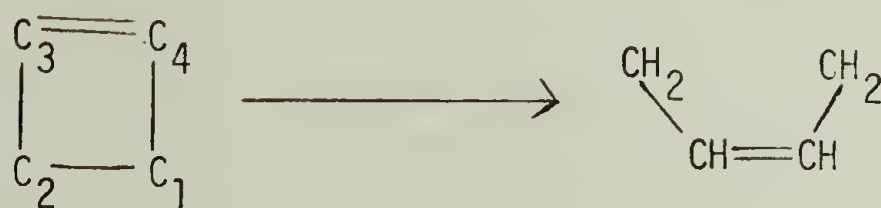


3.b. Crosslinking Reaction by Heat: As briefly mentioned in section 2.a., a patent of the du Pont Company made use of the thermal ring opening reaction of poly(3-methylenecyclobutene) for the preparation of crosslinkable copolymers [16]. These copolymers contained 1 to 45% of polymerized 3-methylenecyclobutene. Free radical, cationic, anionic and Ziegler-Natta type initiators were all capable of initiating the copolymerization reactions. Crosslinking reactions of the copolymers were effected simply by heat treatment at a moderate temperature between 100°C and 325°C. These crosslinkable copolymers were reportedly applicable in the fields of printing inks, laminates, finishes and fibres where the desired shapes could be made with the soluble copolymers and later converted to insoluble crosslinked products by heating. However, no discussion of the possible crosslinking mechanism was given in the present literature.

In this study, the cationically-prepared polymers all showed a single exothermic peak in the temperature range of 150 - 210°C when studied by differential scanning calorimetry (see Appendix, page 17). There was no endothermic peak for melting up to 300°C in the same thermograms. In the cooling curves, only a straight base line was observed

without any peaks. The irreversible exothermic peak was apparently caused by some chemical reaction, most probably by ring opening resulting in crosslinking.

Cyclobutane is known to undergo unimolecular homogeneous thermal decomposition at 420 - 468°C to form ethylene [47]. From kinetic studies, the energy of activation for the decomposition has been found to be 62.5 kcal/mole and the rate of reaction is  $k = 4.0 \times 10^{15} \exp. (-62,500/RT) \text{ sec}^{-1}$ .

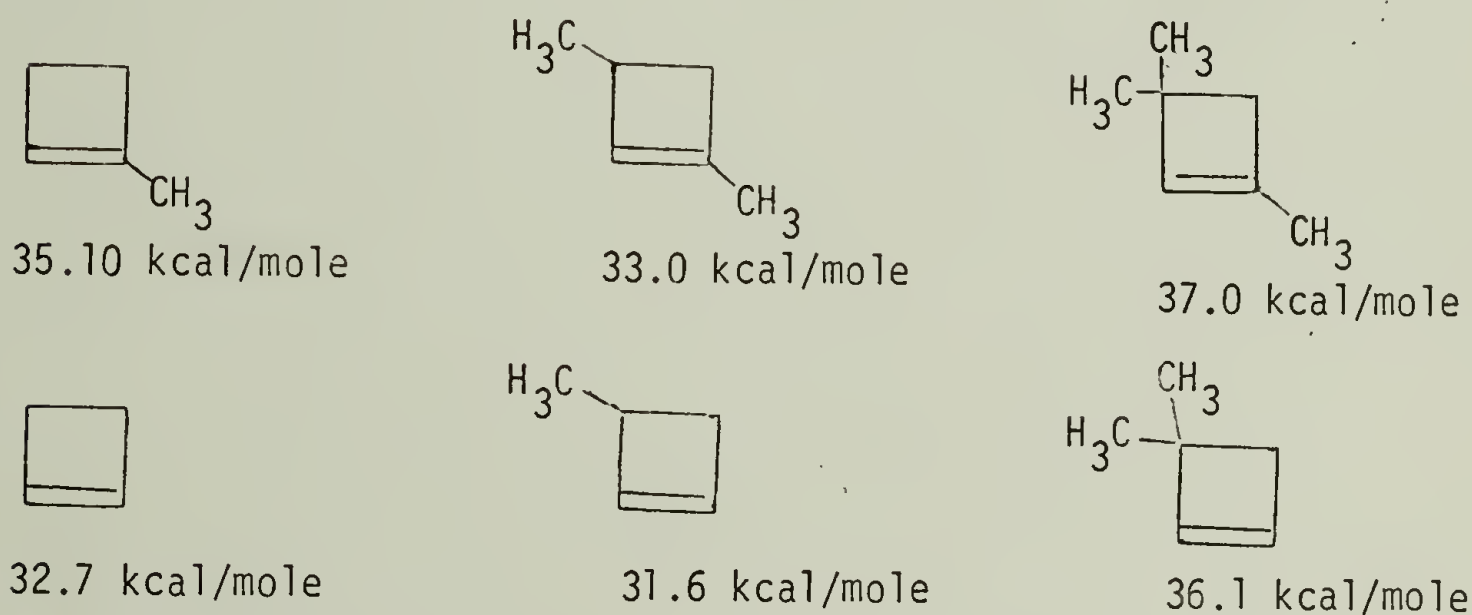


Walters, et al. observed that cyclobutene isomerizes into 1,3-butadiene at temperatures near 150°C [48,49]. From rate studies conducted in temperature range of 130°C - 175°C, it has been found that the thermal isomerization follows first order kinetics with energy of activation of 32.7 kcal/mole and a rate constant of  $1.2 \times 10^{13} \exp. (-32,500/RT) \text{ sec}^{-1}$ .

The considerably smaller energy of activation for the cyclobutene isomerization compared to that for cyclobutane permits the isomerization of cyclobutene to proceed at temperature considerably below that required for cyclobutane. The lability for ring opening of cyclobutene was attributed to the following factors: (a) weakening of carbon-carbon bond in the 3-4 position as a result of the influence of the double bond, (b) high ring strain, (c) the energetically unfavorable constellation of

the hydrogen atoms (or substituents) on carbon 3 and 4 [48].

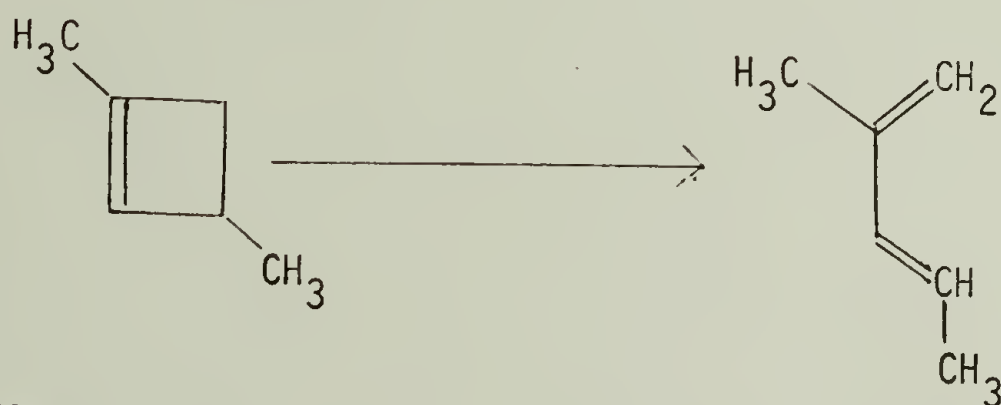
Vogel studied the substituent effect on the thermal stability of cyclobutene and found that electronegative groups such as halogens, acetate, COOH and COOR at carbon atoms 3 and/or 4 tend to enhance the thermal decomposition of cyclobutene [50]. Frey and co-workers conducted a series of thorough investigations of the thermal isomerization of substituted cyclobutene [51,52,53]. They concluded from their studies that substitution of a methyl group on the double bond in cyclobutene raises the energy of activation of the isomerization reaction relative to that of cyclobutene itself. Substitution of two methyl groups, one at each end of the double bond, increases this effect further. Substitution of the methyl group in the 3 or 4 position of the cyclobutene molecule causes a lowering of the energy of activation for the reaction. The energy of activation of some substituted cyclobutenes are listed in the following:



A conrotatory mechanism was postulated [51] to account for both the very low energy of activation values for cyclobutenes and the stereochemistry of the isomerization reaction. With methyl substitution at carbon 3 and/or 4, conrotation of these groups coincide with considerable

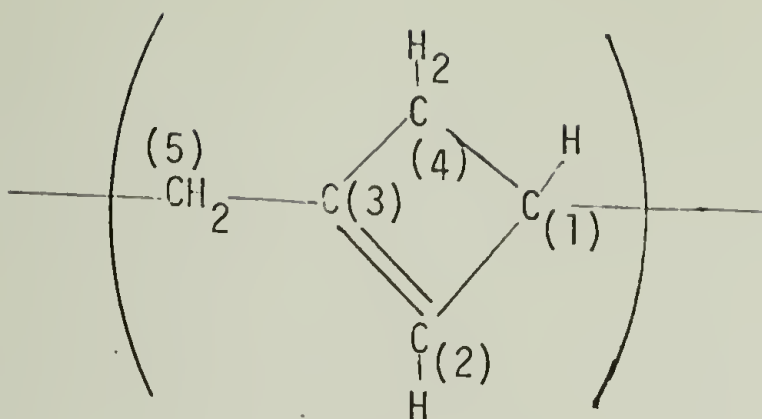
twisting of the cyclobutene ring. Substantial bond overlap occurs which further weakens the  $C_3-C_4$  bond, resulting in the rupture of this bond to form two new double bonds.

Kinetic studies of the thermal isomerization of 1,3-dimethylcyclobutene in the temperature range of  $121^\circ\text{C}$  -  $174^\circ\text{C}$  yielded an energy of activation of 33.0 kcal/mole and rate constant  $k = 10^{13.65} \times \exp. (-3,300/RT)$   $\text{sec}^{-1}$  [51]. The reaction was found to be the first order without any side product to give trans-2-methyl-penta-1,3-diene.



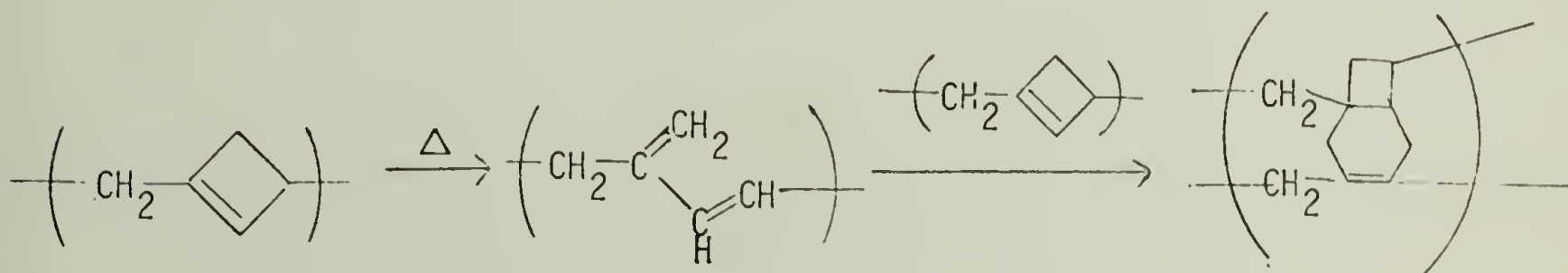
Methyl substitution at carbon 1 in cyclobutene tends to increase the energy of activation of the thermal isomerization, while a methyl substitution at carbon 3 tends to lower the activation energy relative to cyclobutene. These two effects cancelled each other in the compounds above, and consequently the activation energy of 33.0 kcal/mole obtained for the thermal isomerization of 1,3-dimethylcyclobutene was very close to the value of 32.7 kcal/mole for cyclobutene.

The cationic polymerization of 3-methylenecyclobutene was found to proceed by the path of 1,5-propagation so that the repeating units in the polymer chain backbone contained cyclobutene rings as shown by the following structure:



The cyclobutene ring in the repeating unit is substituted by methylene groups at carbon 1 and 3 positions and thus has a similar structure to 1,3-dimethylcyclobutene. The long polymer chain will undoubtedly impart some steric hindrance to rotation of the methylene groups attached to carbon 1 and 3 of the repeating cyclobutene ring so that the activation energy for thermal isomerization of the polymer may be increased slightly to a value higher than that of 33.0 kcal/mole for 1,3-dimethylcyclobutene. In the present study it was observed from calorimetric investigations that the polymer decomposition started to take place at 150°C which is about 30°C higher than that observed for 1,3-dimethylcyclobutene.

From the studies on low molecular weight compounds, it is suggested that a substituted trans-1,3-butadiene structure would be formed in the thermal isomerization of the polymers as depicted in the following equation:



The butadiene repeating units thus formed could react randomly with each other or with cyclobutene units by a Diels-Alder reaction at the temperature of isomerization to produce a highly crosslinked network as shown above. Both the isomerization of the polymers and subsequent crosslinking reaction should give off heat which accounts for the exothermic peak observed in the DSC thermograms. The polymer samples after heating were insoluble in benzene. An IR spectrum of polymer C after a DSC run was taken, but the resolution was not good enough to permit meaningful interpretation possibly because polymer autoxidation takes place along with the above ring opening reaction. The detailed mechanism of crosslinking reaction of poly-3-methylenecyclobutene deserves further investigation and elucidation.

Under a polarizing microscope, the original polymers showed a small amount of birefringence. However, no correlation could be found between the crosslinking reaction and the disappearance of the birefringence when the polymer samples were heated up to 300°C using a hot stage. The small birefringence gradually decreased in intensity with increasing temperature, and the sample turned charcoal brown after the heat treatment.

3.c. Autoxidation: All cationically-initiated polymers were soluble in benzene immediately after preparation but soon turned yellow and became insoluble in benzene if exposed to air or even if stored in nitrogen containing traces of oxygen. When stored in an air atmosphere for four days, polymer B was found to contain 11.51% of oxygen according to an elemental analysis. When the same polymer sample was analyzed again

in three weeks, the oxygen content was found to increase to 28.7%, which was confirmed by an IR spectrum showing the appearance of a broad band at  $3100 - 3600 \text{ cm}^{-1}$  and a carbonyl band at  $1720 \text{ cm}^{-1}$ .

Roberts, et al. prepared samples of poly-3-methylenecyclobutene initiated by a free radical, cationic and anionic initiators [15]. The IR spectra which they published for each of the three polymers unmistakably showed the presence of an OH absorption band around  $3400 \text{ cm}^{-1}$  which can be assigned to hydroperoxide groups, and a band at about  $1720 \text{ cm}^{-1}$  which is probably due to carbonyl groups. Because of the band at  $1720 \text{ cm}^{-1}$  in the IR spectrum of the radical-induced polymer, Roberts and co-workers concluded that 3,5-propagation occurred in the free radical polymerization of 3-methylenecyclobutene. This conclusion also appears to be questionable on other grounds in that 3,5-propagation would give a repeating unit composed of a 3-substituted cyclobutene structure which would have a C=C stretching band at about  $1566 \text{ cm}^{-1}$ . No band was observed at that location, and hence the broad characteristic band of hydroperoxide around  $3400 \text{ cm}^{-1}$  seems to suggest that the band at  $1720 \text{ cm}^{-1}$  was more probably caused by a carbonyl group. Likewise, the  $\text{BF}_3$ -initiated polymer also had a peak at  $1725 \text{ cm}^{-1}$  in its IR spectrum, and again Roberts et al. may not have given this band the proper assignment. Furthermore, as stated above, the insolubility of the above two polymers in common organic solvents was almost certainly caused by polymer autoxidation and cannot be explained on the basis of high molecular weights as suggested by Roberts and co-workers, who apparently failed to take into account the autoxidation phenomenon of poly-3-methylenecyclobutene.

In the present study, the data in Table 2 was collected from experiments designed to determine gel formation time for polymer B in order to elucidate the autoxidation reaction.

Table 2. Gel formation time of polymer B in benzene solution

Vial No.	antioxidant* addition	storage conditions	gel formation time, days
1	No	N <sub>2</sub>	5
2	No	air	1
3	No	air, dark	1
4	yes	N <sub>2</sub>	7
5	yes	air	1
6	yes	air, dark	>14

\*Antioxidant: 2,2'-methylene-bis(4-methyl-6-tert-butylphenol)

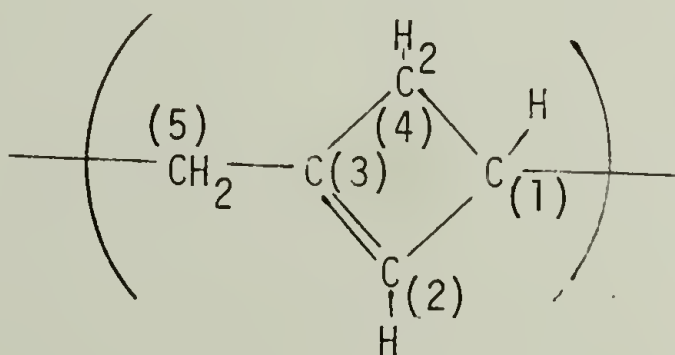
As can be seen from Table 2, in the first series without addition of antioxidant, gel formation occurred in one day for vial 2 in which the polymer was stored in air, and even for vial 3 which contained an air atmosphere with exclusion of light. In contrast, it took 5 days to form a gel in vial 1 because it contained a nitrogen atmosphere having only traces of oxygen.

In the second series with addition of a very small amount of an antioxidant 2,2'-methylene-bis(4-methyl-6-tert-butylphenol) gel formation developed in seven days for vial 4 stored under nitrogen but again took only one day for vial 5 which contained an air atmosphere. Vial 6 being excluded from light and air was found free from gel formation in two weeks. In all of the above experiments, the nitrogen atmosphere in the vials undoubtedly contained a small amount of oxygen.

The results indicate that oxygen was the major cause of gel formation of the polymer solution in benzene. Although the data do not indicate it, it was observed that the combined effect of oxygen and light accelerate the polymer autoxidation. It is shown that the effectiveness of the antioxidant was greatly enhanced by absence of light.

The IR spectra taken from polymer B (see Appendix, pages 5 and 6, IR Spectra Nos. 9, 10 and 11) and other cationically-prepared polymers all clearly showed the characteristic features of the rapid polymer autoxidation. In general, a broad absorption band at  $3100 - 3600 \text{ cm}^{-1}$  was first observed, which gradually increased its intensity and followed by the appearance of a rather sharp carbonyl band around  $1720 \text{ cm}^{-1}$ , and then by broadening of the bands at  $700 - 1450 \text{ cm}^{-1}$  in the spectrum. This ready and rapid autoxidation of the polymers was rather unfortunate because it made polymer characterization difficult.

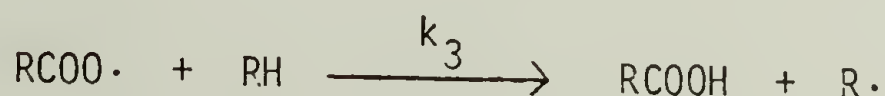
Generally speaking, polymer autoxidation is accelerated by one of the following means: (a) UV or high energy radiation, (b) free radical initiators, (c) metal catalyst [54]. The mechanism operative in the case of poly-3-methylenecyclobutene may require none of these because the polymers possess a double bond in each repeating unit such that there are five labile hydrogen atoms attached to the three allylic positions at carbons 1, 4, and 5 as shown in the following figure:



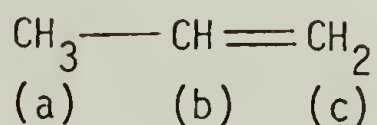
If double bond migration is also considered, all of the six hydrogens at

each carbon atom are equally activated and hence are susceptible to abstraction by the molecular oxygen. This statistical factor may serve to explain in a large part why the polymers are so sensitive to autoxidation.

J. L. Bolland [55] studied the influence of chemical structure on the  $\alpha$ -methylenic reactivity of olefins in the following reaction:



Based upon the results obtained from investigations of the autoxidation at 45°C of twenty-four compounds chosen for study, he concluded by summarizing the results in the form of four rules as follows:



- (i) Replacement of a hydrogen atom by an alkyl group at (a) and/or (c) increases the reactivity by  $3.3^n$ , where  $n$  is the total number of substituent groups introduced at (a) and/or (c). Replacement of a hydrogen at (b) has no effect.
- (ii) Replacement of a hydrogen at (a) by a phenyl group increases  $k_3$  by 23 times.
- (iii) Replacement of a hydrogen at (a) by an alkenyl  $\text{CH=CH-}$  group increases  $k_3$  by 107-fold.
- (iv) The  $k_3$  value appropriate to an  $\alpha$ -group contained in a cyclohexane ring is 1.7 times greater than that contained in the analogous acyclic olefinic group.

If the rule (i) and (iv) are applied to poly-3-methylenecyclobutene, it is to be expected that autoxidation will take place very markedly as found in this study.

Considering the repeating unit structure of 1,5-propagation, it is seen that there are three possible combinations of substituted allylic structures as follows: (I) consisting of carbons 1, 2 and 3, (II) consisting of carbons 2, 3 and 4 and (III) consisting of carbons 2, 3 and 5. In combination I there are four effective substituent groups, while there are two effective groups in either II or III. Therefore, there are a total of eight effective substituent groups in each repeating unit of the polymer which accounts for its great susceptibility to an autoxidation reaction.

The reactivity of each hydrogen in the polymer repeating unit is not equal, and the hydrogen abstraction by oxygen will occur preferentially at the point containing the most labile hydrogen atom. The hydrogen attached to carbon atom 1 is both tertiary and allylic in nature, and as such it will be preferentially abstracted because the most stable radical will be formed at this site. Hence, if autoxidation takes place at carbon 1 by abstracting the tertiary hydrogen, there are four effective substituent groups which will increase the autoxidation reactivity to a great extent.

It is interesting to note that a simple application of Bolland's first rule to poly-3-methylenecyclobutene, poly-1,4-butadiene and poly-1,4-isoprene, it is expected that poly-3-methylenecyclobutene will be at least  $3.3^{(4-2)} = 10.9$  times more reactive toward oxidation than the former, which has only two substituent groups present. Compared to poly-1,4-

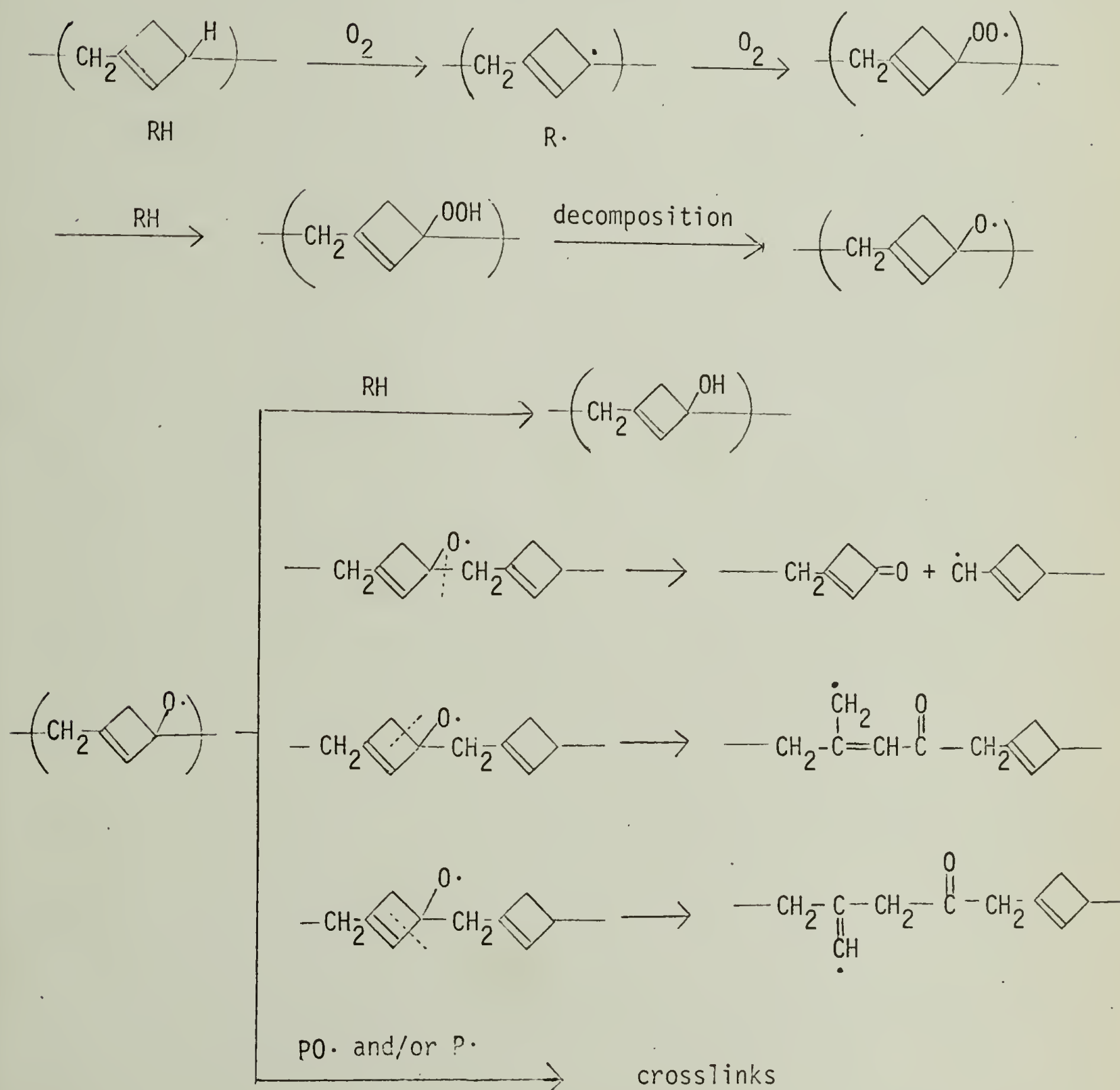
isoprene which has three effective substituent groups for the most labile hydrogen, poly-3-methylenecyclobutene will be  $3.3^{(4-3)} = 3.3$  times more reactive in the polymer autoxidation. By the same reasoning, poly-3-methylenecyclobutene will be  $3.3^{(4-3)} = 3.3$  times more reactive than poly-1,4-cyclopentadiene in the autoxidation reaction.

Bolland's rule (iv) indicates that cyclohexene is 1.7 times more reactive than its acyclic olefinic analogue indicating that some ring effect operates in the oxidation reaction. In this connection, polycyclopentadienes were also found to undergo rapid autoxidation [22,25], and if autoxidation reactivity parallels ring strain, cyclobutene will be even more reactive than cyclopentene and cyclohexene. In summary, therefore, by application of Bolland's rules (i) and (iv) to this study, it is to be expected that poly-3-methylenecyclobutene prepared by cationic initiators will be very sensitive to autoxidation, in good agreement with the experimental results.

The experimental results point out that a combination of light and air can cause rapid autoxidation of the polymer because abstraction of the labile allylic hydrogen requires a relatively small activation energy. On the basis of the above theoretical considerations as well as the experimental findings, it is suggested that the tertiary hydrogen at carbon 1 is the most labile one to be abstracted by oxygen with the aid of light. Once the radical is formed, it will rapidly combine with molecular oxygen to give a peroxy radical, which will then lead to the formation of a hydroperoxide by abstraction of another hydrogen. The crosslinking reaction may take place by combination of any two radical species mentioned above as well as with alkoxy radicals formed by

decomposition of hydroperoxide groups. The decomposition of hydroperoxide can also produce ketone groups, which was confirmed in the IR spectra of the polymers.

From these considerations, the overall mechanism of the polymer autoxidation can be postulated as shown in the following equation.



### III. Anionic Polymerization

The bulk polymerization of 3-methylenecyclobutene at 0°C initiated by *n*-BuLi gave 40% yield of a polymer having a number average molecular weight of 3,000. Again chain transfer to monomer may have occurred to a certain degree by formation of the cyclobutadienylcarbinyl anion which is also predicted to be stable [15,42].

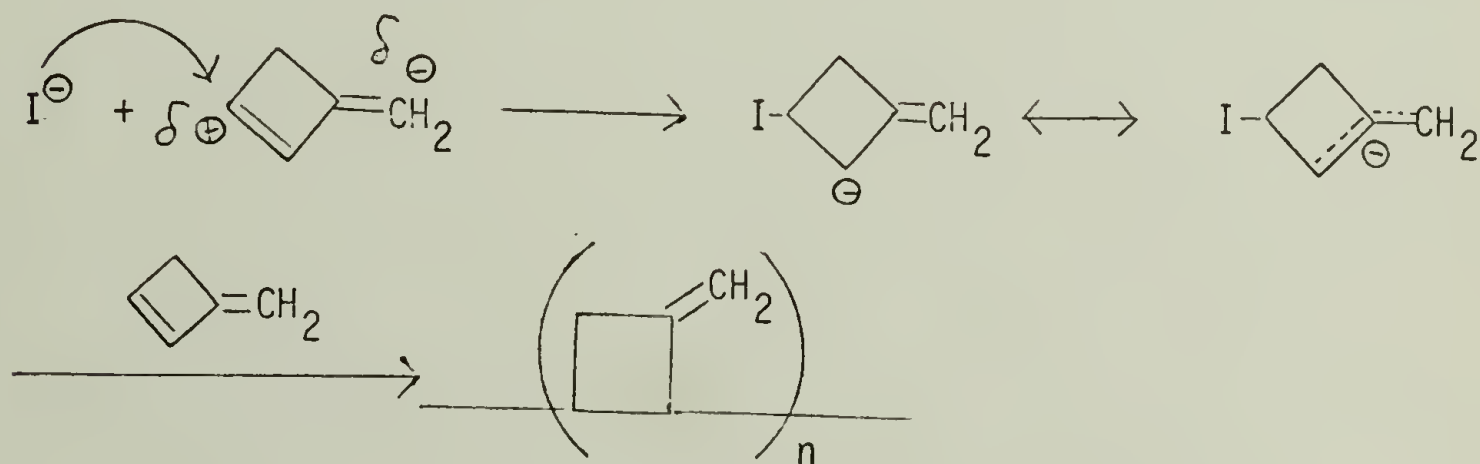
The IR spectrum of the original polymer in this case (see Appendix, page 6, IR Spectra No. 12), showed strong absorption bands at  $1670\text{ cm}^{-1}$  which are characteristic of exocyclic methylene groups, and the band at  $1630\text{ cm}^{-1}$  was very weak. Therefore, it is concluded that the polymer was formed mainly by 1,3-propagation leaving the exocyclic double bond intact.

In the NMR spectrum of the polymer (see Appendix, page 13, NMR Spectra No. 8), the single peak at  $5.75\tau$  was assigned to exocyclic methylene protons, and the peak around  $4.0\tau$  expected for olefinic proton(s) attached to the endocyclic double bond was absent. These observations support the suggestion above that the repeating unit of the polymer chain consists of a methylenecyclobutane ring formed by chains growing through carbons 1 and 2 only. The rather small peaks at  $4.74\tau$  and  $7.15\tau$  were probably due to impurities. The area under the peak at  $5.75\tau$  and that under the broad multiple peaks at  $7.50 - 8.80\tau$  is in the ratio of 3:8 whereas a calculated ratio of 3:6 is expected from the polymer structure resulting from 1,2-polymerization.

In 1956, Roberts and co-workers accidentally carried out an anionic polymerization of 3-methylenecyclobutene in an attempt to metallate the monomer with  $\text{KNH}_2$  in liquid ammonia [15], which happens to be a good

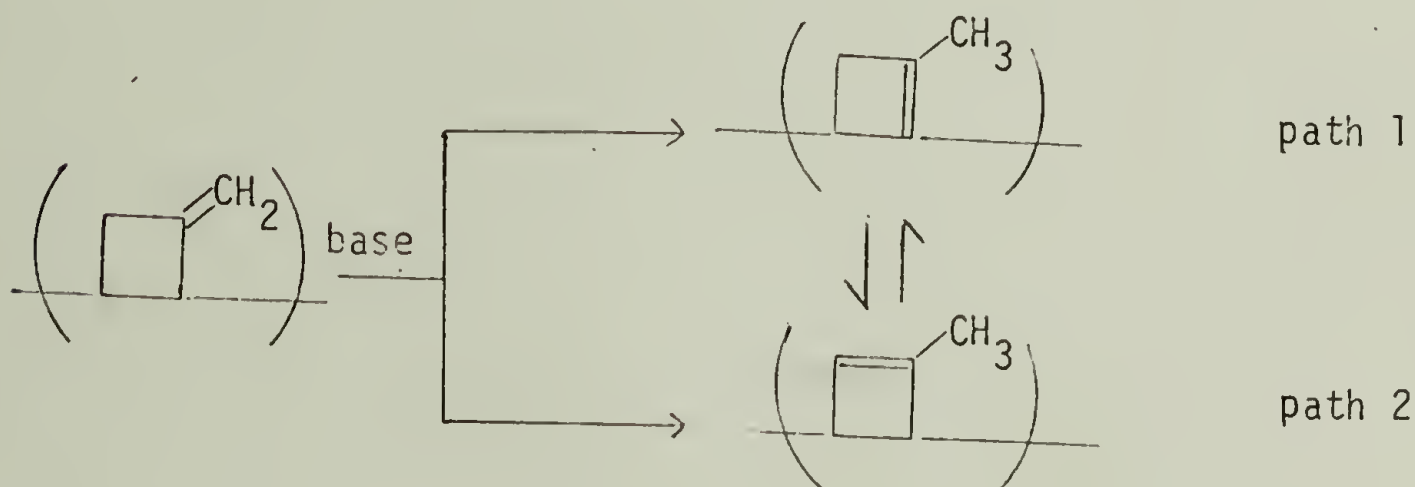
anionic polymerization system. According to their IR spectroscopic analysis, the polymer was obtained by 1,2-addition of 3-methylenecyclobutene, and it was proposed that the anionic initiator attacks the carbon 1 position because it bears a partial positive charge as predicted by molecular orbital calculations [15,42]. The intermediate thus formed would be  $\text{I}-\text{C}_4\text{H}_5\text{CH}_2^- \leftrightarrow \text{I}-\text{C}_4\text{H}_5\text{CH}_2$ , which then attacks another monomer to preferentially leaving an exocyclic double bond. The initiator would not be expected to attack carbon atom 5 because it carries a partial negative charge [15,42]. In addition, if the initiator attacks carbon atom 5, the intermediate  $\text{ICH}_2\text{-C}_4\text{H}_5^-$  is expected to be unstable because of its anti-aromatic character. Anti-aromaticity is defined as the decreased  $\pi$ -electron stability in cyclic compounds compared to their open-chain analogues [61]. Again, Roberts et al. did not make note of autoxidation associated with  $n\text{-BuLi}$ -initiated polymer although their IR spectrum of the polymer also showed the presence of a hydroperoxide group.

The mechanism of anionic polymerization of 3-methylenecyclobutene is presented in the following equation:



The exocyclic double bond in this repeating unit should be susceptible

to isomerization because 1-methylcyclobutene is known to be 0.9 kcal/mole more stable than methylenecyclobutane [45]. Moreover, Gil-Av, et al. investigated the equilibrium isomerization of  $\text{CH}_2=\text{Cyclobutane}$  and  $\text{CH}_3\text{-Cyclobutene}$  at 25°C under basic conditions, and found that a rapid isomerization took place starting from pure methylenecyclobutane to achieve an equilibrium concentration of 85% methylenecyclobutane and 15% 1-methylcyclobutene [56]. In view of these findings, the 1,2-addition polymer should be subject to some degree of isomerization as shown in the following:

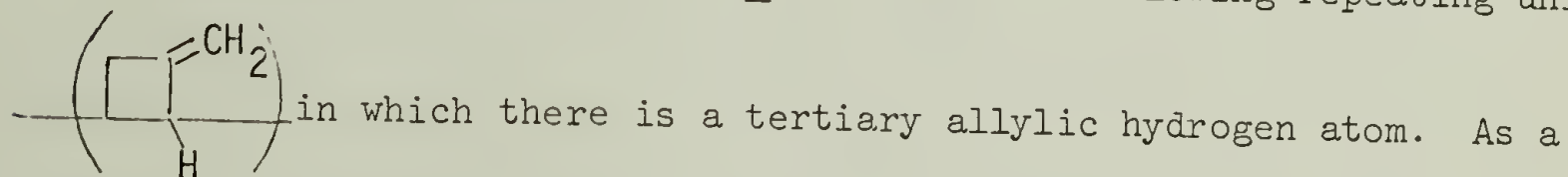


The isomerization could follow either of the above two possible paths. In both cases, the IR spectrum of the polymer would show a methyl band at  $1380\text{ cm}^{-1}$  and a C=C stretching band of the endocyclic double bond at about  $1635\text{ cm}^{-1}$ , which were indeed found in the spectrum but with very weak intensity. Path 1 would give a tetrasubstituted internal double bond with absence of an out-of-plane C-H bending vibration band around  $800\text{ cm}^{-1}$ . The IR spectrum of the polymer showed the absence of this particular band, which can be interpreted to mean that isomerization via path 1 does occur to some degree.

No clear-cut assignment can be made to the three overlapped peaks at  $7.50 - 8.80\tau$  in the NMR spectrum of the polymer. The area under

these peaks and that under the single peak at  $5.75\tau$  are in the ratio of 8:3. If the polymer is composed of only  $\left( \text{cyclobutene-1,2-dimethylene} \right)_n$ , the area ratio should be 6:3. Considering the possible mechanisms of isomerization of the polymer repeating unit into the more stable cyclobutene isomers, the intensity of the peaks at  $7.50 - 8.80\tau$  will be expected to increase because of the presence of a peak for the methyl group and the cyclobutene ring. This interesting subject of isomerization requires further studies in the future.

The polymer prepared with  $n\text{-BuLi}$  has the following repeating unit



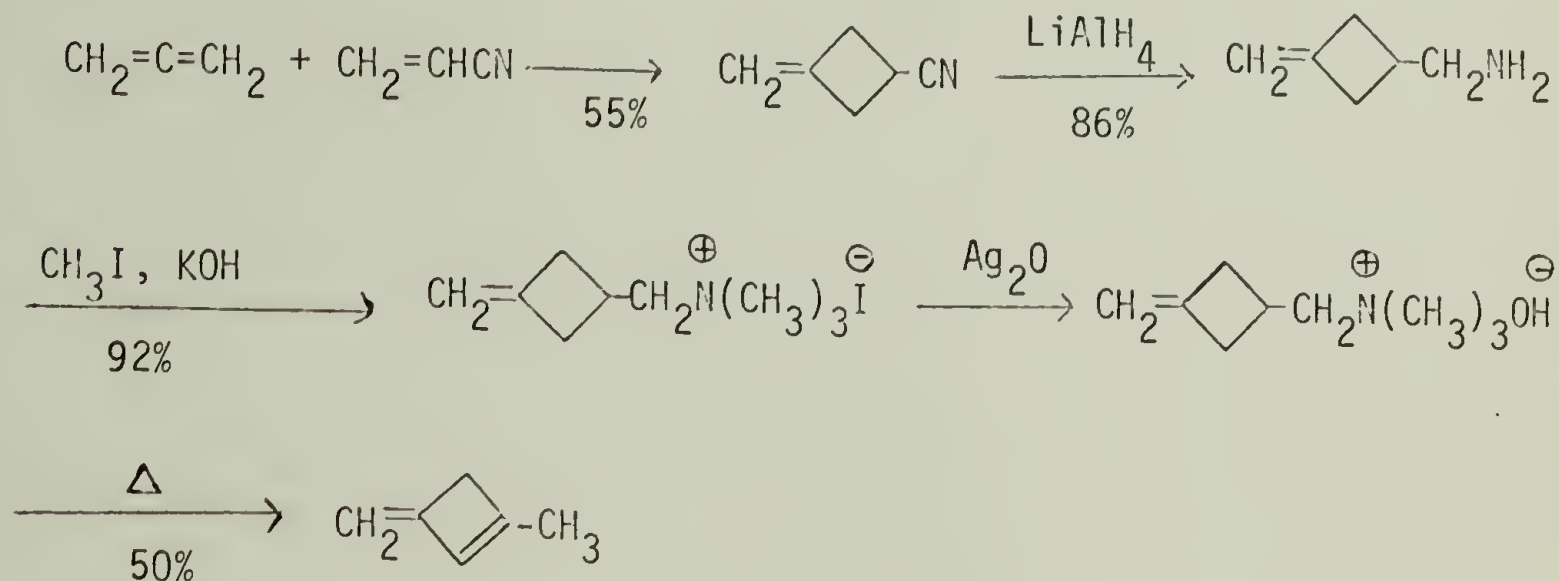
result, the polymer is again expected to undergo a rapid autoxidation reaction, and this was found to be the case in the present study. The IR spectra of the polymer (see Appendix, page 7, IR Spectra No. 13) showed a broad band at  $3100 - 3600 \text{ cm}^{-1}$  assignable to hydroperoxide groups and a band at  $1720 \text{ cm}^{-1}$  for carbonyl groups.

As with polycyclobutene, poly-3-methylenecyclobutene derived from 1,2-propagation has the possibility of achieving stereoregular structures. However, structural determination for stereoregularity of the 1,2-addition polymer is difficult because of the rather poorer resolution of the NMR spectrum obtained, and very little NMR data on four-membered ring compounds are available.

## Part II. Poly-1-methyl-3-methylenecyclobutene

### I. Monomer Synthesis and Structure Determination

In 1958, Roberts and co-workers synthesized 1-methyl-3-methylenecyclobutene by way of 3-methylenecyclobutanecarboxylic acid and 3-methylenecyclobutylcarbonyl dimethylamine [26]. Their synthetic steps are presented in the following equation:



The du Pont Company in U. S. Patent 2,995,543 issued in 1961 [17] disclosed the preparation of the above diene and many of its alkyl and aryl substituted compounds following the general scheme employed by Roberts and co-workers.

Butler and Griesbaum made the subject monomer compound by the dehydrobromination of 1,3-dibromo-1,3-dimethylcyclobutane [57]. However, the details of their complete syntheses were not reported in that paper.

The monomer in the present study was prepared according to the routes of Roberts and co-workers with slight modifications. Because it has a boiling point at 69 - 70°C and is stable if stored under its own vapor pressure [26] or in nitrogen atmosphere, the subject monomer can be handled with ease, in contrast to the difficult problem posed by

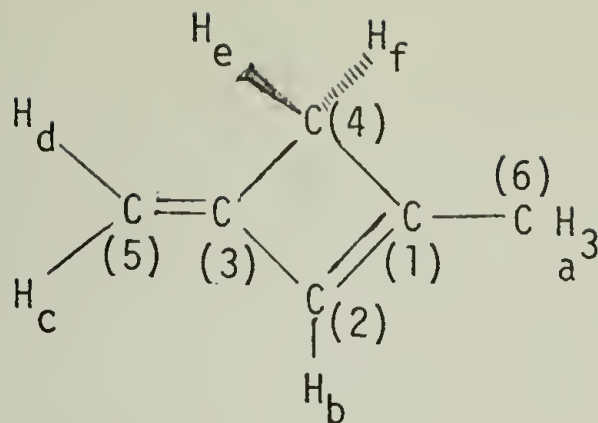
3-methylenecyclobutene which is both very volatile at room temperature, having a boiling point of  $35^{\circ}\text{C}$ , and sensitive to self polymerization. In this study, the bulk monomer was prepared and stored in a slightly positive nitrogen atmosphere at  $-78^{\circ}\text{C}$ . When a polymerization reaction was to be performed, the monomer was warmed up to  $0^{\circ}\text{C}$  before the required amount was taken out from the storage flask by a syringe.

The monomer purification caused no serious difficulty. The crude monomer contained a small amount of water and trimethylamine, and most of the water impurity could be removed by drying the monomer with calcium chloride at  $0^{\circ}\text{C}$ . The pure monomer could then be obtained by further distillation of this crude diene in a nitrogen stream using a semi-micro still equipped with a heating jacket.

The IR spectrum of the monomer (see Appendix, page 1, IR Spectra No. 2) is exactly the same as that reported by Roberts, et al. [26]. The characteristic absorption bands of the exocyclic methylene appear at  $3080\text{ cm}^{-1}$ ,  $1688\text{ cm}^{-1}$  and  $851\text{ cm}^{-1}$ . The small peak at  $3058\text{ cm}^{-1}$  is assigned to the C-H stretching vibration of the olefinic hydrogen attached to the endocyclic double bond. The C=C stretching of the internal double bond with a methyl substitution is seen at  $1593\text{ cm}^{-1}$ . The typical methyl band appears at  $1370\text{ cm}^{-1}$ .

Roberts and co-workers reported an NMR spectrum of the monomer recorded on a 40 MHz spectrometer [26]. Different proton groups were clearly separated in the spectrum, but the resolution was not as good as can be expected.

The structure of the monomer with numbering of the carbons and hydrogens is shown as follows:



The monomer presumably has a planar structure, and as a result,  $H_b$ ,  $H_c$  and  $H_d$  should lie in the same plane formed by the six carbon atoms, while  $H_e$  and  $H_f$  should project above and below the plane. The NMR spectrum of 1-methyl-3-methylenecyclobutene (see Appendix, page 12, NMR Spectra No. 6) consists of single peaks at  $3.83\tau$ ,  $5.42\tau$ ,  $5.63\tau$ ,  $7.18\tau$  and  $8.03\tau$  having an area ratio of 1:1:1:2:3.

The three methyl protons appear at  $8.03\tau$ .  $H_e$  and  $H_f$  are in the same chemical environment, hence they show as a singlet at  $7.18\tau$ . The singlet at  $3.83\tau$  is assigned  $H_b$ , olefinic proton attached to the endocyclic double bond.  $H_c$  and  $H_d$  of exocyclic methylene protons are in different electronic surrounding and are expected to appear as two singlets observed at  $5.42\tau$  and  $5.62\tau$ . However,  $H_c$  is expected to experience the deshielding effect of the endocyclic double bond and the peak at  $5.42\tau$  can be assigned to  $H_c$  while the one at  $5.62\tau$  to  $H_d$ .

The above assignment of  $H_c$  and  $H_d$  peaks is opposite to that made by Butler and Griesbaum [57]. They based their assignment on a proposed diamagnetic shift experienced by  $H_c$  relative to  $H_d$  due to the anisotropy of the eclipsed carbon-hydrogen in the former. However, it would seem to be more important to consider that  $H_c$  is more in the deshielding zone of the  $C_3-C_4$  bond than is  $H_d$ , however small that effect may be. To what extent, if any, C-H bond anisotropy may contribute to shift differences is still not certain [58]. Therefore, it is suggested here that the deshielding effect of a double bond is more important in this

case and hence should be used to account for the NMR spectrum of the monomer. Accordingly, the lower field peak at 5.42 $\tau$  should be assigned  $H_c$ .

The four different types of protons of the monomer:  $H_a$ ,  $H_b$ ,  $H_c-H_d$ , and  $H_e-H_f$ , are all at least three carbon atoms away from each other. As such, the coupling constants among them are expected to be small, which is reflected in the rather simple NMR spectrum of the monomer. Using a 100 MHz spectrometer, Butler and Griesbaum were able to obtain an NMR spectrum of the monomer with very good resolution. By double and triple irradiation techniques, they also derived the coupling constants of the five sets of mutually coupled non-equivalent protons [57]. The results are as follows:  $J_{bc}=0.77$  Hz,  $J_{be,bf}=0.50$  Hz,  $J_{ab}=1.55$  Hz,  $J_{cd}=0$  Hz,  $J_{de,df}=1.28$  Hz,  $J_{ad}=0.60$  Hz,  $J_{ce,cf}=0.83$  Hz,  $J_{ac}=0.65$  Hz,  $J_{ae,af}=1.31$  Hz.

## II. Cationic Polymerization

The data obtained for the cationic polymerizations of 1-methyl-3-methylenecyclobutene with various initiators are collected in Table 3. In general, these polymerization reactions proceeded fast and resulted in high yield of polymers of unusually high molecular weight for a diene monomer, particularly in contrast to the low yields of low molecular weight polymers obtained with 3-methylenecyclobutene.

### 1. Polymer Structure

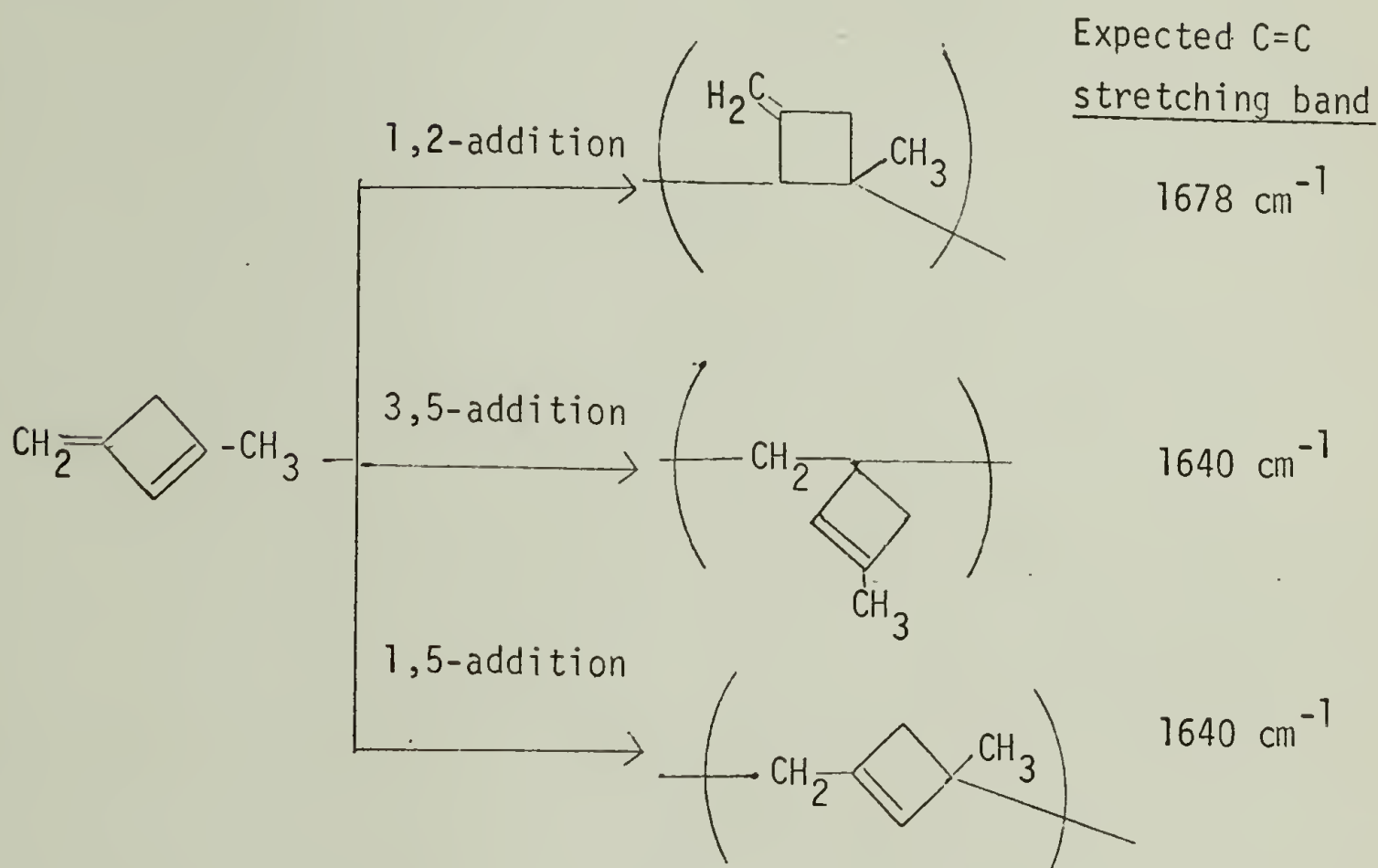
1.a. IR Spectra The IR spectra of the polymers E, F, and G taken in a benzene solution (see Appendix, pages 7 and 8, IR Spectra Nos. 14, 15, and 16) and they all show essentially the same features irrespective of the initiators and solvents. Just like the polymerization of 3-methylenecyclobutene, there are three possible modes of propagation in the polymerization of 1-methyl-3-methylenecyclobutene.

Table 3. Cationic Polymerizations of 1-Methyl-3-Methylenecyclobutene

Polymer	Monomer mmole	Initiator	Solvent	Temperature °C	Time, hours	Yield, %	$\bar{M}_n$
E	3.87	BF <sub>3</sub> , 1 ml	-	-78	1/6	66	3,800
F	11.2	BF <sub>3</sub> ·OEt <sub>2</sub> 0.48 mmole	n-hexane 15 ml	-78	5.5	71	19,200
G*	18.1	AlEt <sub>2</sub> Cl, 0.26 mmole HBr, 2.5 ml	toluene 20 ml	-78	5.5	77	16,200

\*This polymerization was run three times and the best result is reported herewith.

As a result, three different repeating units in the polymer chain may be formed, and the characteristic absorption bands generally associated with the respective double bonds are shown in the following:



The 1,2-propagation reaction would give rise to a repeating unit containing an exocyclic methylene group which is expected to show strong bands at  $1678 \text{ cm}^{-1}$  and  $870 \text{ cm}^{-1}$ . From the absence of these two bands, the possibility of significant amounts of 1,2-polymerization is thus ruled out.

A medium band at  $1630 \text{ cm}^{-1}$  was observed for these polymers, apparently arising from the repeating units containing either 3,5- or 1,5-structures. However, the IR spectra seem incapable of making the distinction between these two repeating units. The  $\text{CH}_3$  band from 3,5-addition polymer may appear in a lower wavenumber region, but the results are not conclusive. The medium band at  $800 \text{ cm}^{-1}$  is caused by the out-of-plane vibration of C-H attached to the trisubstituted double bond.

1.b. NMR Spectra The NMR spectra of polymers E, F, and G (see Appendix, pages 14 and 15, NMR Spectra Nos. 9, 10, and 11) were recorded in a deuterated benzene solution at room temperature. All spectra show essentially the same features consisting of three single peaks at  $3.85\tau$ ,  $7.67\tau$  and  $8.67\tau$  in the ratio of 1:4:3.

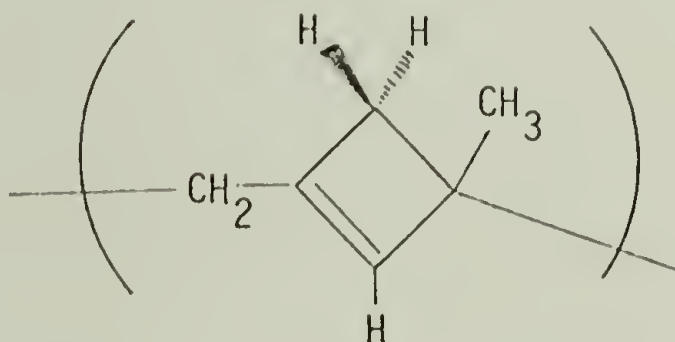
The absence of a peak near  $5.3\tau$  which would be expected for exocyclic methylene protons, also eliminates the possibility of 1,2-addition polymerization. The singlet at  $3.85\tau$  is assigned to an olefinic proton attached to a trisubstituted cyclobutene ring. Again, the chemical shift of this peak cannot differentiate the polymer structures resulting from 3,5- or 1,5- propagation.

In terms of their relation to the double bond, the chemical shifts of the methyl and methylene groups in the 3,5- and 1,5- structures are expected to be different. The chemical shift of a methyl attached to a double bond is expected to appear in the region of  $8.0\tau$ , while that of an allylic methyl should be near  $8.4\tau$  [59]. The NMR spectra of the polymers have a singlet at  $8.67\tau$  assigned from area integration to the methyl protons. Hence, the expected chemical shift of an allylic methyl near  $8.4\tau$  is closer to  $8.67\tau$  found for the methyl protons in the polymer NMR spectra. Hence, 1,5-propagation appears to predominate in the cationic polymerizations of 1-methyl-3-methylenecyclobutene.

The remaining single peak at  $7.67\tau$  representing four protons is assigned to the two remaining methylene groups. The cyclic and acyclic methylene protons in the 3,5-addition repeating unit are in different chemical environments, and thus the acyclic methylene protons are expected to appear around  $8.3\tau$  which is at a little higher field strength than that expected for the cyclic analogues,  $7.4\tau$ . However, both the

cyclic and acyclic methylene protons in the repeating unit obtained from 1,5-propagation are in more or less identical chemical surroundings by being both allylic to the double bond and adjacent to a tertiary methyl group. Hence, they appear close together as a single peak at  $7.67\tau$ .

From the combined analyses of olefinic, methyl, and methylene protons in the NMR spectra, a reasonable conclusion is again that cationic polymerizations of 1-methyl-3-methylenecyclobutene takes place predominantly by a 1,5-propagation mechanism. The repeating unit of these polymers is shown as follows:



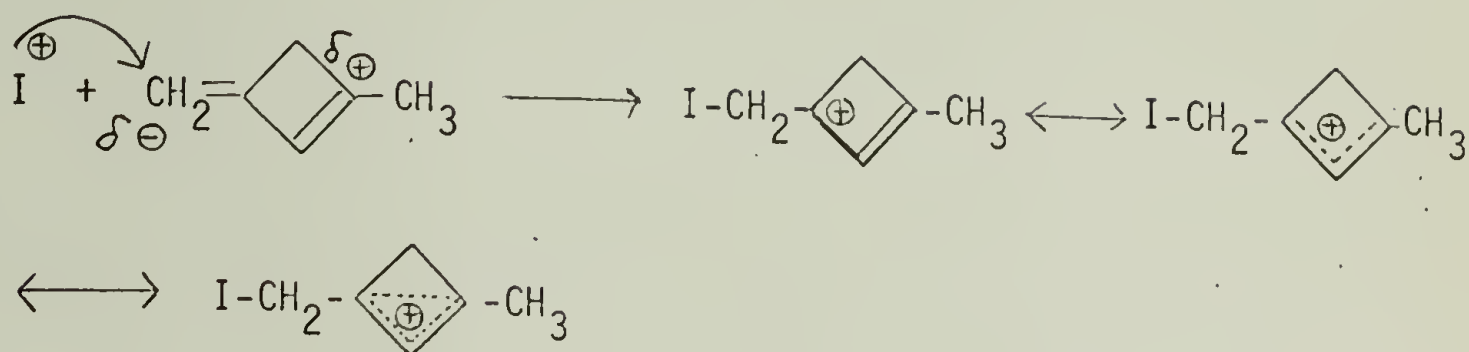
The long range spin-spin coupling of the four different types of protons are not noticeable because the protons are at least three carbons away from each other. Consequently, the NMR spectra show a rather clean three-singlet pattern, although the unambiguous assignment of the several small peaks at  $7.3 - 8.9\tau$  deserves further study.

The 1961 du Pont Company patent [17] describes copolymers of 1-methyl-3-methylenecyclobutene with a number of ethylenically unsaturated monomers, but the details of the polymer structure were not disclosed in the patent literature.

## 2. Polymerizations Mechanism

From the IR and NMR spectroscopic analyses, it appears established that cationic polymerizations of 1-methyl-3-methylenecyclobutene occurs mainly by the path of 1,5-propagation. The initiating cation probably

attacks the exocyclic double bond at carbon 5 to form the stable intermediate as depicted in the following figure:



The intermediate thus formed may be homoaromatic in character because the structure fits Hückel's  $(4n+2)$  rule for a conjugated ring molecule. Moreover, the inductive effect of the methyl group greatly enhances the stability of intermediate. The introduction of a methyl group at carbon 1 of 3-methylenecyclobutene apparently brings about two striking results in the cationic polymerization reactions of this monomer compared to 3-methylenecyclobutene. Firstly, the methyl group increases the stability of the propagating intermediate relative to that of the carbonium ion which would form from chain transfer at carbon 4. Secondly, the methyl group probably polarizes the electron pair of the intermediate allylic carbonium ion away from the tertiary carbon 1, thus directing a nucleophilic attack by another monomer to carbon 1 to facilitate 1,5-addition. These rationalizations account for the cationic polymerization reaction of the 1-methyl monomer taking place rapidly and producing comparatively high yields of polymers with unusually high molecular weight in comparison to the low yield, low molecular weight polymers obtained from the unsubstituted diene and to diene monomers in general. Indeed, the molecular weights obtained from the 1-methyl monomer are significantly higher than those reported for the homogeneous

cationic polymerization reactions of most dienes, particularly 1,3-butadiene and isoprene [60].

The cationic polymerizations of butadiene and isoprene generally give low molecular weight polymers mainly of trans-1,4 structure, together with insoluble polymers containing cyclized structures [1,60]. The polymerization reactions of these monomers are complicated by the different possible carbonium ion intermediates and extensive chain transfer reactions. The polymerization of isoprene in ethyl chloride by stannic chloride, for example, produces only low molecular weight polymer in the range of 900-3,800 [60].

The bulk polymerization initiated by  $\text{BF}_3$  gas yielded a product in which about one half of the polymer was insoluble in benzene. This insolubility was probably caused by a crosslinking reaction inherent with  $\text{BF}_3$ . The low molecular weight of the soluble polymer ( $\bar{M}_n = 3,800$ ) may be due either to the crosslinking reaction removing the higher molecular weight fraction or because the polymerization reaction was run for only 10 minutes, compared to 5.5 hours for corresponding experiments in the solution polymerization reactions.

The monomer is known to have a high ring strain of 54.9 kcal/mole [45], which undoubtedly provides some of the driving force of the polymerization reaction because about half of the strain is relieved during the process.

### 3. Polymer Reactions

#### 3.a. Hydrogenations of Polymer G

Method A: An IR spectrum was taken directly of a sample from the reaction mixture, after the palladium catalyst was removed, when the attempted hydrogenation was run for three days at 50 psi hydrogen pressure. The spectrum showed a substantial decrease in the C=C stretching

band, and the reaction was stopped. After the polymer was reprecipitated and dried, an IR spectrum was recorded again, but the fairly strong C=C stretching band at  $1635\text{ cm}^{-1}$  still remained. Under the same conditions, cationically-initiated poly-3-methylenecyclobutene underwent not only hydrogenation but hydrogenolysis reaction, as already described in Part I, section 3.a. Thus poly-1-methyl-3-methylenecyclobutene appears to be more resistant to hydrogenation, probably because the cyclobutene ring is more stable in this polymer compared to that in poly-3-methylenecyclobutene.

Method B: The hydrogenation of polymer G by toluenesulfonyl hydrazide was run at reflux temperature of o-xylene for three hours. A longer reaction time was avoided because thermal isomerization of the polymer might occur. After this attempted hydrogenation, an IR spectrum was taken which now showed the disappearance of the C=C stretching band. However, the NMR spectrum of the hydrogenated polymer (See Appendix, page 15, NMR Spectra No. 12) still showed the presence of a olefinic proton at  $3.48\tau$ . As calculated from the area ratio in the NMR spectrum, about 28% of the polymer remained unreacted in the hydrogenation reaction. Singlets were observed at  $3.48\tau$ ,  $7.91\tau$  and  $9.04\tau$  which are probably due to the 1,5-structure of the original polymer sample. A new singlet observed at  $9.15\tau$  was assigned to the methyl protons in the hydrogenated polymer. New multiplets observed at  $8.0 - 8.9\tau$  were apparently due to the cyclobutane and open chain methylene protons. However, an unambiguous assignment of the multiplet was difficult because the spectrum resolution was rather poor. The peak at  $8.67\tau$  was probably caused by the four cyclic methylene protons of the saturated cyclobutane ring.

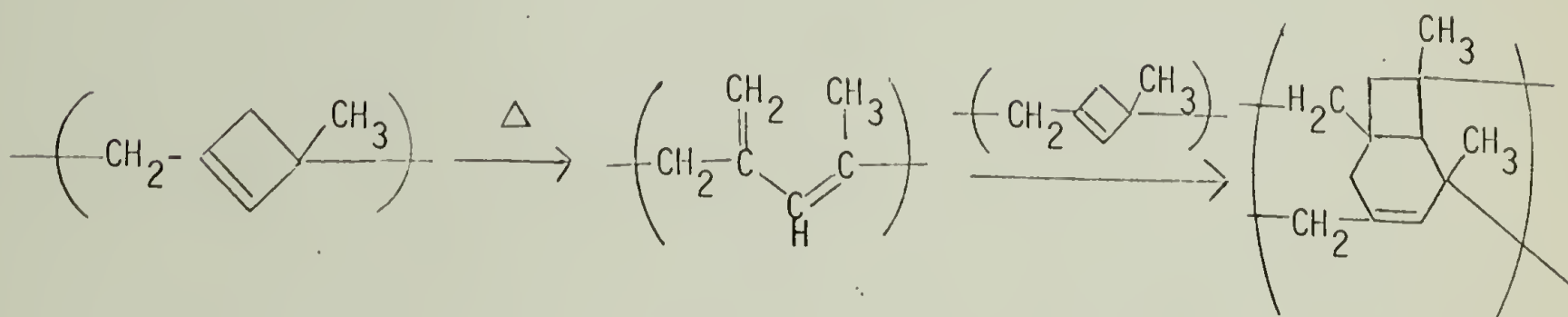
The 1,5-structure of the polymer will have two asymmetric centers assuming a complete hydrogenation of the endocyclic double bond. A di-tacticity is therefore expected, but the determination of the tacticity problem appears to be very difficult in view of the poor resolution of the NMR spectrum obtained and sparsely available NMR data on four-membered ring compounds. 100 MHz and 220 MHz spectrometers should be used to provide a better resolution of the hydrogenated polymer if this information would be of interest.

### 3.b. Crosslinking Reaction by Heat Treatment

The DSC thermograms of the cationically-initiated polymers all show a broad exothermic peak in temperature range of 190 - 250°C (see Appendix, page 17), which is 40°C higher than that observed for poly-3-methylenecyclobutene prepared from cationic initiators. The increased stability of the former is expected because the methyl group at the carbon 1 position would increase the stability of the cyclobutene repeating units of this polymer relative to that in poly-3-methylenecyclobutene obtained by the same mode of propagation.

The repeating unit of this polymer consists of a structure very similar to 1,3,3-trimethylcyclobutene. The activation energy for thermal isomerization of 1,3,3-trimethylcyclobutene in the temperature range of 172 - 213°C was found to be 37.0 kcal/mole [52], compared to 33.0 kcal/mole for 1,3-dimethylcyclobutene. The introduction of a methyl group at carbon 3 both reduces ring strain and causes steric hindrance to rotation in the thermal isomerization of 1,3,3-trimethylcyclobutene, and thus the compound requires higher activation energy for the overall reaction. The bulky polymer chain units should further increase the steric effect, so the polymers having a 1,5-structure will require an even

higher temperature than the model compounds for the thermal decomposition, and the subsequent crosslinking reaction, to occur. A possible mechanism of the exothermic reaction of the polymers is postulated in the following equation:



On the basis of a standard benzoic acid, the exothermic reaction of polymer G in the DSC thermogram is calculated to be 195 calories per gram of polymer, compared to about 178 calories for polymer D. The weight loss involved in the DSC run amounts to only 3.4%, indicating that little volatilization occurs in the process.

A du Pont Company 1961 patent [17] claimed the utilization of a small percentage of 1-methyl-3-methylenecyclobutene comonomer for the preparation of crosslinkable copolymers with other vinyl monomers. The soluble copolymers are capable of being crosslinked to insoluble and infusible polymers on heating in the temperature range of 100 - 325°C. However, a mechanism for the crosslinking reaction was not offered in that patent.

### 3.c. Autoxidation Reaction

It has been established in this study that poly-3-methylenecyclobutene with 1,5-addition repeating units is sensitive to rapid autoxidation, and presumably the allylic tertiary hydrogen at carbon 1 plays a major role in this reaction. Partly to eliminate this reactive site for the autoxidation reaction, a methyl group was introduced at carbon 1 to form 1-methyl-3-methylenecyclobutene monomer. It is expected that autoxidation of this polymer containing the 1,5-structure should then be greatly depressed compared to that from the unsubstituted monomer. This expectation seemed to be confirmed almost immediately as the polymer characterizations encountered no problem with this product resulting from insolubility caused by rapid crosslinking during isolation. The elemental analyses of polymer F and G showed values very close to the calculated analyses, that is within 0.3%. Although the tertiary hydrogen atom is removed, the repeating units still contain two allylic carbons with four reactive hydrogen atoms which will be subject to autoxidation reaction, but qualitative observations indicate that the autoxidation phenomenon is much less pronounced than for poly-3-methylenecyclobutene.

By simple application of Bolland's rule (i) to poly-3-methylenecyclobutene and Poly-1-methyl-3-methylenecyclobutene prepared cationally without consideration of double bond migration, it is noted that there are a total of eight substituent groups operative for each repeating unit of the former while there are four such groups for the latter. Qualitatively speaking the poly-1-methyl-3-methylenecyclobutene should therefore be  $3.3^{(8-4)} = 3.3^4$ , that is about 100 times less sensitive to overall autoxidation reaction when compared with poly-3-methylenecyclobutene. If hydrogen abstraction is limited to the most labile site, then

poly-1-methyl-3-methylenecyclobutene is at least  $3.3^{(4-2)}=10.9$  times less reactive in the polymer autoxidation than poly-3-methylenecyclobutene.

### III. Anionic Polymerization

The bulk and solution polymerizations of 1-methyl-3-methylenecyclobutene initiated by *n*-BuLi failed to produce any polymer probably because of the following reasons: (i) the methyl group at carbon 1 causes a steric hindrance to the approach of the initiating anion to that site; (ii) a unstable tertiary anion is formed if the initiator attacks carbon 2; (iii) an unstable anion is produced, which is tertiary and anti-aromatic in nature, if the initiator attacks carbon 5; (iv) chain transfer to form a stable cyclobutadienylcarbinyl anion at carbon 4 could take place to a considerable extent.

It is not known which of the above mechanisms is more important to account for the unsuccessful anionic polymerization of 1-methyl-3-methylenecyclobutene. It is of interest to note, however, that cyclopentadiene also will not polymerize by an anionic mechanism but will polymerize readily by a cationic reaction [60]. On the other hand, the polymerization reactions of acyclic dienes such as butadiene, isoprene and piperylene proceed very well with anionic initiators but not with cationic initiators. 1-Methyl-3-methylenecyclobutene, but not 3-methylenecyclobutene seems to be an exception to the behavior of dienes in general in the formation of unusually high molecular weight polymers for this type of monomer.

### IV. Polymerizations by Ziegler-Natta Catalysts

The data of the polymerizations of 1-methyl-3-methylene-cyclobutene by Ziegler-Natta catalysts are collected in Table 4.

Table 4. Polymerizations of 1-Methyl-3-Methylenecyclobutene by Ziegler-Natta Catalysts

Polymer	Monomer (mmole)	Initiator (mmole)	Solvent ml	Temperature °C	Time, hours	Yield, %	$\bar{M}_n$
H*	19.0	Al( <i>i</i> -Bu) <sub>3</sub> , 2.4 VCl <sub>3</sub> , 0.96	<u>n</u> -hexane 9 ml	22	24	75	-
I	25.2	Al( <i>i</i> -Bu) <sub>3</sub> , 0.48 VCl <sub>3</sub> , 0.19	<u>n</u> -hexane 12 ml	22	24	50	19,500
J*	20.0	AlEt <sub>2</sub> Cl, 1.0 Co(acac) <sub>3</sub> , 0.002	benzene 12 ml	0	22	48	-

\*These polymerizations were run twice.

The heterogeneous catalysts of  $\text{AlEt}_3$  with  $\text{VCl}_3$  in *n*-heptane was used by Natta to make crystalline trans-1,4 polypentadiene [3]. When 12.5 mole % of  $\text{Al}(\text{i-Bu})_3$  catalyst, based on monomer, was employed in the polymerization, a white fluffy polymer G was obtained in 75% yield. Polymer H was insoluble in benzene or even in refluxing toluene, hexachlorobutadiene and  $\alpha$ -chloronaphthalene. When the  $\text{Al}(\text{i-Bu})_3$  concentration was reduced to 1.9 mole % of that monomer, a slightly yellowish polymer I was produced, which was soluble in benzene. It is therefore reasoned that excess of the catalyst caused a secondary crosslinking reaction through the unsaturated unit of the polymer chain in addition to the regular propagation reaction. Reduction of the catalyst concentration to 1.9 mole % of that of the monomer apparently avoids the crosslinking reaction and permits the formation of a linear polymer which is soluble in benzene. According to an elemental analysis, polymer H contains 23.1% oxygen, and its insolubility may also result from autoxidation reaction.

On the basis of same IR and NMR spectroscopic analyses applied to the cationically-initiated poly-1-methyl-3-methylenecyclobutene, the IR and NMR spectra of polymer I (see Appendix, pages 9 and 16, IR Spectra No. 17, NMR Spectra No. 13) clearly show that heterogeneous Ziegler-Natta polymerizations of 1-methyl-3-methylenecyclobutene proceeded by a 1,5-addition mechanism as in the case of the cationic polymerization reactions. The number average molecular weight of polymer I was about 19,500, demonstrating the ready polymerization by heterogeneous catalysts.

The homogeneous catalysts of  $\text{AlEt}_2\text{Cl}$  with  $\text{Co}(\text{acac})_3$  in benzene was used by Natta to prepare crystalline syndiotactic cis-1,4 polypenta-

diene [3]. The same catalyst system used here produced polymer J in 48% yield, but the polymer was not completely soluble in benzene. The IR and NMR spectra of polymer J were taken in benzene and hexachlorobutadiene respectively (see Appendix, pages 9 and 16, IR Spectra No. 18 and NMR Spectra No. 14) and show again that 1,5-propagation predominates but a crosslinking reaction occurs to some extent because the area ratio of olefinic proton to the other protons was found to be 1:9.5 instead of the theoretical 1:7 for linear polymer. No molecular weight measurement was made because the polymer was only partially soluble in benzene.

The DSC thermograms of polymers H, I and J did not show an endothermic melting peak up to 300°C. As usual, a characteristic exothermic peak in the temperature range of 190-250°C was observed which is attributed to the ring-opening reaction of repeating units and crosslinking of the polymers.

A small amount of birefringence was found in the polymers when observed on a polarizing microscope, but it gradually disappeared when the polymer samples were heated and there seemed to be no correlation with the above crosslinking reaction.

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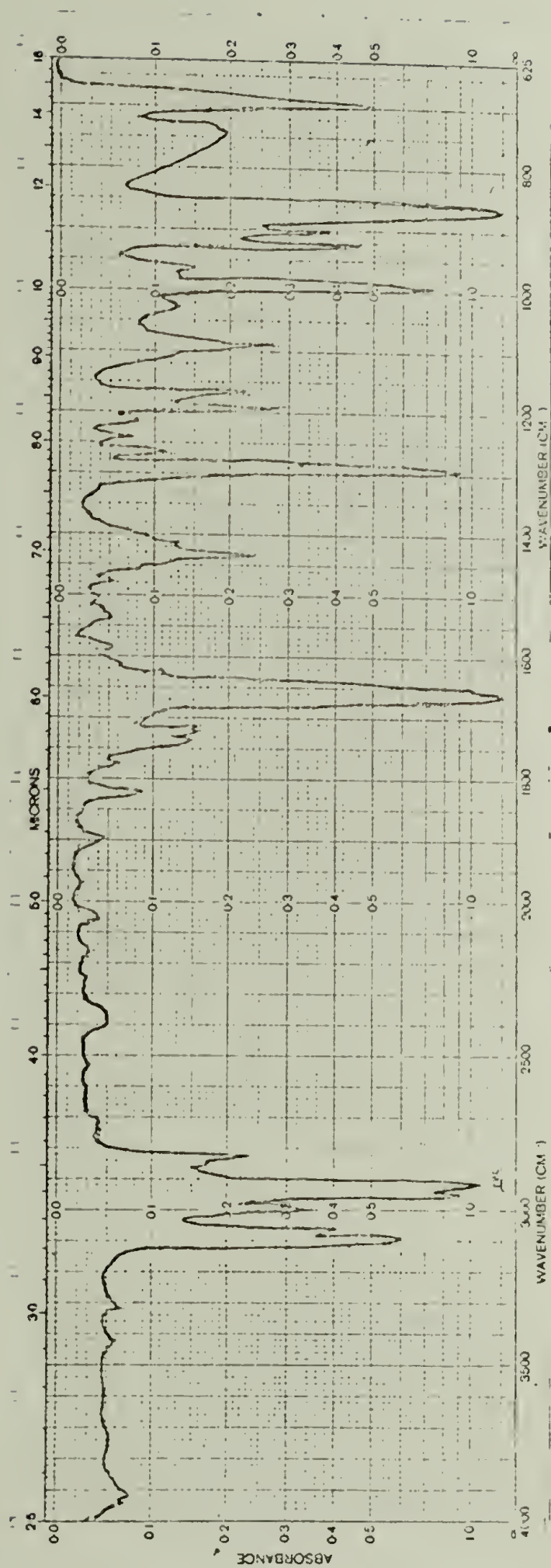
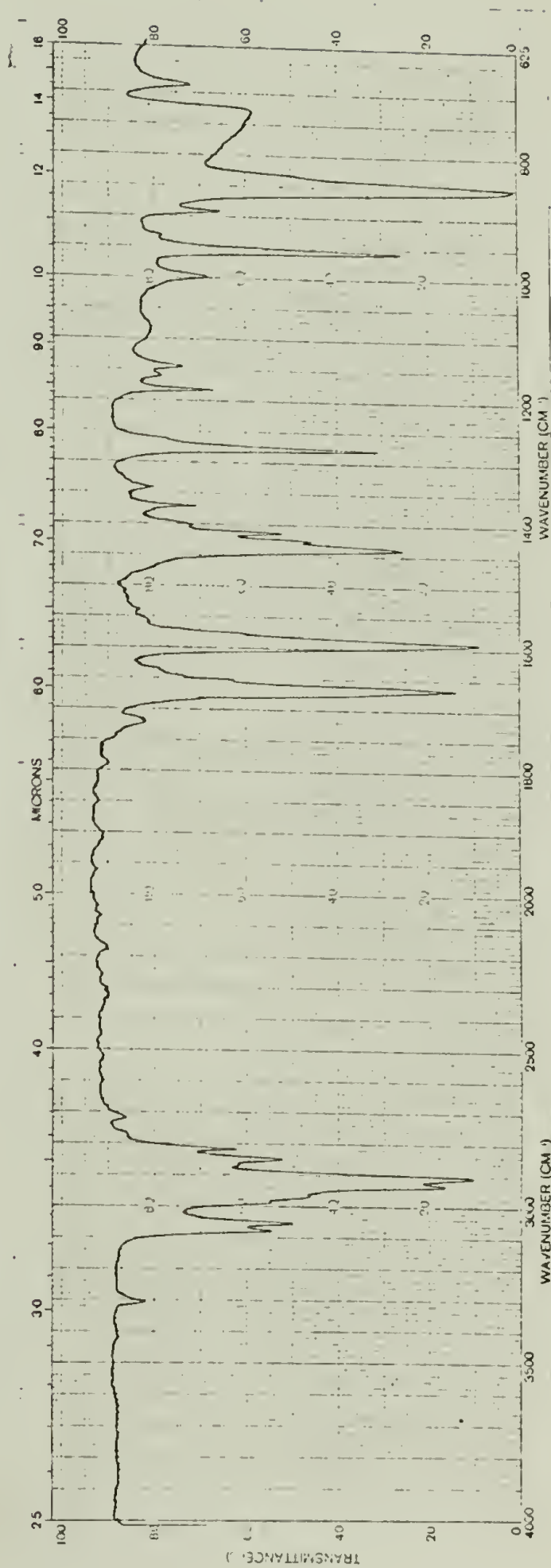
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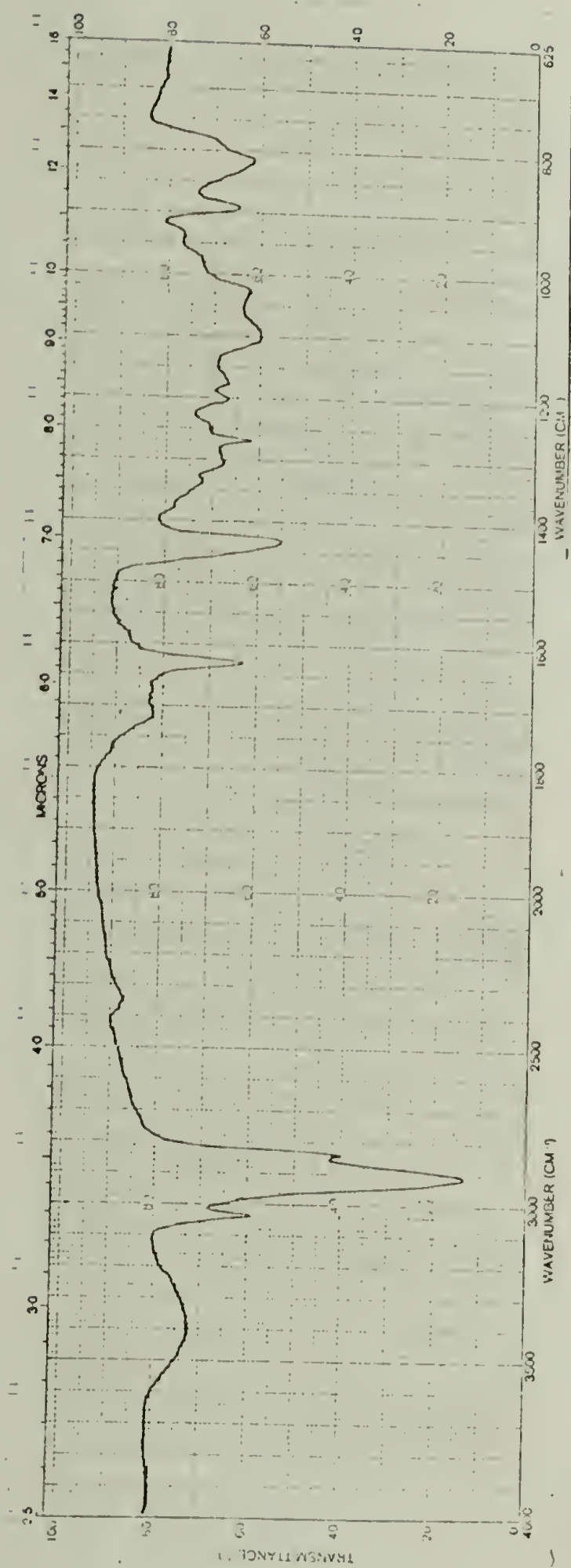
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## APPENDIX

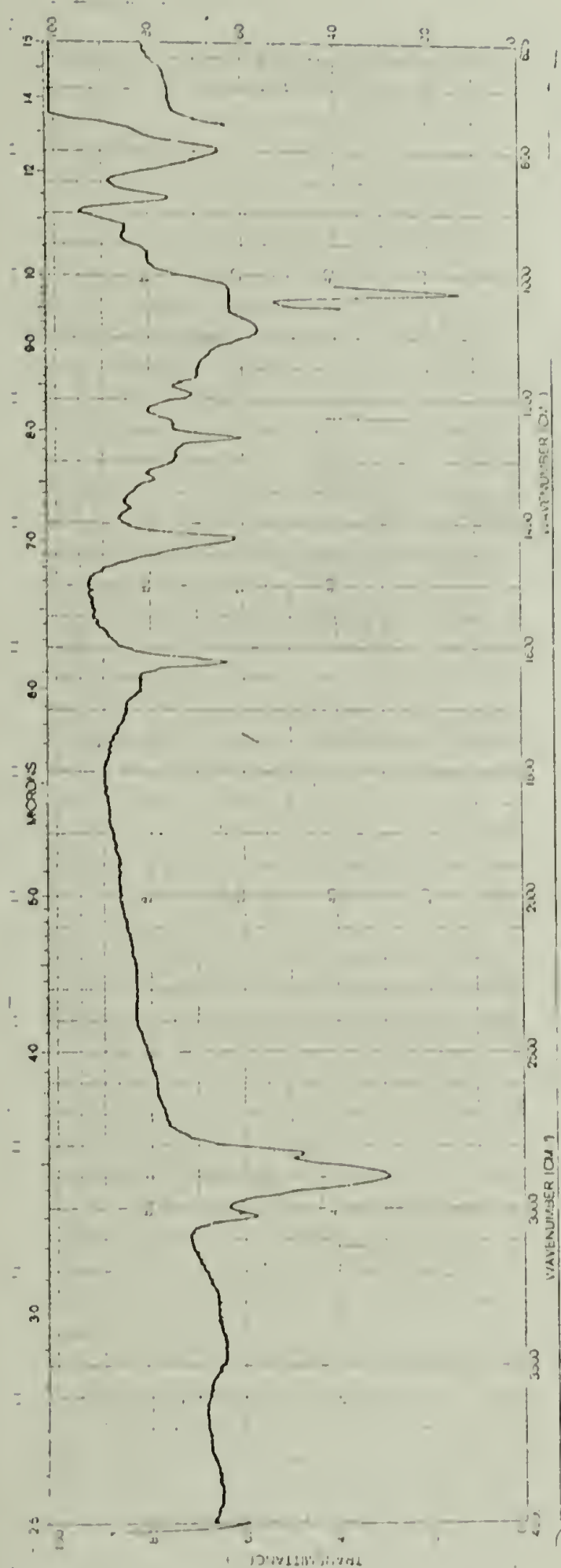
IR Spectrum No. 1. 3-Methylenecyclobutene, about 10% in  $\text{CCl}_4$ , 0.2 mm pathIR Spectrum No. 2. 1-Methyl-3-methylenecyclobutene, about 10% in  $\text{CCl}_4$ , 0.2 mm path.



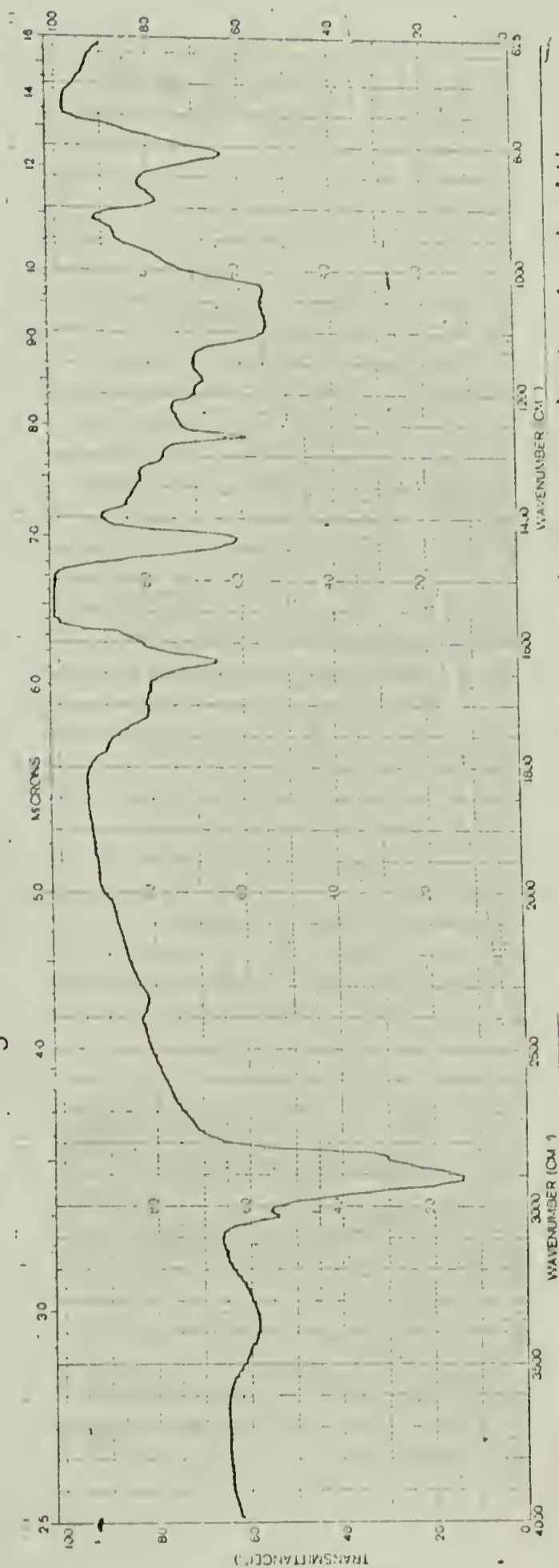
IR Spectra No. 3. Poly-3-methylenecyclobutene obtained with  $\text{BF}_3$ -etherate  
at  $22^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$ , KBr disk.



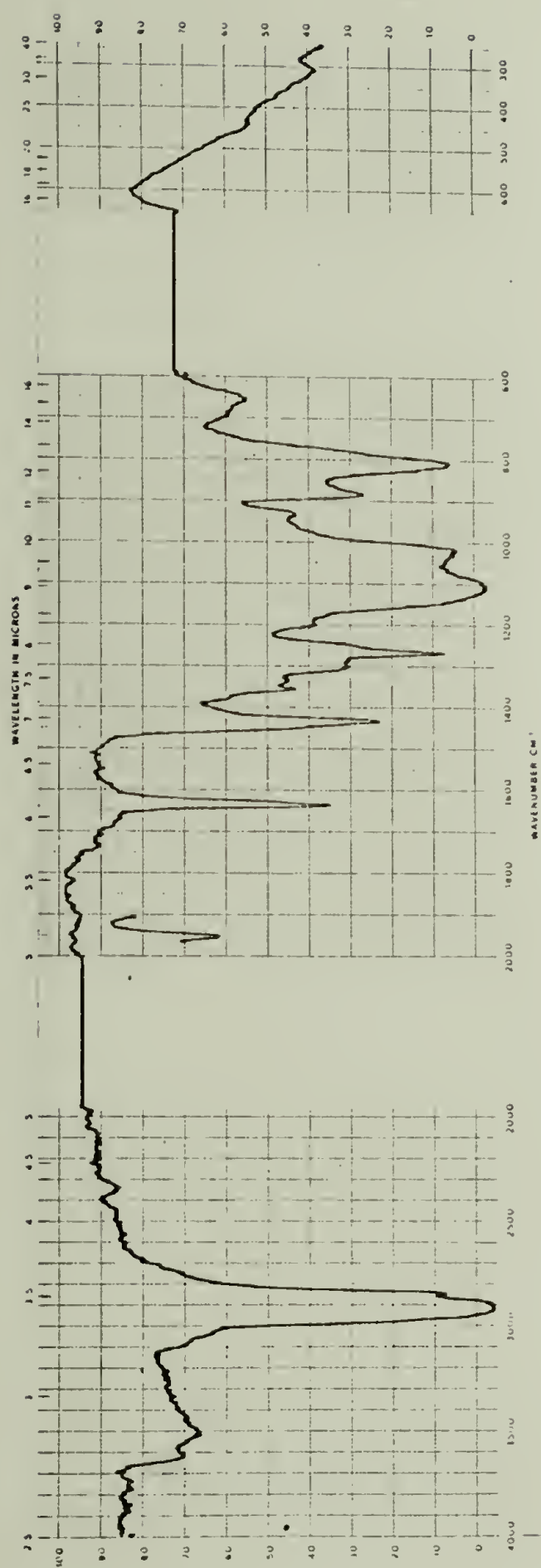
IR Spectra No. 4. Poly-3-methylenecyclobutene obtained with  $\text{AlEt}_2\text{Cl-H}_2\text{O}$   
at  $-78^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$ , KBr disk.



IR Spectra No. 5. Poly-3-methylenecyclobutene (Polymer A) obtained with  $\text{BF}_3$  at  $-78^\circ\text{C}$ , KBr disk.

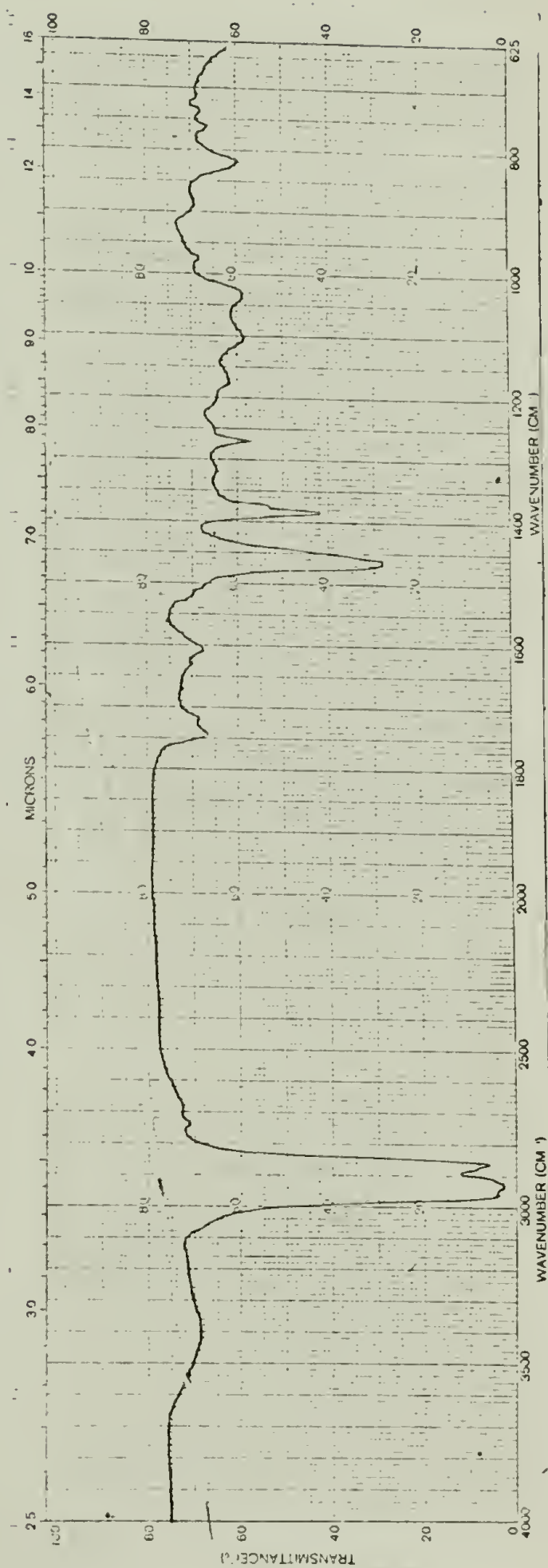


IR Spectra No. 6. Poly-3-methylenecyclobutene (Polymer B) obtained with  $\text{BF}_3 \cdot \text{OEt}_2$  at  $22^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$ , KBr disk.

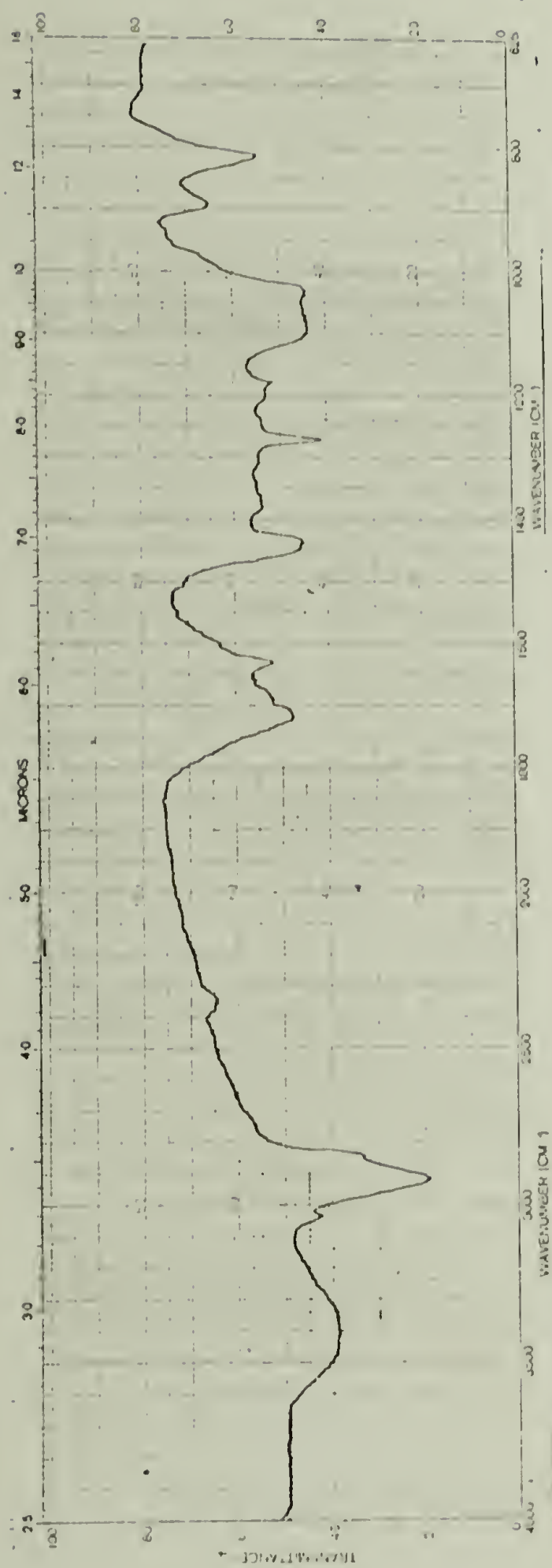


IR Spectra No. 7. Poly-3-methylenecyclobutene (Polymer C) obtained with  $\text{AlEt}_2\text{Cl}$ -

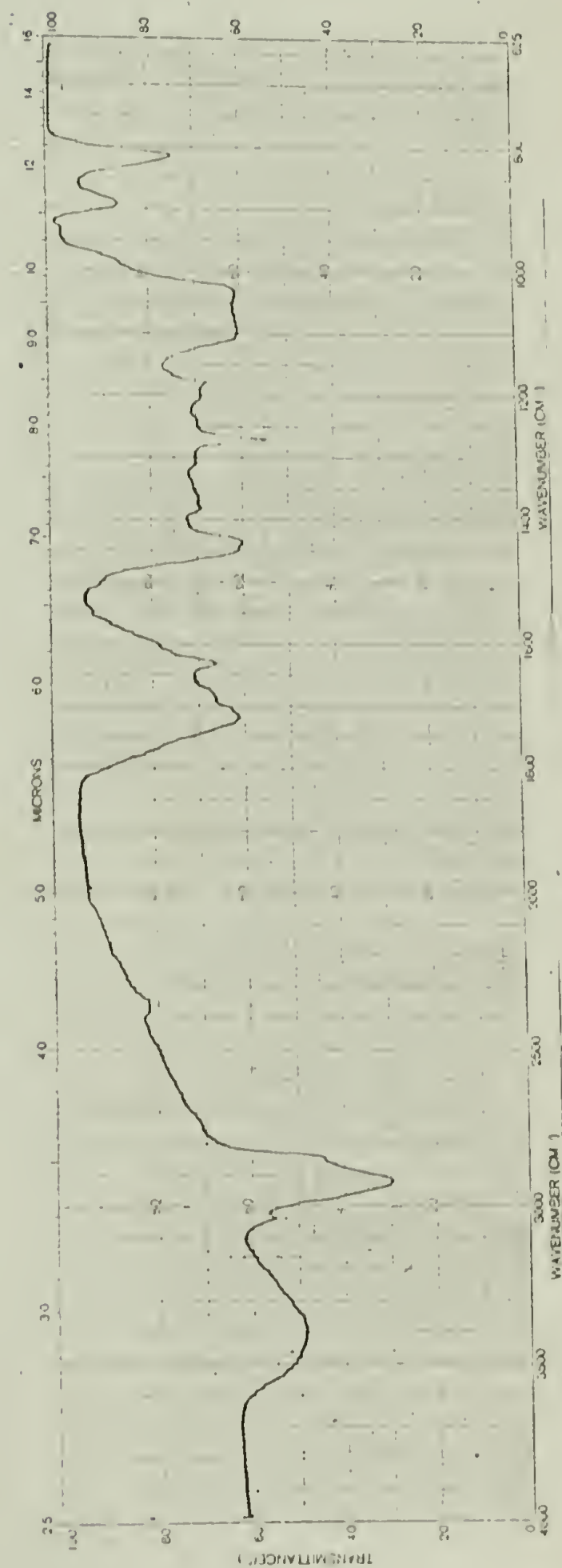
$\text{HBr}$  at  $-78^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$ ; about 10% in benzene, 0.2 mm path.



IR Spectra No. 8. Polymer C after hydrogenation, liquid film.



IR Spectra No. 9. Oxidized Polymer B, exposed to air one day, KBr disk.

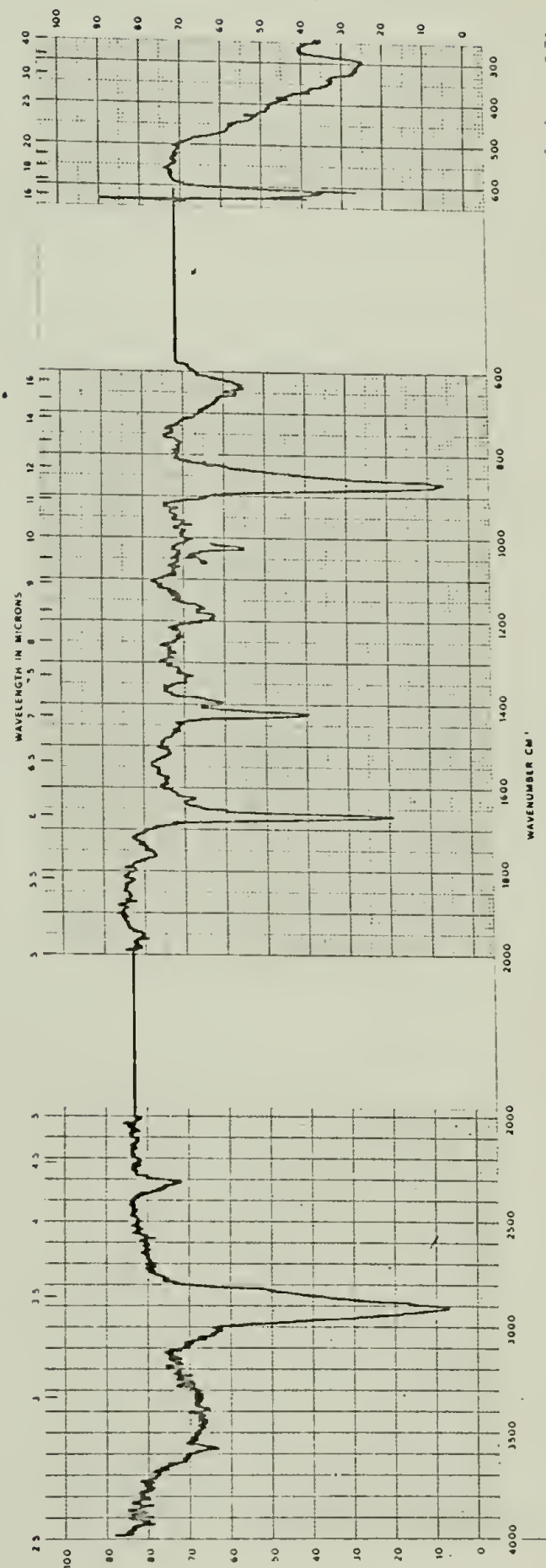


IR Spectra No. 10. Oxidized Polymer B, exposed to air two days, KBr disk.



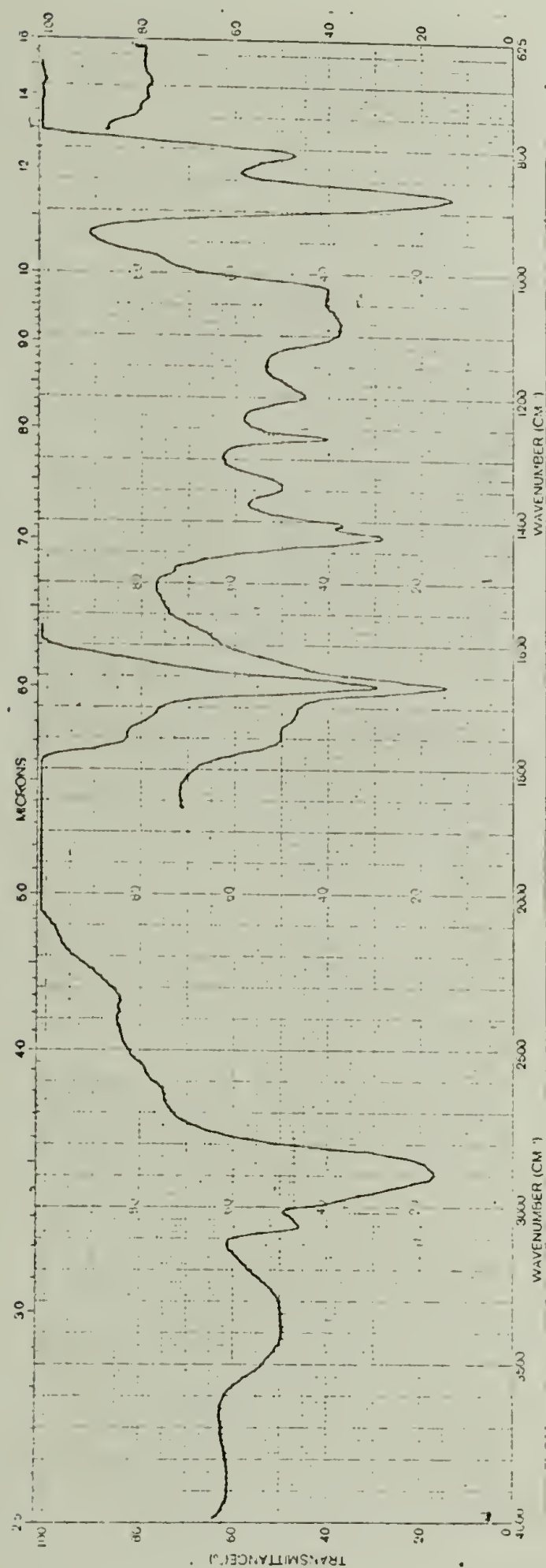
IR Spectrum No. 11.

Oxidized Polymer B, exposed to air 14 days, KBr disk.

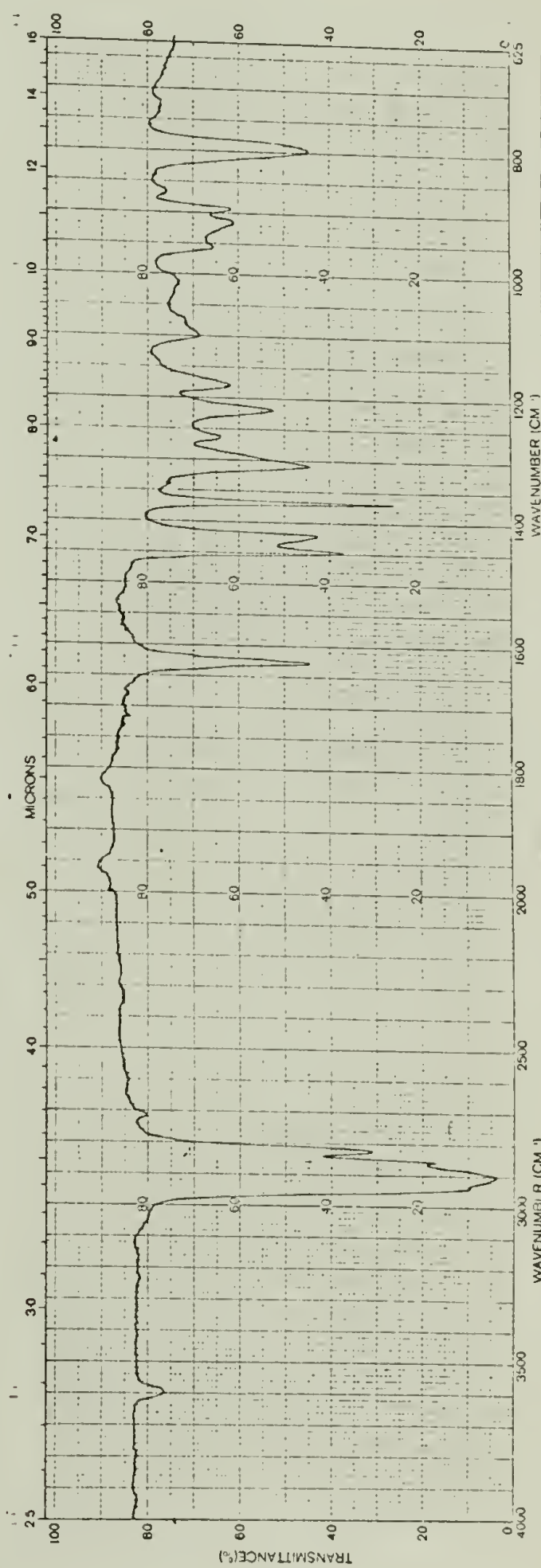


IR Spectrum No. 12.

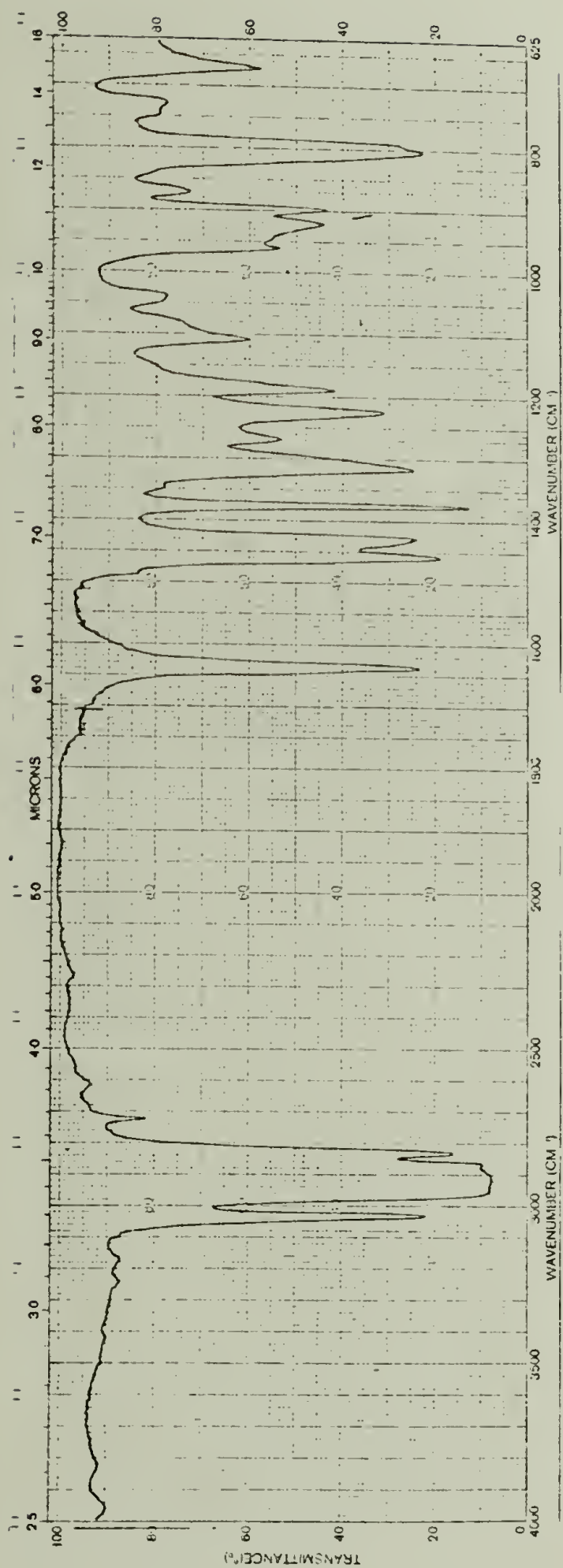
Poly-3-methylenecyclobutene obtained with  $n\text{-BuLi}$  at  $0^\circ\text{C}$ ;  
about 10% in benzene, 0.2 mm path.



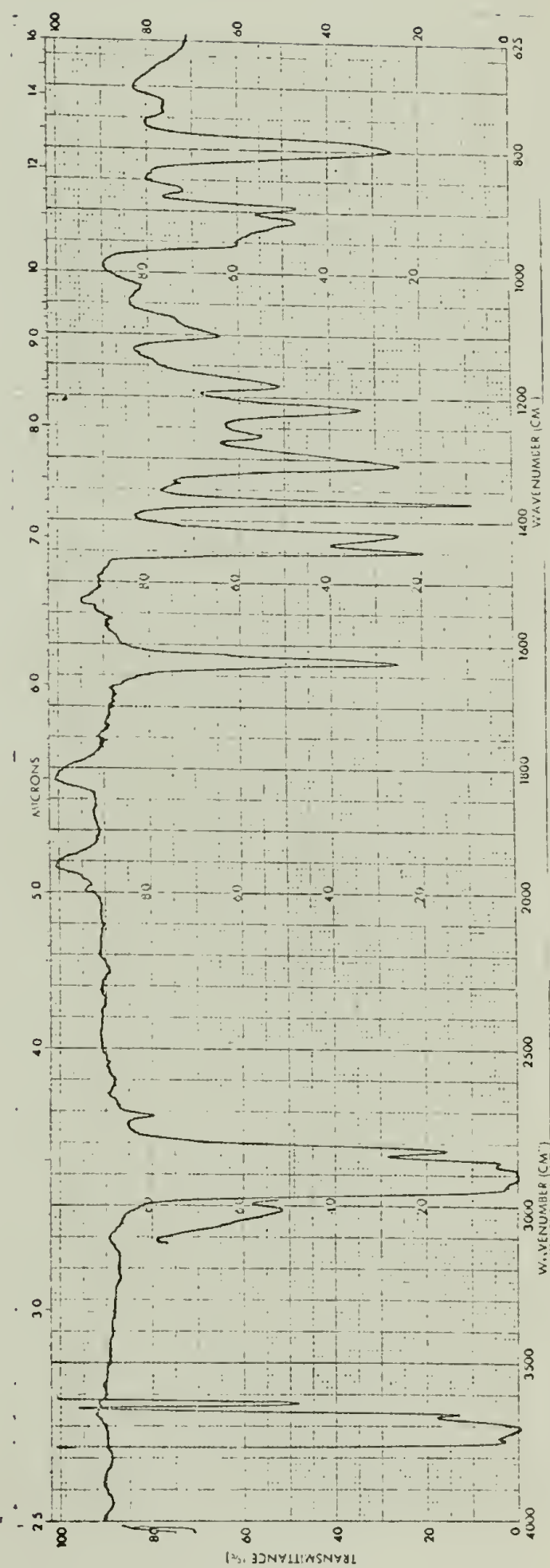
IR Spectra No. 13. Oxidized Poly-3-methylenecyclobutene obtained with n-BuLi at 0°C, KBr disk.



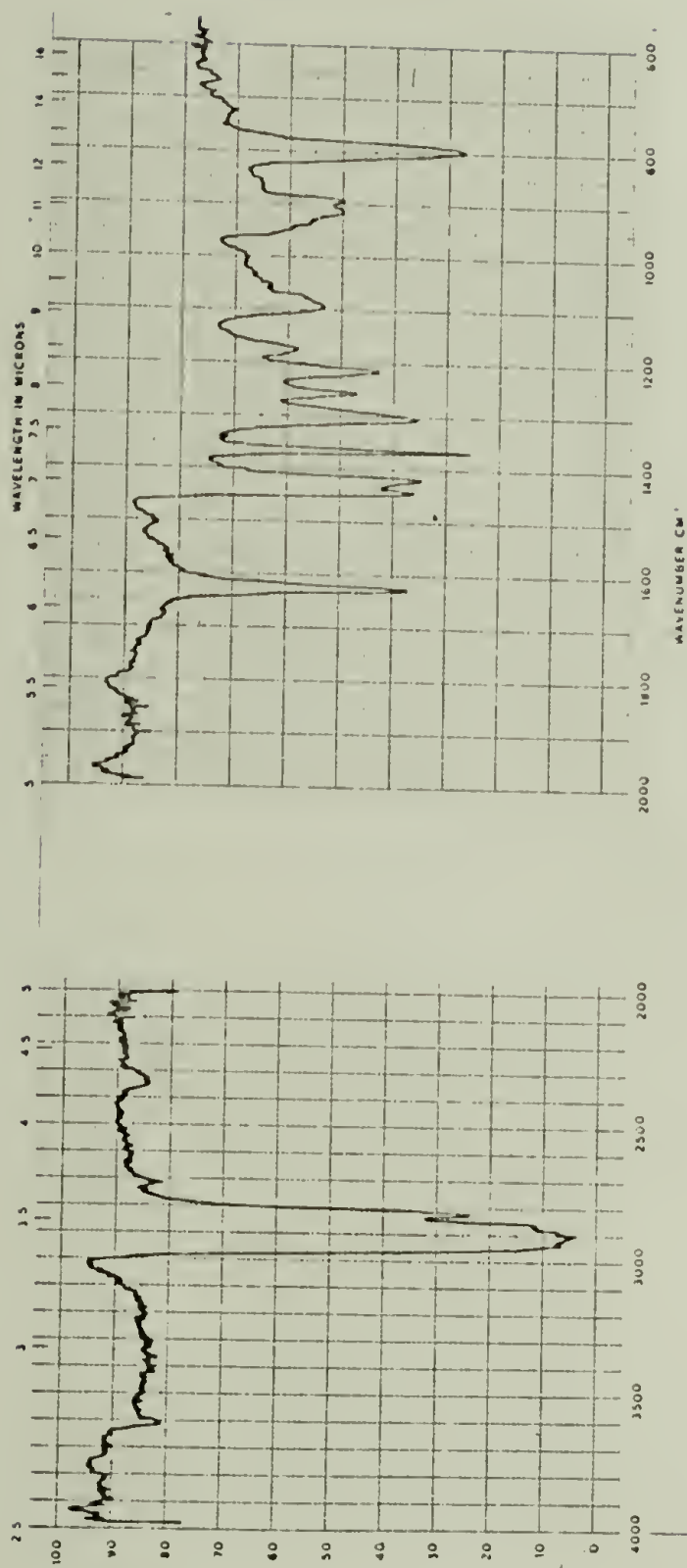
IR Spectra No. 14. Poly-1-methyl-3-methylenecyclobutene (Polymer E) obtained with  $\text{BF}_3$  at  $-78^\circ\text{C}$ ; about 10% in benzene, 0.2 mm path.



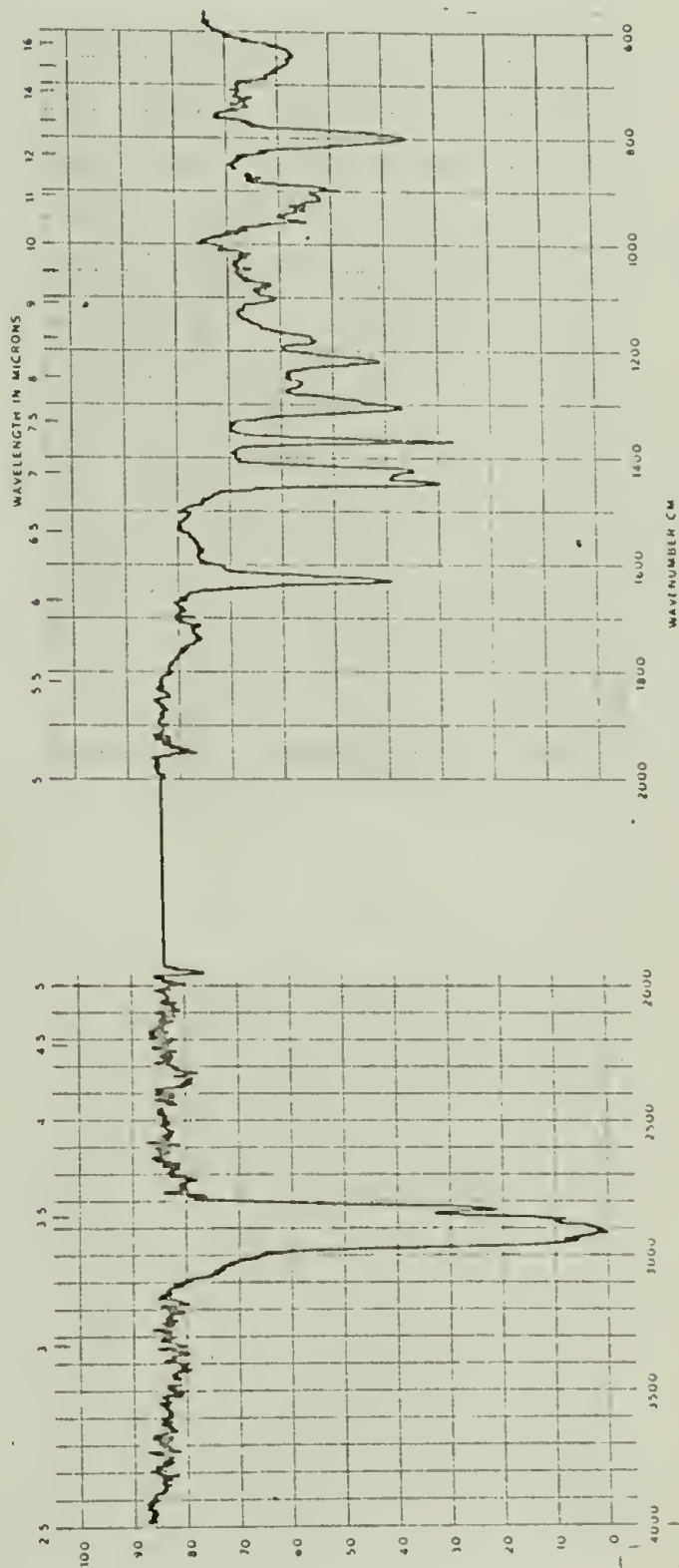
IR Spectra No. 15. Poly-1-methyl-3-methylenecyclobutene (Polymer F) obtained with  $\text{BF}_3 \cdot \text{OEt}_2$  at  $-78^\circ\text{C}$  in  $n$ -hexane; thin film on salt plate.



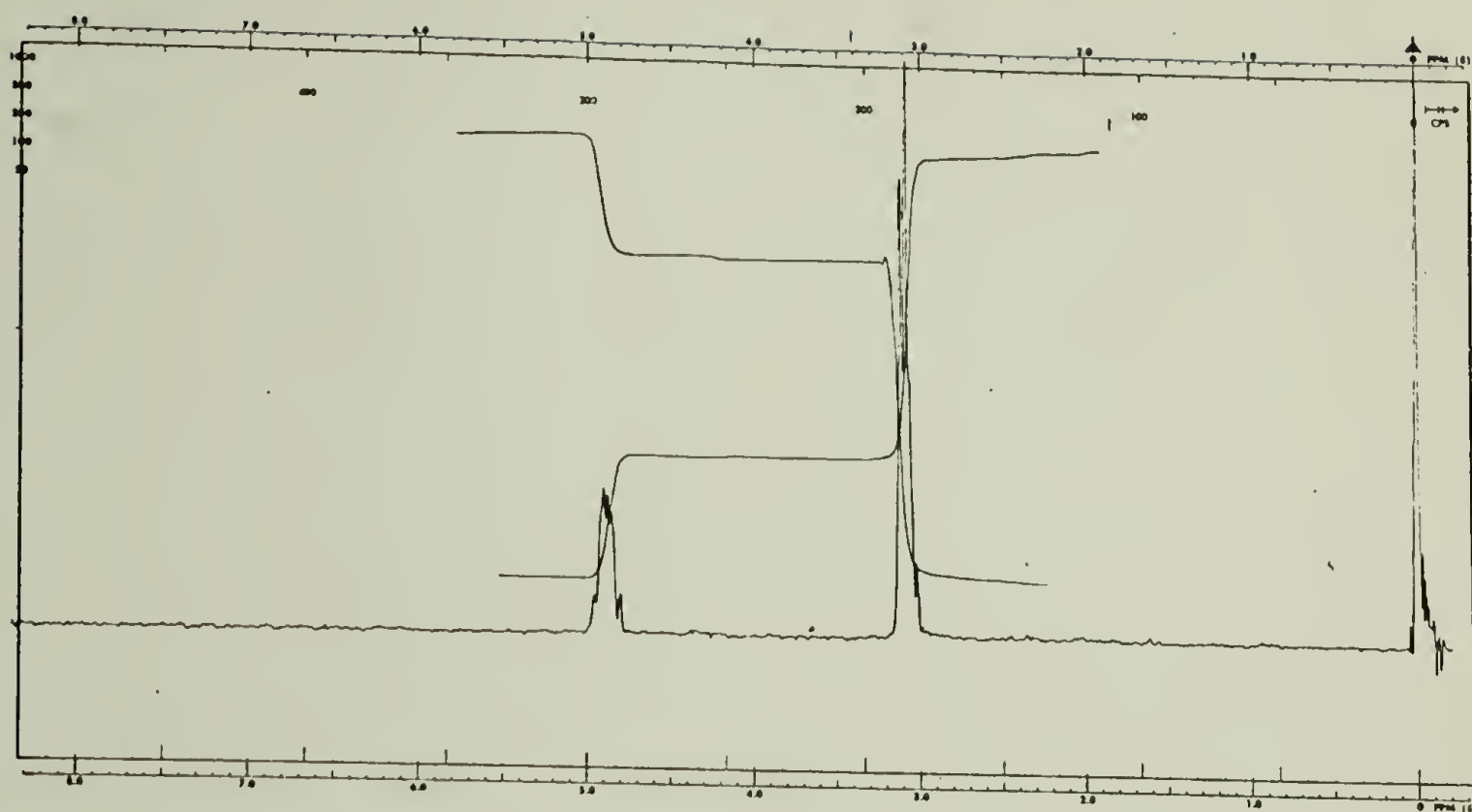
IR Spectra No. 16. Poly-1-methyl-3-methylenecyclobutene (Polymer G) obtained with  $\text{AlEt}_2\text{Cl-HBr}$  at  $-78^\circ\text{C}$  in toluene; about 10% in benzene, 0.2 mm path.



IR Spectra No. 17. Poly-1-methyl-3-methylenecyclobutene (Polymer I) obtained with  $\text{Al}(\text{i-Bu})_3\text{-VCl}_3$  at  $22^\circ\text{C}$  in n-hexane; about 10% in benzene, 0.2 mm path.



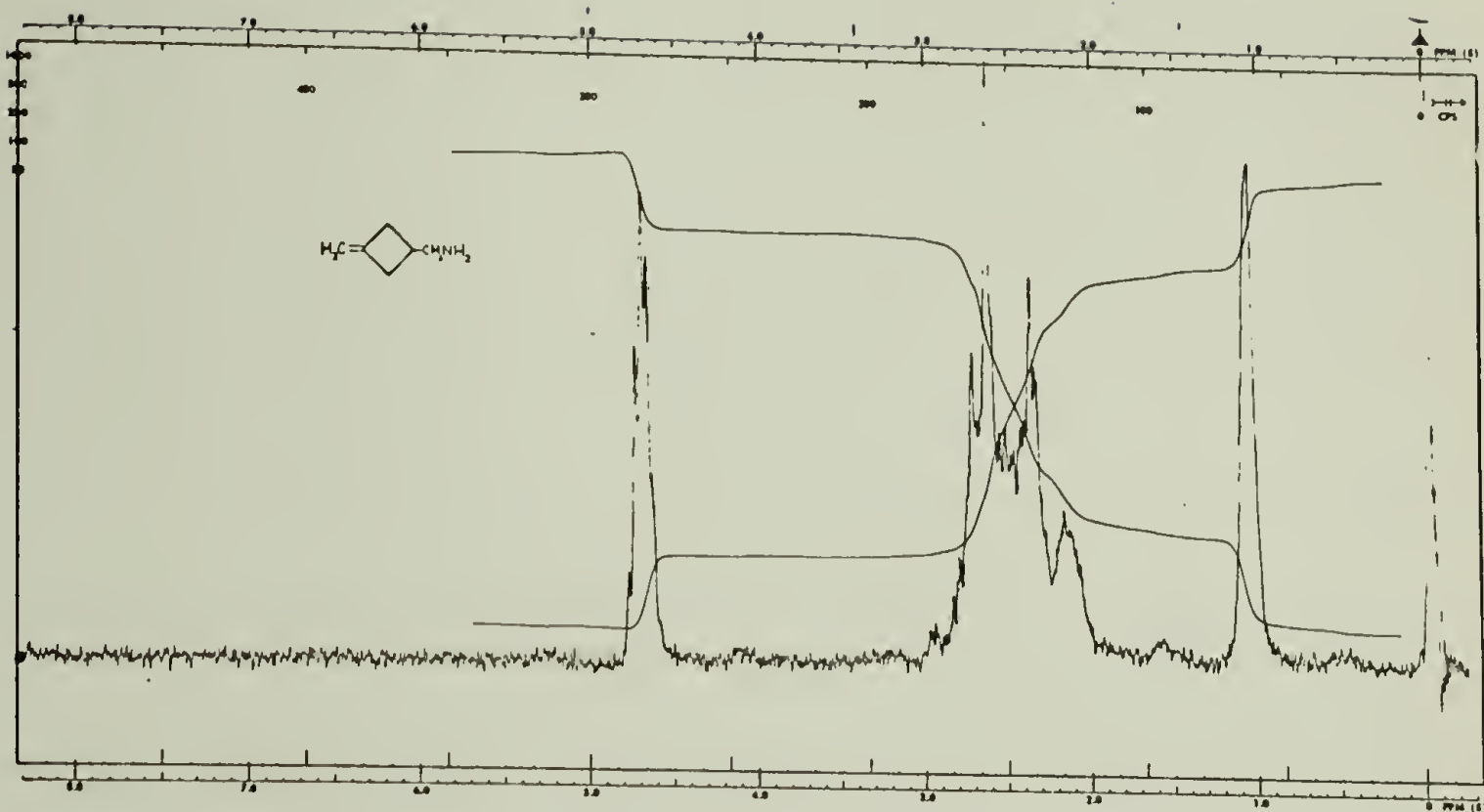
IR Spectra No. 18. Poly-1-methyl-3-methylenecyclobutene (Polymer J) obtained with  $\text{AlEt}_2\text{Cl-Co(acac)}_3$  at  $0^\circ\text{C}$  in benzene; about 10% in benzene, 0.2 mm path.



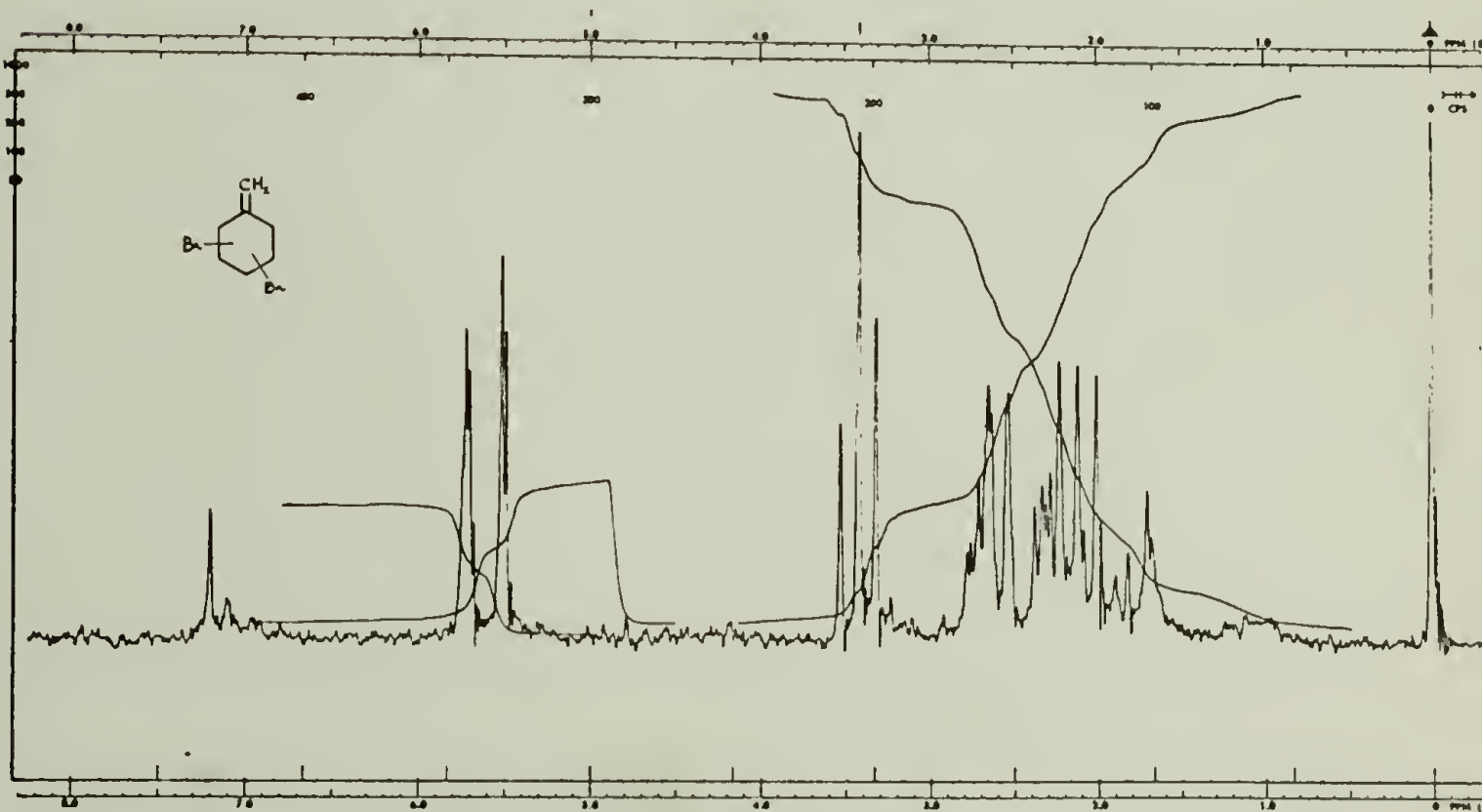
NMR Spectra No. 1. 3-Methylenecyclobutanecarbonitrile in carbon tetrachloride, 500 cps sweep width.



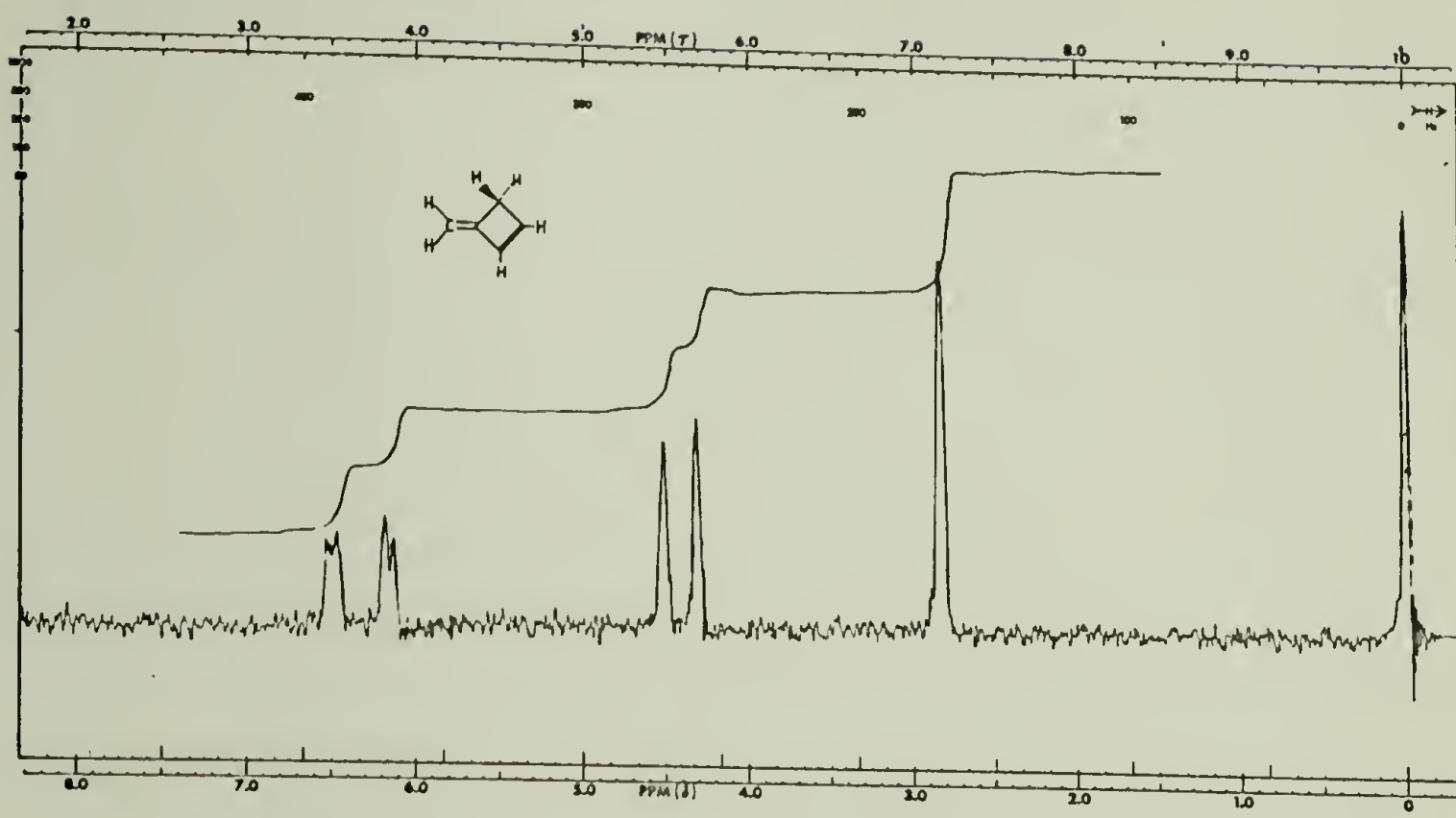
NMR Spectra No. 2. 3-methylenecyclobutanecarboxylic acid in carbon tetrachloride, 1000 cps sweep width.



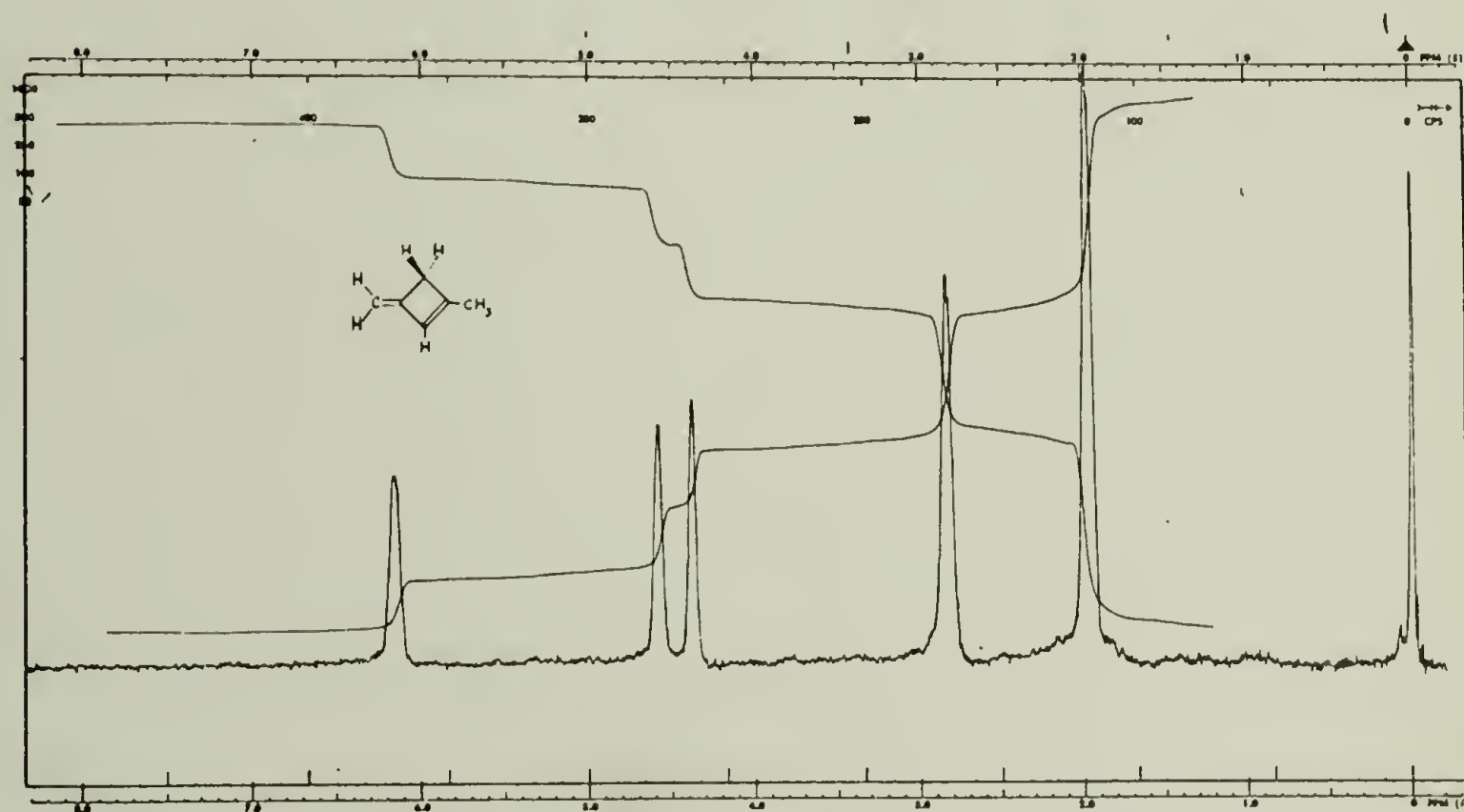
NMR Spectra No. 3. 3-Methylenecyclobutylcarbinylamine in carbon tetrachloride, 500 cps sweep width.



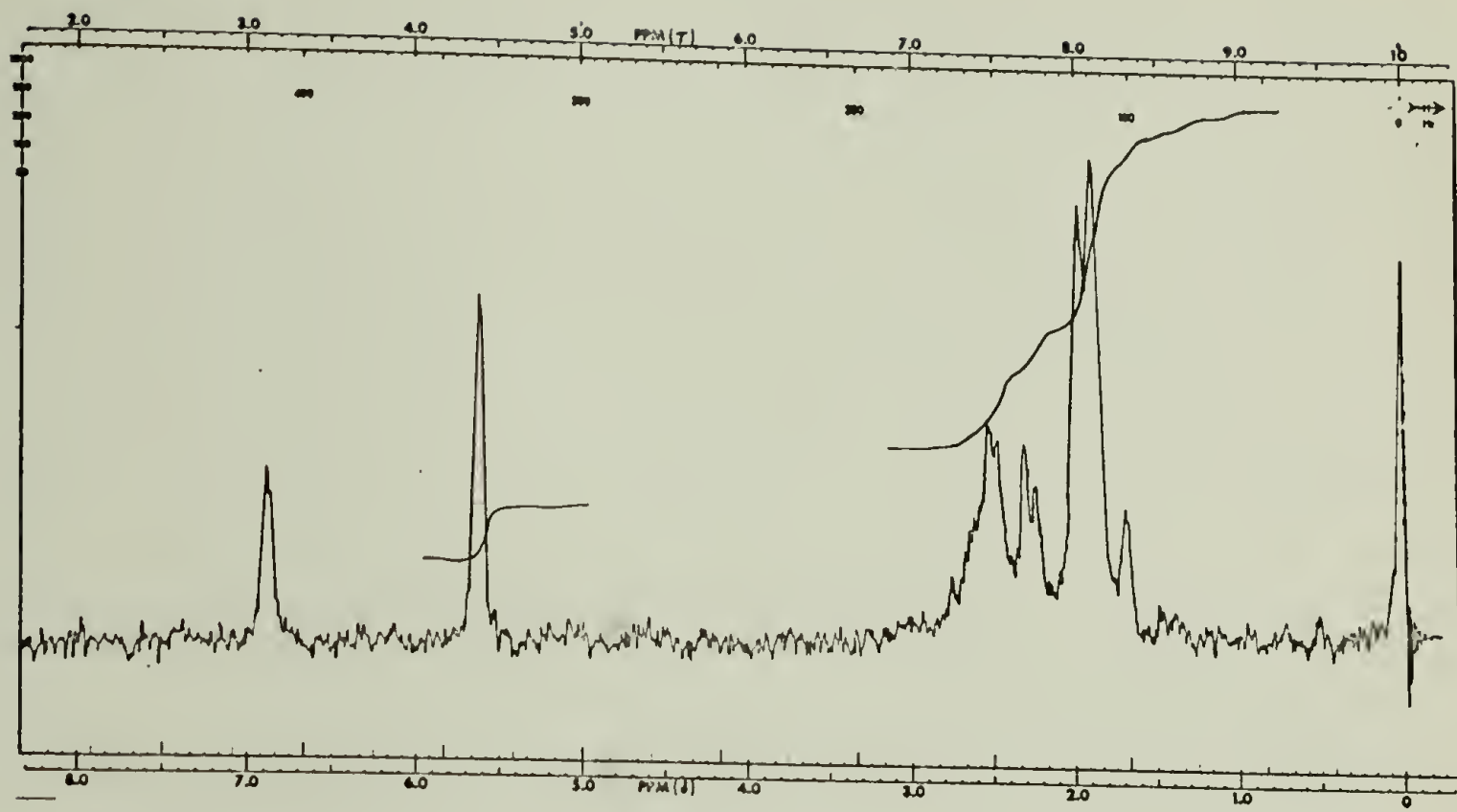
NMR Spectra No. 4. Reaction product of allene and vinylbromide in carbon tetrachloride, 500 cps sweep width.



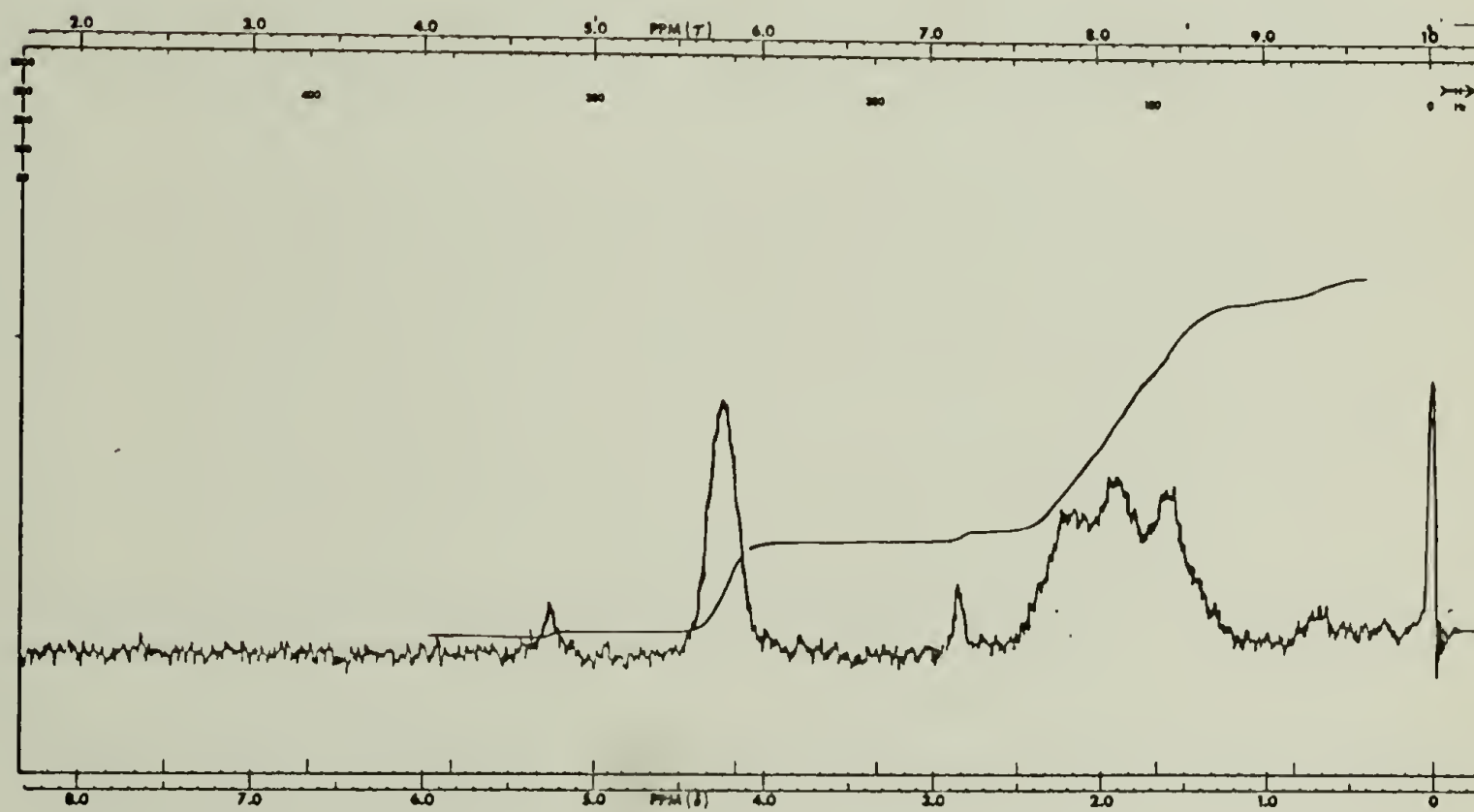
NMR Spectra No. 5. 3-Methylenecyclobutene in carbon tetrachloride, 500 cps sweep width.



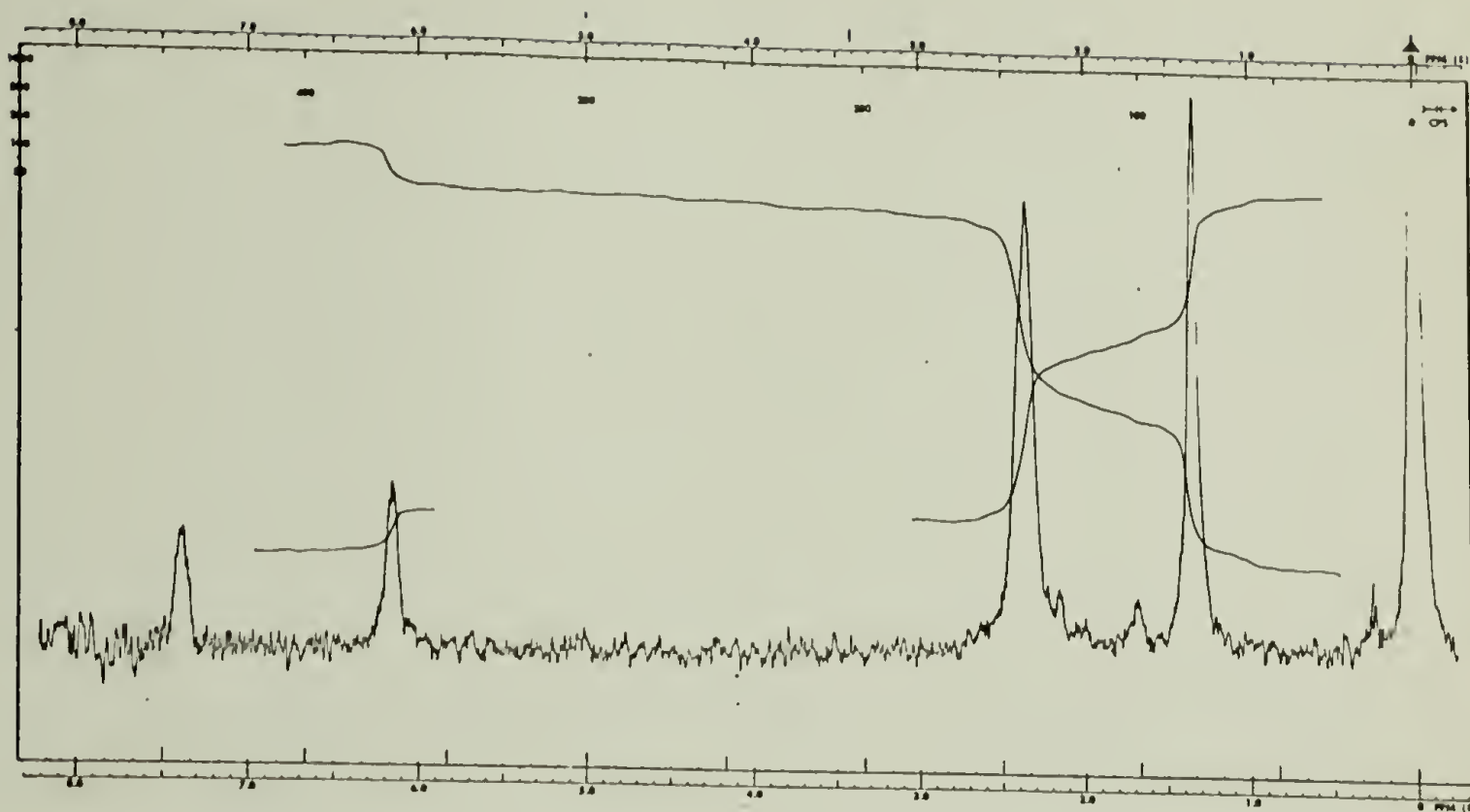
NMR Spectra No. 6. 1-Methyl-3-methylenecyclobutene in carbon tetrachloride, 500 cps sweep width.



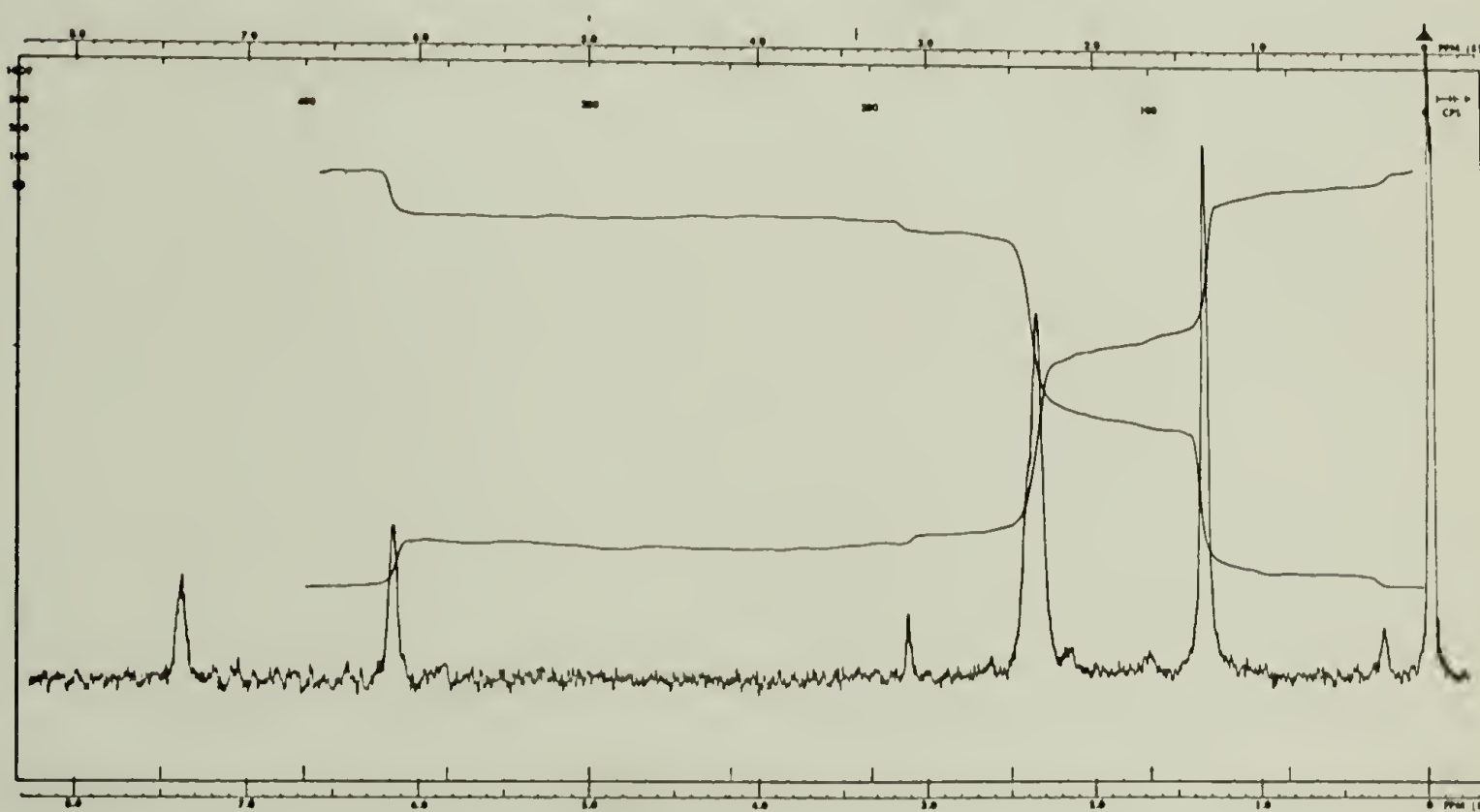
NMR Spectra No. 7. Poly-3-methylenecyclobutene (Polymer C) obtained with  $\text{AlEt}_2\text{Cl-HBr}$  at  $-78^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$ ; in deuterated benzene at room temperature, 500 cps sweep width.



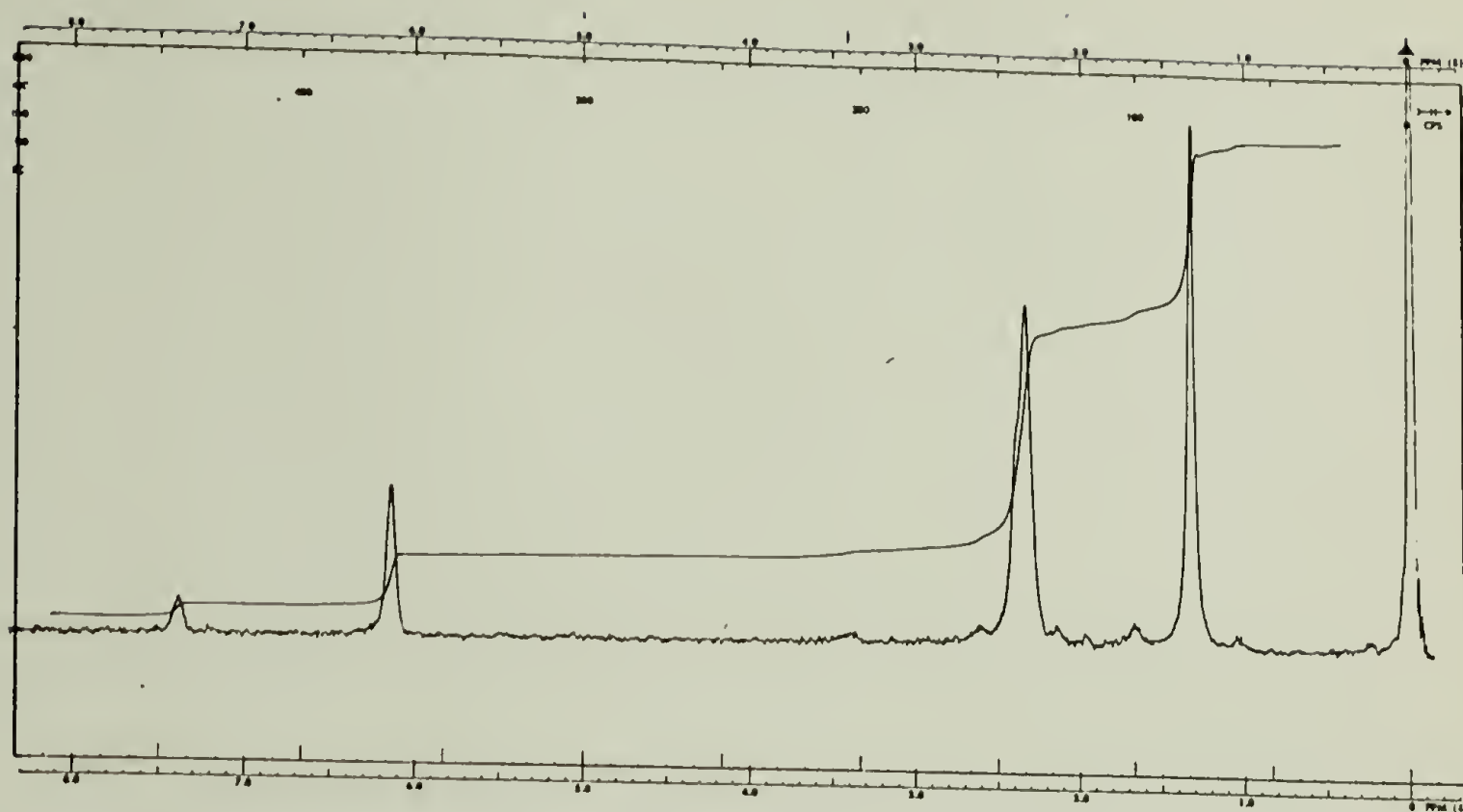
NMR Spectra No. 8. Poly-3-methylenecyclobutene obtained with  $n\text{-BuLi}$  at  $0^\circ\text{C}$ ; in carbon tetrachloride at room temperature, 500 cps sweep width.



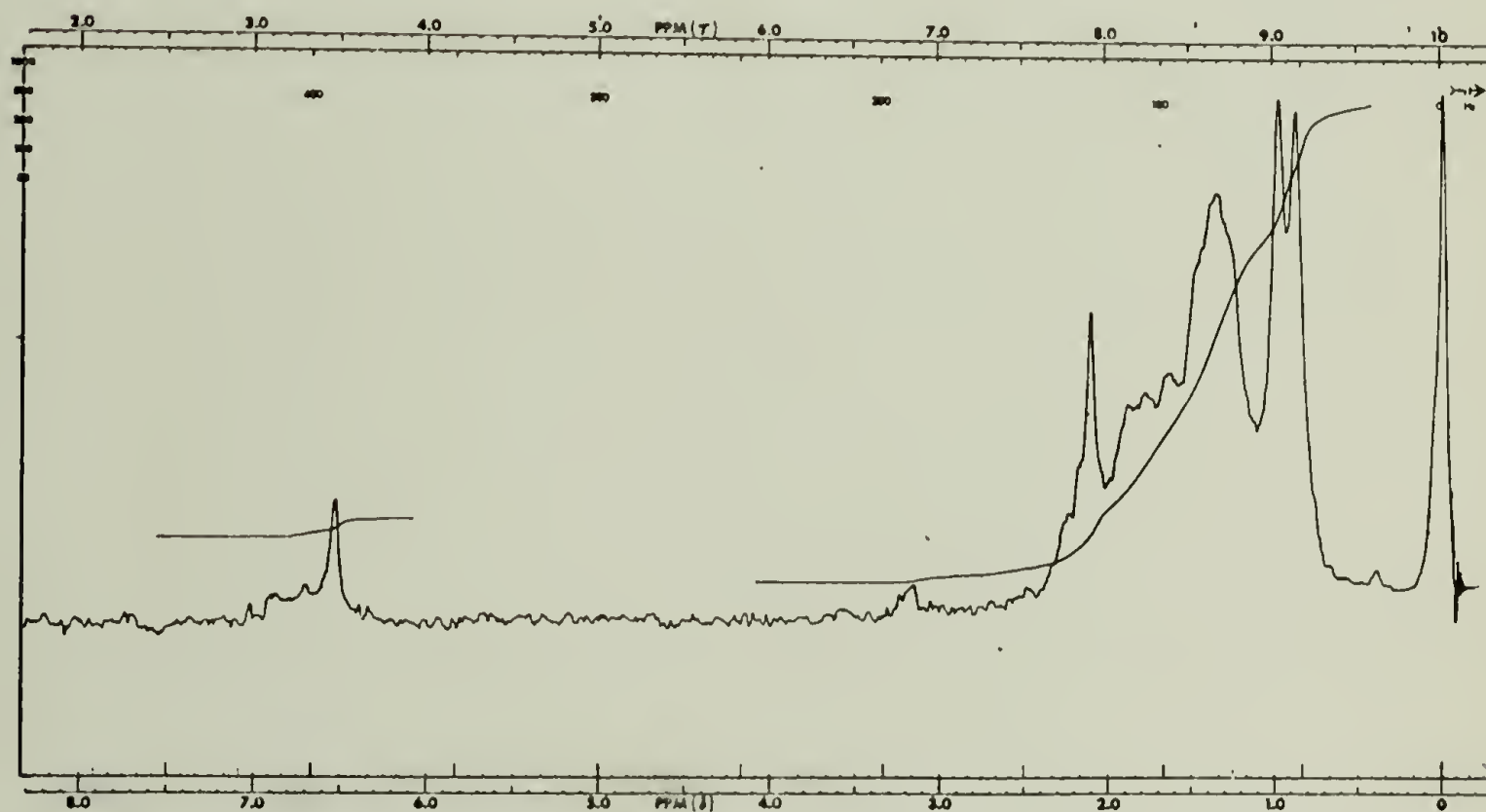
NMR Spectra No. 9. Poly-1-methyl-3-methylenecyclobutene (Polymer E) obtained with  $\text{BF}_3$  at  $-78^\circ\text{C}$ ; in deuterated benzene at room temperature, 500 cps sweep width.



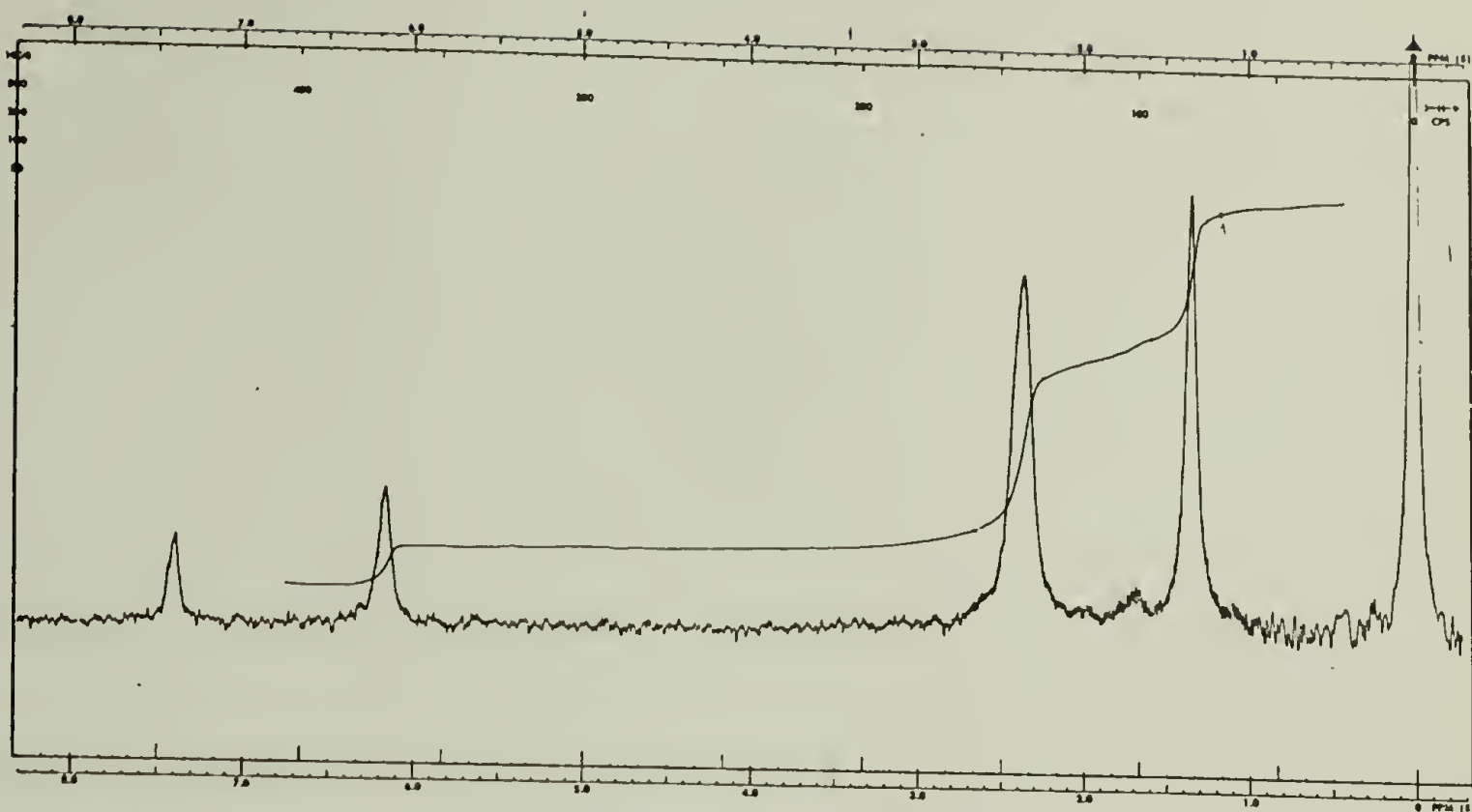
NMR Spectra No. 10. Poly-1-methyl-3-methylenecyclobutene (Polymer F) obtained with  $\text{BF}_3$ -etherate at  $-78^\circ\text{C}$  in n-hexane; in deuterated benzene at room temperature, 500 cps sweep width.



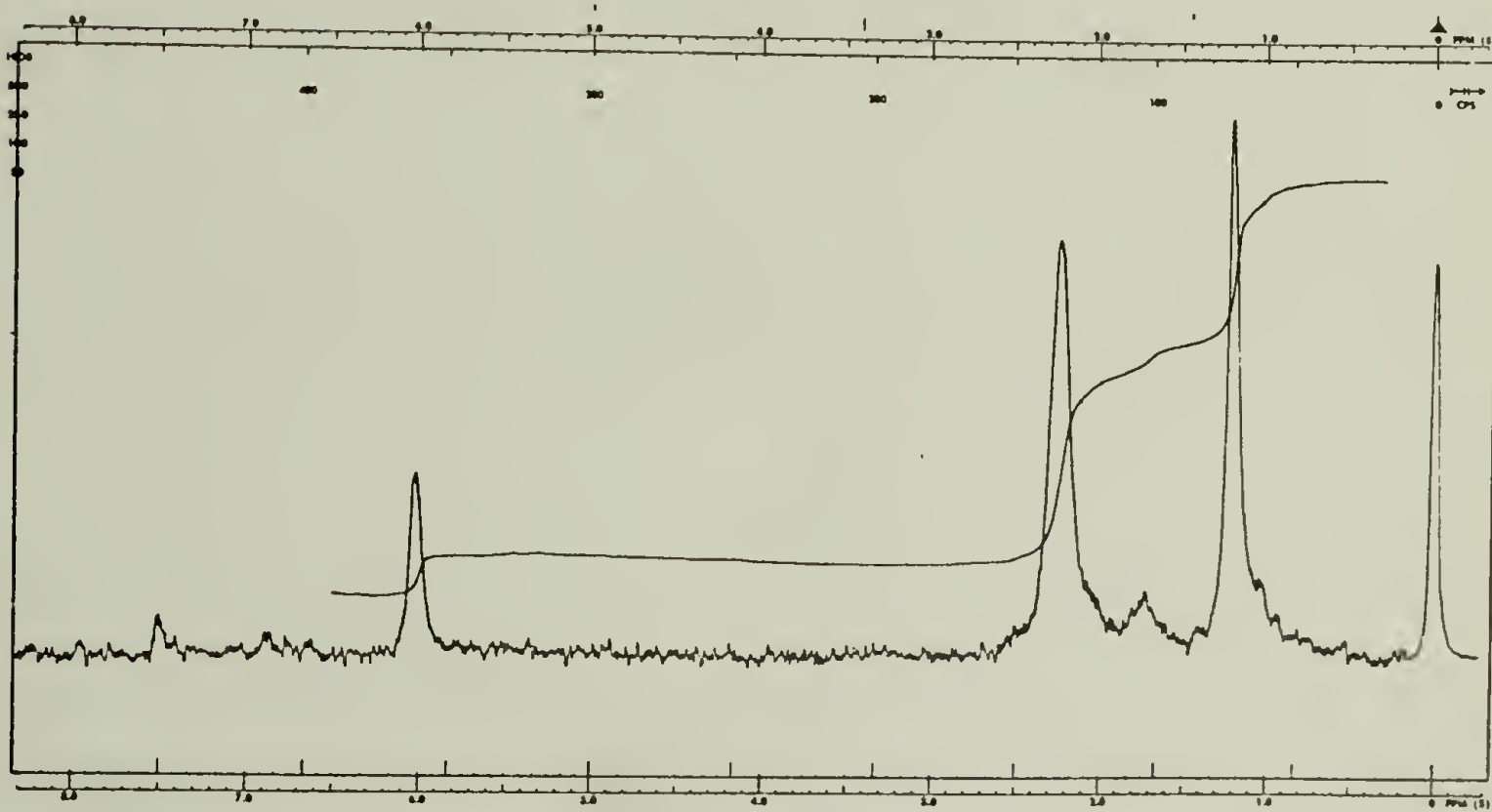
NMR Spectra No. 11. Poly-1-methyl-3-methylenecyclobutene (Polymer G) obtained with  $\text{AlEt}_2\text{Cl-HBr}$  at  $-78^\circ\text{C}$  in toluene; in deuterated benzene at room temperature, 500 cps sweep width.



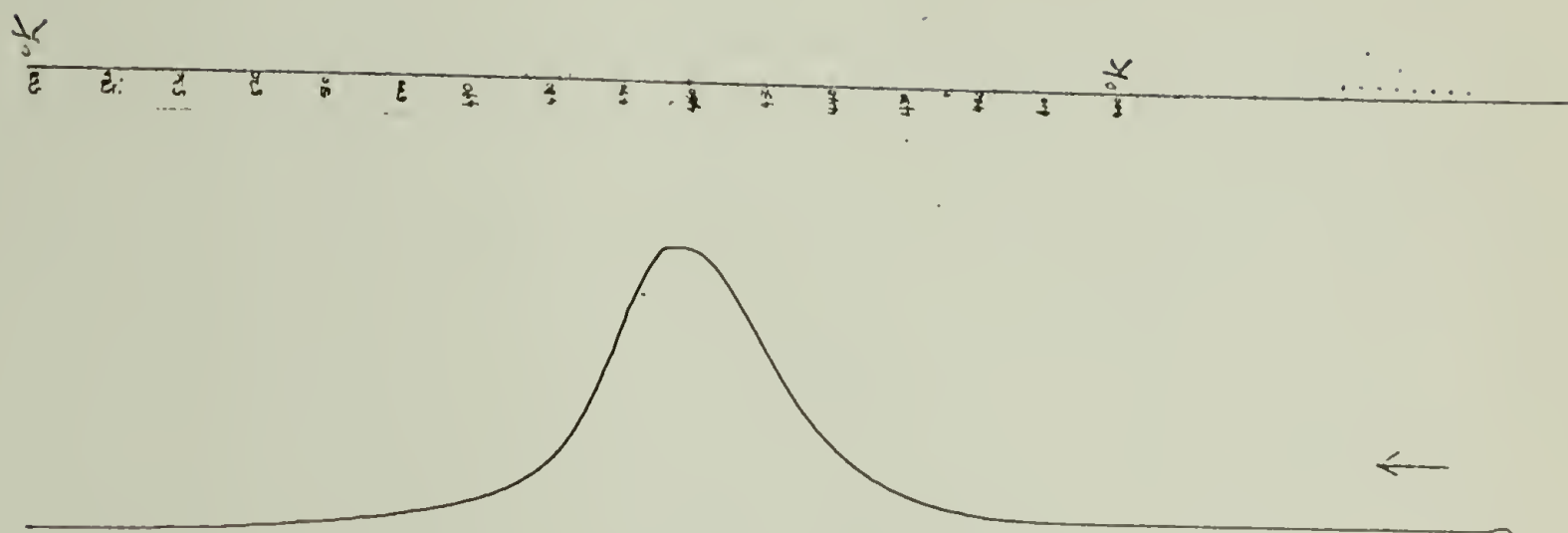
NMR Spectra No. 12. Polymer G after partial hydrogenation; in carbon tetrachloride, 500 cps sweep width.



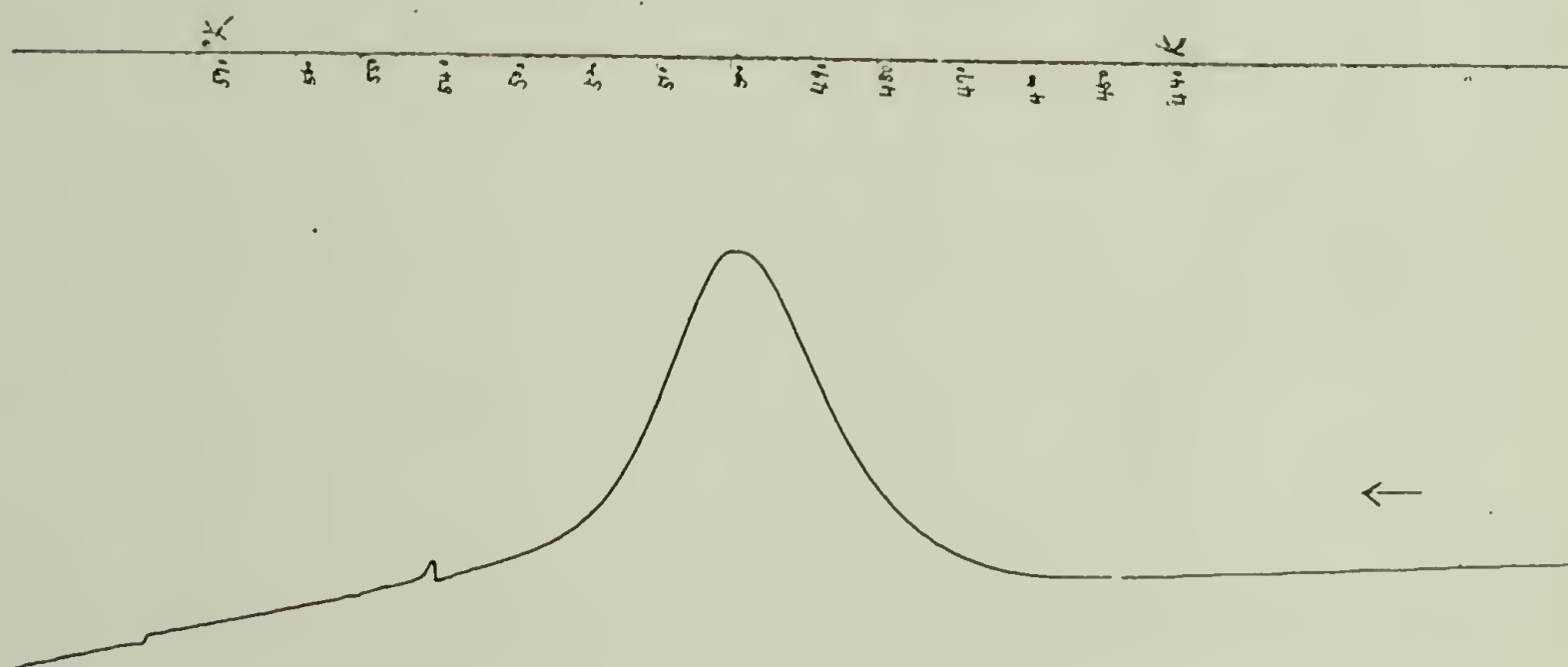
NMR Spectra No. 13. Poly-1-methyl-3-methylenecyclobutene (Polymer I) obtained with  $\text{Al}(\text{i-Bu})_3\text{-VCl}_3$  at  $22^\circ\text{C}$  in hexane; in deuterated benzene at room temperature, 500 cps sweep width.



NMR Spectra No. 14. Poly-1-methyl-3-methylenecyclobutene (Polymer J) obtained with  $\text{AlEt}_2\text{Cl-Co(acac)}_3$  at  $0^\circ\text{C}$  in benzene; in hexachlorobutadiene at room temperature, 500 cps sweep width.

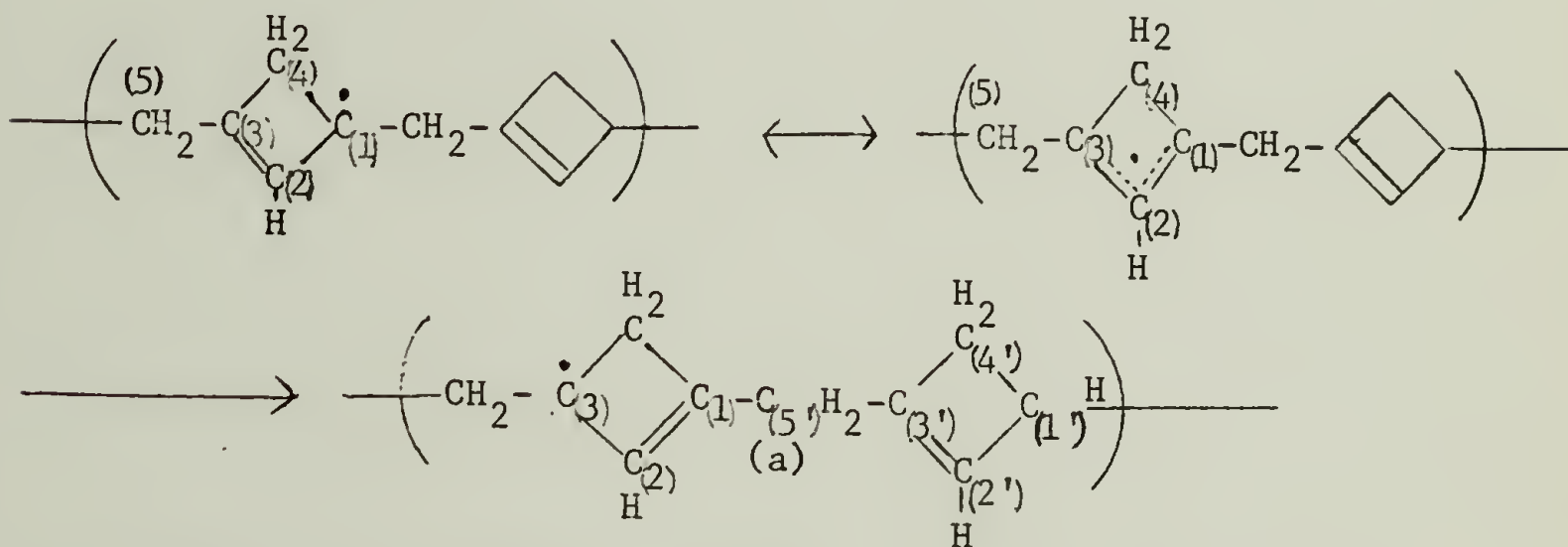


DSC thermogram of poly-3-methylenecyclobutene (Polymer D), 10°C/minute heating rate.



DSC thermogram of poly-1-methyl-3-methylenecyclobutene (Polymer F), 10°C/minute heating rate.

Autoxidation: (A). The allylic tertiary hydrogen atom at carbon 1 of the repeating unit of poly-3-methylenecyclobutene prepared cationically is most susceptible to abstraction by a radical. The radical so formed at carbon 1 can be delocalized by resonance stabilization, and the radical may therefore migrate to carbon 3 with simultaneous shift of double bond to C<sub>1</sub> and C<sub>2</sub> as shown in the following equation:



As a result of this possible migration of the double bond, the H-abstraction reactivity of the propylene combination of C<sub>5</sub>', C<sub>3</sub>', and C<sub>2</sub>', at the neighboring repeating unit will increase by 107 fold, according to Bolland's rule (iii) mentioned on page 69, because a hydrogen atom at position (a) is replaced by an alkenyl group. This mechanism may in part explain the great sensitivity of the subject polymer to autoxidation.

Any radical produced in the process of autoxidation of poly-3-methylenecyclobutene can attack the double bond of another nearby repeating unit, causing the formation of crosslinks through carbon-carbon, ether and peroxide bridges.

(B). Poly-1-methyl-3-methylenecyclobutene obtained cationically is relatively stable to autoxidation because the labile allylic tertiary hydrogen at  $C_1$  is now replaced by a methyl substituent. The IR spectrum of Polymer F film on salt plate does not show any change after two weeks of exposure to air and light, and there appears only small absorption bands due to hydroperoxide and carbonyl groups after three months. Moreover, the color of the film remains unchanged throughout the above period.

(C). Poly-1-methyl-3-methylenecyclobutenes prepared with Ziegler-Natta catalysts (Polymers H, I, and J) are subject to autoxidation catalyzed by the transition metal salts of cobalt and vanadium which have at least two readily accessible oxidation states differing by one unit. The traces of these two metals in the polymers undergo the alternating one-electron oxidation and reduction reaction with hydroperoxide to supply a continuous flow of new radical to the system. The higher concentration of  $VCl_3$  catalyst employed in Polymer H apparently results in higher rate of polymer autoxidation. Therefore, Polymer H is found to contain 23.1% of oxygen according to an elemental analysis. The polymer insolubility is probably due to the effects of autoxidation.

Crystallinity: Cationic polymerization of 3-methylenecyclobutene and 1-methyl-3-methylenecyclobutene through 1,5-propagation gives rise to an asymmetric center at carbon 1 of each polymer repeating unit, hence crystalline stereoregular polymers are possible. However,

under the experimental conditions, there seems to be lack of stereo-regulating control to yield the desired crystalline polymers. Any structural change resulting from autoxidation will probably further disrupt the ordered placement, if any, in the polymer chain.

