

# Catalyzed Polymerization of Cycloolefins

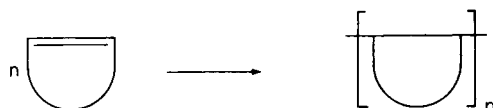
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## Synopsis

The catalyzed polymerization of cycloolefins may lead to a ring retention polymer product or to a polyalkenamer. The homogeneous catalysts, derived from V, W, Mo, and Re transition metal complexes, normally require the synergistic use of an alkylaluminum cocatalyst. *Trans*-1, 5-polyalkenamers exhibit elastomeric properties and might be suitable for tire manufacture.

## INTRODUCTION

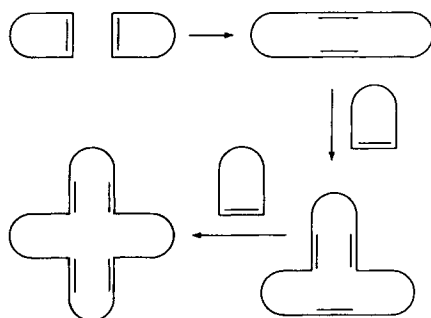
Cycloolefin monomers have been recognized to homopolymerize by two distinct mechanisms. The first and older is the conventional addition polymerization path through the double bond (Scheme 1). This process is analogous to the



Scheme 1.

addition polymerization of terminal alkenes. The polymer produced by the addition polymerization retains the cyclic ring.

The second process involves a ring-opening polymerization reaction. In this process, for every double bond that opens in the cyclic monomer, a new double bond is formed in the polymer (Scheme 2). Therefore, the total number and



Scheme 2.

type of carbon-carbon bonds is the same before and after the polymerization.

## DOUBLE-BOND OPENING POLYMERIZATION

Very few systems have been effective in polymerizing cycloalkenes via the double-bond opening process. The initial double bonds are generally inert

TABLE I  
Polymerizability of Cycloolefins by Various Catalysts<sup>5</sup>

Cycloolefin	AlCl <sub>3</sub> in C <sub>2</sub> H <sub>5</sub> Cl	Al(CH <sub>3</sub> ) <sub>3</sub> or Al(CH <sub>3</sub> ) <sub>3</sub> with VCl <sub>4</sub>	Al(CH <sub>3</sub> ) <sub>3</sub> or Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> with TiCl <sub>3</sub> AA <sup>a</sup>
Cyclopentene	no	yes	yes
3-Methylcyclopentene	yes	no	no
Cyclohexene	no	no	no
3-Methylcyclohexene	yes	yes	no

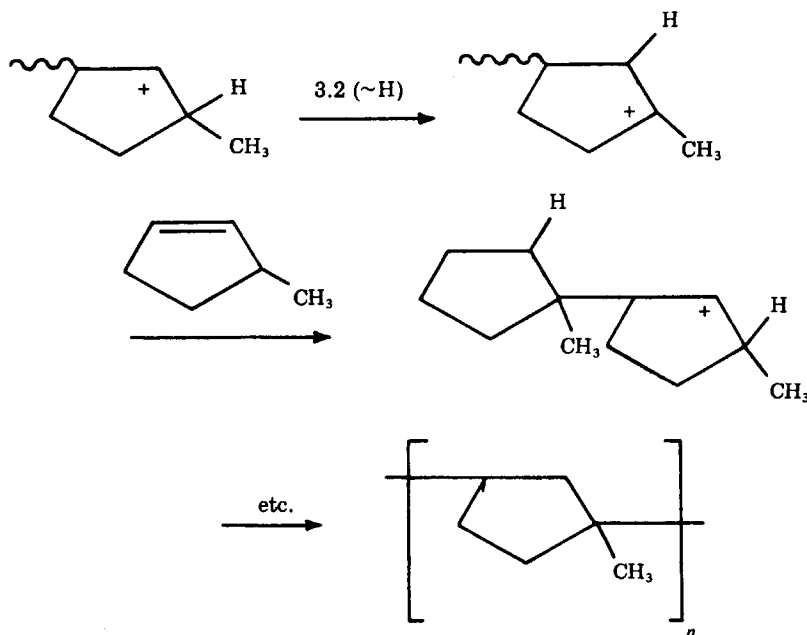
<sup>a</sup> The commercial product, Aluminum-reduced TiCl<sub>3</sub>AA, of Stauffer Chemical Co., Richmond, CA, is prepared by reducing TiCl<sub>4</sub> with an aluminum and then activating the product.

toward homopolymerization, and only in special cases where the internal bonds are constituents of highly strained ring systems have normal addition homopolymerizations been accomplished. For example, cyclopropene,<sup>1</sup> cyclobutene,<sup>2,3</sup> and certain strained five-member unsaturated rings such as bicyclo (2.2.1) hept-2-ene<sup>4</sup> have been polymerized through the double bond.

Boor et al.<sup>5,6</sup> have carried out a systematic study on the polymerization of cycloolefins such as cyclopentene, 3-methylcyclopentene, cyclohexene, and 3-methylcyclohexene by Ziegler-Natta and cationic catalysts. Table I summarizes the results of this study.

Cyclopentene is polymerized very slowly by VCl<sub>4</sub>/Al(CH<sub>2</sub>)<sub>3</sub>, VCl<sub>4</sub>/Al(CH<sub>3</sub>)<sub>2</sub>Cl, TiCl<sub>3</sub>AA/Al(CH<sub>3</sub>)<sub>3</sub>, and TiCl<sub>3</sub>AA/Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> to give a mixture of polycyclopentene ring retention product and cis-trans polypentenamers.

The 3-methylcyclopentene monomers polymerized cationically only. The mechanism probably proceeds by cationic 1,3-addition preceded by a 3,2-hydride shift (Scheme 3).



Scheme 3.

The 3-methylcyclohexene has been polymerized by  $\text{AlCl}_3$  and by the  $\text{VCl}_4/\text{Al}(\text{CH}_3)_2\text{Cl}$  system, while  $\text{TiCl}_4\text{AA}/\text{Al}(\text{CH}_3)_3$  was ineffective. As with 3-methylcyclopentene ring-opening polymerization did not take place; the poly(3-methylcyclohexene) was obtained. It is interesting to note that while the  $\text{VCl}_4/\text{Al}(\text{CH}_3)_2\text{Cl}$  system was effective in polymerization 3-methyl cyclohexene, the same catalyst did not polymerize 3-methylcyclopentene.

As shown in Table I, cyclohexene was not polymerizable by any of the catalysts employed in this study.

The conventional addition polymerization for parent cyclopentene and cyclohexene has been cited in two short reports. In one of these, Hoffman<sup>7</sup> discussed briefly the polymerization of cyclopentene and cyclohexene. These monomers were homooligomerized in the presence of the  $\text{BF}_3/\text{HF}$  system to some dimers, trimers, and tetramers. Also, in another report<sup>8</sup> it is claimed that cyclopentene and cyclohexene were polymerizable under very harsh conditions (300°C, 6500 atm). The products were saturated polymers which contained cyclic monomeric units.

Numerous unsuccessful attempts have been made to homopolymerize cyclohexene under mild conditions either by ring-opening or by double bond-opening mechanism.<sup>9-11</sup> The reason for this failure has been attributed to the high ring stability. Recently, however, we discovered<sup>12-14</sup> that the  $\text{Re}(\text{CO})_5\text{Cl}/\text{C}_2\text{H}_5\text{AlCl}_2$  system promotes the homopolymerization of cyclohexene via the double-bond opening process. The weight average molecular weight of the polymer was about 2500 (500-500 range). Cyclic olefins containing five-, six-, seven-, and eight-member rings were also polymerized by the above homogeneous catalyst system.

As shown in Table II, five-, six-, seven-, and eight-member rings are all polymerized, provided no steric hindrance is encountered. Methyl groups as close to the double bond as the allylic carbon render the cycloolefin inert to polymerization.

Physical measurements such as IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR indicate that the cyclic ring is retained and that the final polymer products are made up of repeating 1,2-, or a combination of 1,2-, and isomerized single-bond units. Further support for ring retention was provided by pyrolysis and gas chromatographic studies of polycyclohexene.

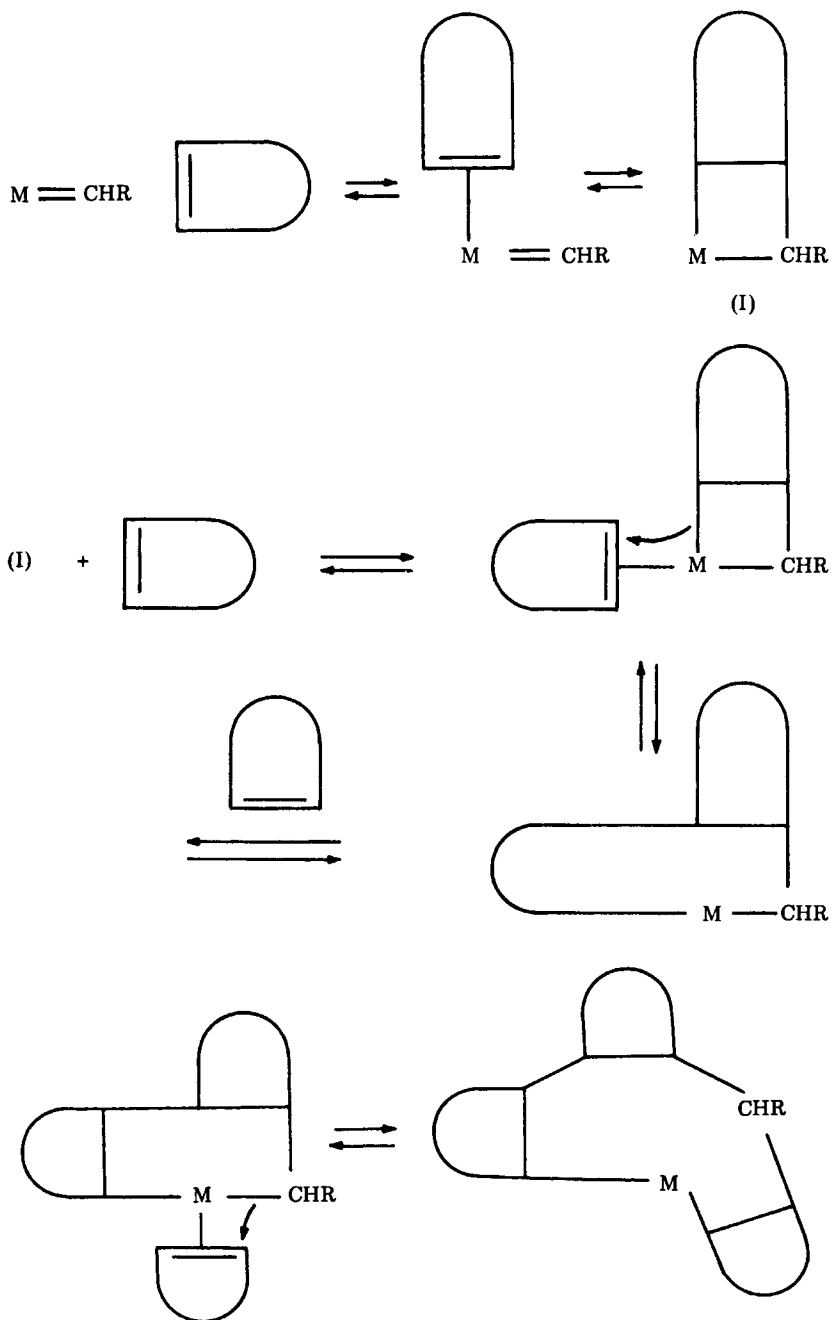
TABLE II  
Polymerization of Cycloolefins by  $\text{Re}(\text{CO})_5\text{Cl}/\text{C}_2\text{H}_5\text{AlCl}_2$  System<sup>14</sup>

Cycloolefin	Polymerizability <sup>a</sup>
Cyclopentene	yes
3-Methylcyclopentene	no
Cyclohexene	yes
3-Methylcyclohexene	no
4-Methylcyclohexene	yes
1,2-Dimethylcyclohexene	no
4,4-Dimethylcyclohexene	yes
Cycloheptene	yes
Cyclooctene	yes

<sup>a</sup> Conditions: All reactions were carried out with a  $\text{Re}(\text{CO})_5\text{Cl}/\text{C}_2\text{H}_5\text{AlCl}_2$  molar ratio of 1:2 at 110°C.

## MECHANISM

It was demonstrated<sup>15,16</sup> earlier in the metathesis reaction of internal and terminal linear alkenes that, although  $\text{Re}(\text{CO})_5\text{Cl}/\text{C}_2\text{H}_5\text{AlCl}_2$  was added in the reaction mixture  $\{(\text{CO})_4\text{Re}^+ = \text{CHCH}_2\text{CH}_3\}$  appears to be the initiated and propagated species. This coordinated carbene was deduced from gas evolution



Scheme 4.

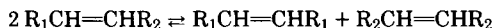
studies and examination of the first-formed products in the metathesis of 1,7-octadiene. The main difference in the conditions between the metathesis reaction of linear alkenes and polymerization of cycloolefins is the temperature at which reaction occurs: 90°C for metathesis, 110°C for polymerization.

Therefore, it is possible that the first steps of polymerization are similar to those of metathesis, in that a four-member metallocycle species is produced. Thus, where  $M=CHR$  denotes the catalyst initiator, the sequence of events shown in Scheme 4 takes place.

Species (I) represents the first step in metathesis, i.e., the four-member metallocycle. In addition, rather than ring-opening, addition polymerization can result from a slight modification of the metathesis mechanism when the second molecule of cycloalkene coordinates. The mechanism incorporates a metathesis-type initiator but a Ziegler–Natta type propagation.

### RING-OPENING POLYMERIZATION

The ring-opening polymerization of cycloolefins is closely related to the metathesis reaction of acyclic olefins:



Scheme 5.

Since the discovery by Eleuterio,<sup>17</sup> in 1957, of an alumina-supported molybdenum catalyst for the first ring-opening polymerization, several workers undertook the task of investigating numerous transition metal complexes for the metathesis reaction of cycloolefins.

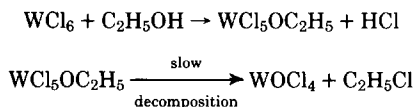
However, catalysts of practical importance for cycloolefin ring-opening polymerization were discovered in the early 1960's. In 1963, Ziegler–Natta type catalysts were prepared<sup>18</sup> from tungsten and molybdenum halides and organometallic compounds, for the ring-opening polymerization of cyclopentene. The catalysts were also tested<sup>19</sup> with higher-membered cycloolefins ranging from cyclohexene through cyclododecene. Cyclohexene was nonpolymerizable with these systems.

The two-component Ziegler–Natta catalysts for cycloolefin ring-opening polymerization have not been completely satisfactory for industrial applications, mainly because of their relative instability and the poor reproducibility of the results.

A basic improvement to the stable catalysts and reproducible results was accomplished in the late 1960's with the discovery<sup>20,21</sup> of the three-component systems. Oxygen-containing compounds were highly effective in strongly activating Ziegler–Natta systems, especially those made from tungsten halides and organometallic activators, with promoters such as alcohols, water, molecular oxygen, and peroxides. One of these catalysts systems,  $WCl_6-C_2H_5OH-C_2H_5AlCl_2$ , has been widely employed by different workers in ring-opening polymerization reactions of cycloolefins<sup>22</sup> as well as in acyclic olefin metathesis reactions.<sup>23,24</sup>

The chemical importance of the action of such oxygen-containing activators is not well understood. However, the system is activated by allowing the activator to react with the transition metal halide before adding the organometallic component. In the case of alcohols the first reaction step is believed<sup>25,26</sup> to be

a chlorine-alkoxide exchange accompanied by the evolution of a stoichiometric amount of hydrochloric acid (Scheme 6). This moderately stable  $\text{WCl}_5\text{OC}_2\text{H}_5$  slowly decomposes into  $\text{C}_2\text{H}_5\text{Cl}$  and an orange crystalline precipitate, presumably  $\text{WOCl}_4$ . When the organoaluminum compound comes into contact with the tungsten component, an active catalyst is formed instantaneously.



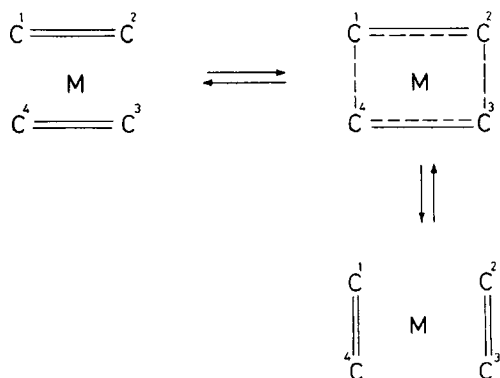
Scheme 6.

Organometallic-free systems are also active cocatalysts for the cycloolefin ring-opening polymerization reactions. For example, mixtures of tungsten halides and Lewis acids such as aluminum chloride are fairly active catalysts.<sup>26</sup> However, recently it was reported<sup>27</sup> that a bimetallic component catalyst system is not essential for the ring-opening polymerization of cycloolefins since tungsten hexachloride alone was effective as a metathesis catalyst. Although the polymerization rate was slower than that normally obtained with two metallic component systems, the polyalkenamer yields were the same.

The ring-opening polymerization is not limited to parent cycloolefin monomers. Fluorine substituted bicyclo[2.2.1]hept-2-enes and hepta-2,5-dienes have been reported<sup>28</sup> to undergo ring-opening polymerization using a variety of metathesis catalysts, derived from tungsten hexachloride. However, the fluorine substituents have to be far away from the double bond which participates in the metathesis reaction. Cycloolefin monomers with electron-withdrawing substituents are also known<sup>29-31</sup> to undergo ring-opening polymerization by metathesis catalysts.

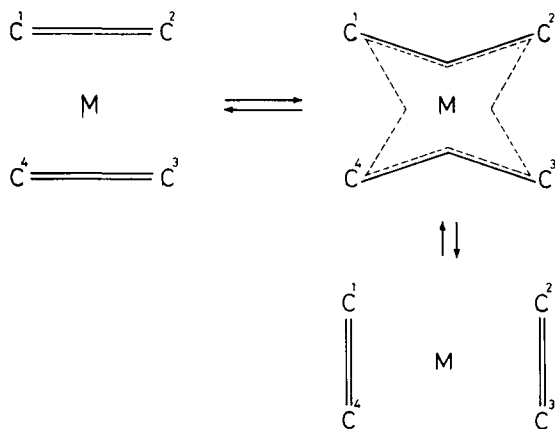
### METATHESIS REACTION MECHANISM

Several mechanistic studies have been carried out on the metathesis reaction of linear olefins. The first of these was done in the later 1960's by Calderon et al.,<sup>23,25</sup> who proposed a "quasicyclobutane" transition state as shown by Scheme 7. However, this mechanism was not very popular because of the fact that cyclobutane were never detected in the metathesis reaction. Furthermore, cyclobutanes did not metathesize to linear alkenes in the presence of metathesis catalysts.



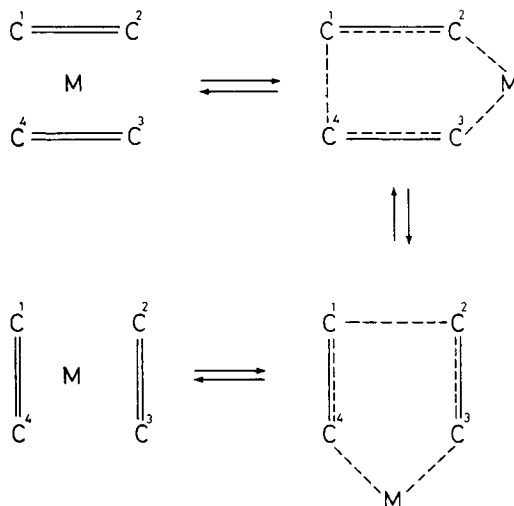
Scheme 7.

During the 1970's several workers undertook the task of investigating the metathesis reaction mechanism more seriously. Lewandos and Pettit<sup>32,33</sup> proposed a transition state which involves the concurrent breaking of the carbon-carbon sigma and Pi bonds (Scheme 8). The four methylene units act as an

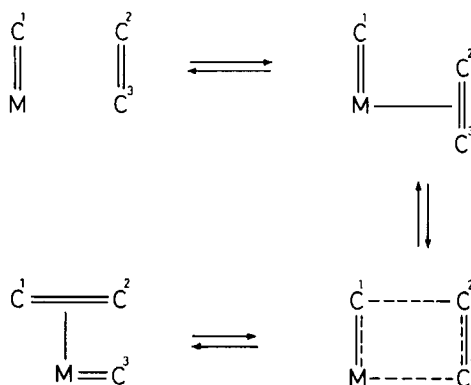


eight-electron donor system, but this requires to neglect the ligands on the transition metal so that the effective atomic number rule is obeyed.

In 1972, Grubbs and Brunk<sup>34</sup> proposed a fluxional five-member metallocycle. This intermediate can yield the starting materials or the metathesis products (Scheme 9).

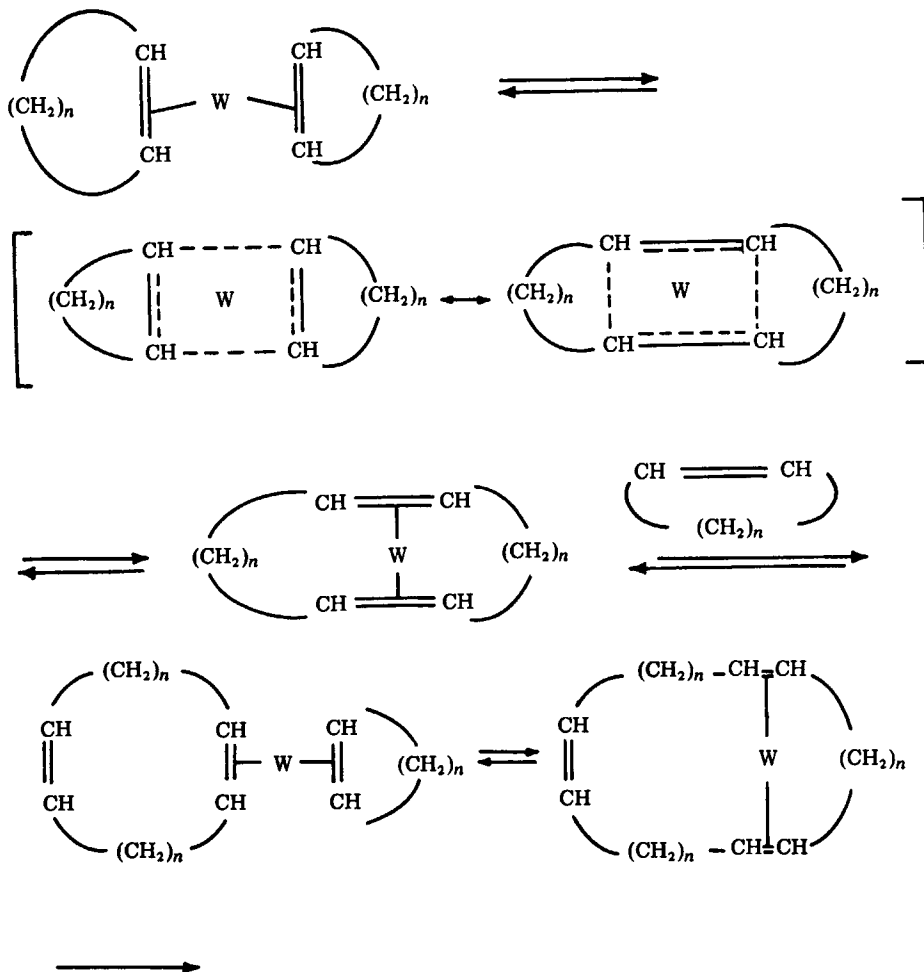


All the above three paths involve a concerted mechanism. However, the most widely accepted mechanism is the one involving a stepwise process.<sup>35</sup> This process involves the initial formation of a metal carbene which produces a four-member metallocycle species, the breakdown of which gives the reactants or products (Scheme 10). Support of the carbene mechanism for olefin metathesis was reported later by several workers.<sup>36-39</sup>



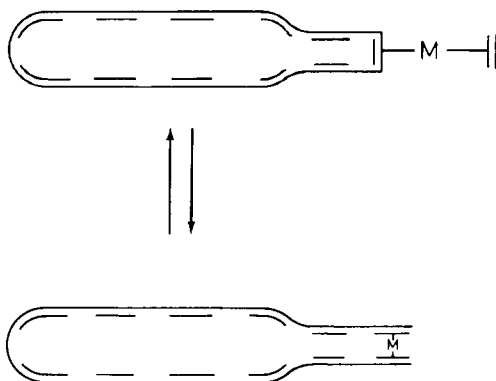
Scheme 10.

It appears that a metal coordinated carbene is definitely involved in the metathesis reaction of linear alkenes. However, one should ask whether any of the cyclic alkenes are polymerized by the accepted linear olefin metathesis mechanism.



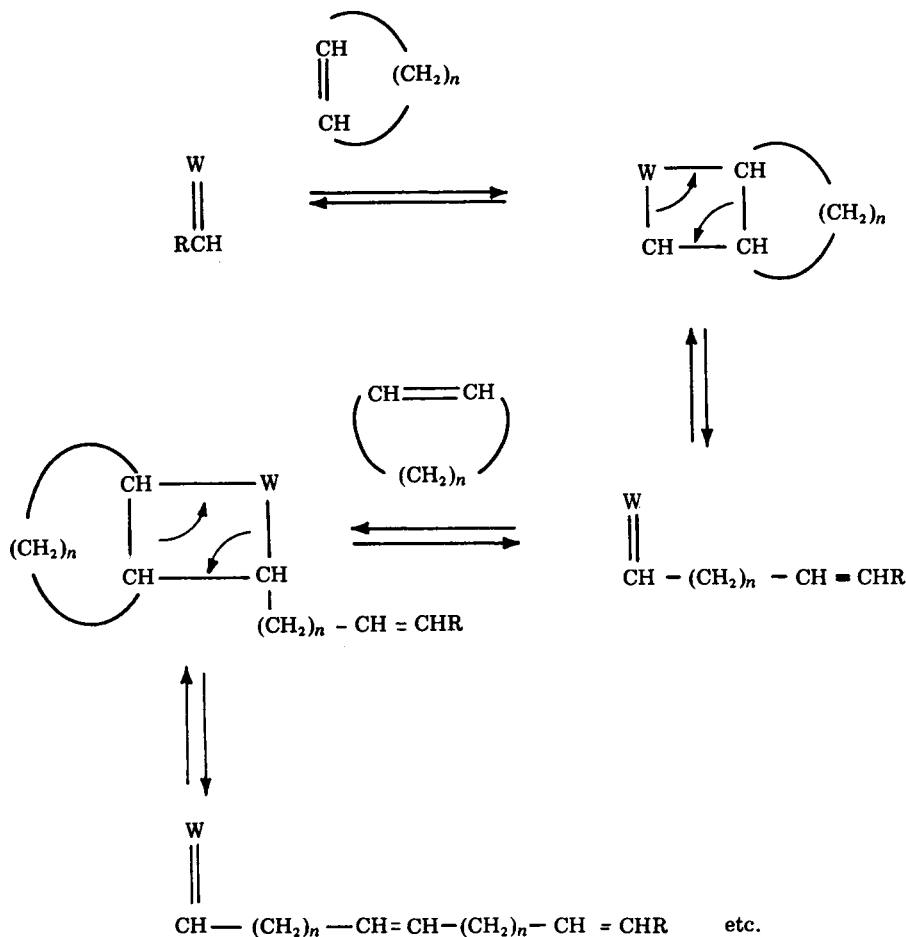
Scheme 11.





Scheme 12.

The ring-opening polymerization mechanism of cycloolefins has received less attention than that of the metathesis reaction of linear alkenes mainly because of the fact that most workers are interesting in the properties of the polyalkenamers synthesized by this reaction. For example, trans-1, 5-polypentamer

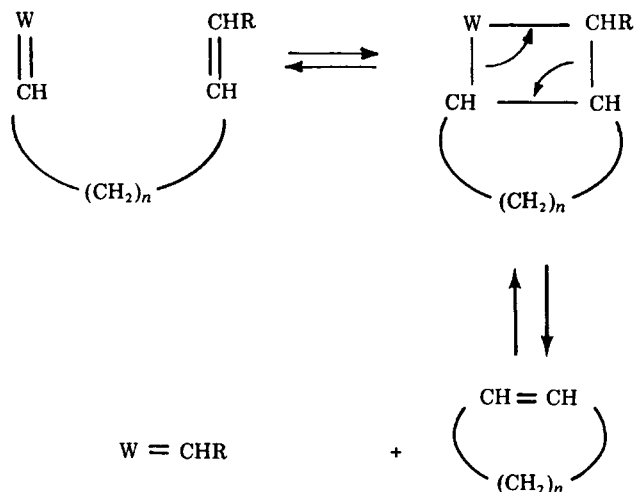


Scheme 13.

which is produced from cyclopentene by a ring-opening mechanism has elastomeric properties<sup>40</sup> and may be suitable for tyre manufacture.<sup>41,42</sup>

Although the cycloolefin ring-opening polymerization mechanism has not been studied in detail, two mechanisms have been proposed. The first and less popular mechanism is the "quasicyclobutane" type proposed by Scott and Calderon<sup>22</sup> (Scheme 11). According to this scheme, chain propagation proceeds with ring expansion through successive metathesis reactions reversible in each step. Termination in this polymerization is not complete since the species formed may participate again in an equilibrium process. According to this mechanism a macrocyclic structure is obtained but even traces of any acyclic olefin, present as impurity, or derived from the decomposition of the organometallic catalyst can act as agents for the cleavage of the macrocycles (Scheme 12).

The most popular cycloolefin ring-opening polymerization mechanism is the one involving the formation of a metal carbene.<sup>43-45</sup> Once a metal carbene is formed, it acts as the catalytic intermediate and the reaction proceeds as in Scheme 13. This mechanism would give a linear macrostructural polymer. A cyclic polymer could be formed by the mechanisms shown in:



Scheme 14.

## TECHNOLOGICAL ASPECTS OF CYCLOOLEFIN POLYMERS

As a conclusion of this review, it may be interesting to point out some general features concerning the technological aspects of cycloolefin polymers.

The possibility of polymerizing cycloolefins to linear *cis*- and *trans*-polyalkenamers makes available now a series of stereoregular linear polyhydrocarbons. The starting materials of these linear polyhydrocarbons are derived from inexpensive petrochemicals.

The length of the methylene sequence of each structural unit, that is, the number of methylene groups between the subsequent carbon-carbon double bonds, directly depends on the size of the starting cycloolefin. The polyhexamer ( $n = 4$ ) is not obtainable by ring-opening polymerization of cyclohexene, but it can be synthesized<sup>46</sup> by stereospecific alternating copolymerization of

TABLE III  
*Trans* Polyalkenamers and Preparation Method

<i>Trans</i> polyalkenamer	$-\{CH=CH-(CH_2)_n\}-_n$	Preparation method
Polyacetylene	0	polymerization of acetylene
Polypropenamer	1	unknown
1,4-Polybutadiene	2	polymerization of butadiene
Polypentenamer	3	cyclopentene polymerization
Polyhexenamer	4	butadiene-ethylene copolymerization
Polyheptenamer	5	cycloheptene polymerization
Polyoctenamer	6	cyclooctene polymerization
Polydodecenamer	10	cyclododecene polymerization
Polyethylene	$\infty$	ethylene polymerization

butadiene with ethylene. This then provides a series of *trans*-polyalkenamers as shown in Table III.

Although *cis*-polyalkenamers melt at relatively low temperatures, the linear polyalkenamers that come from cycloolefins and have a *trans*-double-bond content higher than 75% of the total amount of double bonds, are crystalline and have higher melting points than do the *cis*-polymers. The *trans*-tactic polyalkenamers from cycloolefins having a number  $n = 4$  of methylene groups between two subsequent double bonds give well-defined powder spectra.

Conversely, *trans*-polypentenamer ( $n = 3$ ) is elastomeric at room temperature and is generally amorphous but it crystallizes either when stretched at room temperature or cooled below  $-20^\circ\text{C}$ .

From all polyalkenamers synthesized from cycloolefins by a ring-opening mechanism only *trans*-1, 5-polyalkenamer shows elastomeric properties that might be suitable for tyre manufacture. This elastomer appears to offer the desirable processing properties of natural rubber and aging resistance of various synthetic rubbers. However, it has not yet become commercially available.

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