# On the Ring-Opening Polymerization of Methylenecyclobutane

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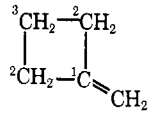
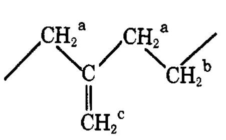
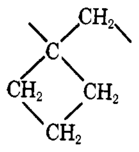
ABSTRACT: Methylenecyclobutane (I) has been polymerized via ring opening by several transition metal catalysts such as $Al(i\text{-}Bu)_3$–$TiCl_3ARA$, $Ti(CH_2C_6H_5)_4$ $RhCl_3$–ethanol. The polymers are predominantly constituted of units $-CH_2-C(=CH_2)CH_2CH_2-$ (II). Ethylene–methylenecyclobutane copolymers have been prepared with $Ti(CH_2C_6H_5)_4$. Moreover, I has been found to react with $PdCl_2$ and $[Rh(CO)_2Cl]_2$ at 60° to give, *via* ring opening, π-allyl complexes of those metals. The results suggest that the polymerization of I proceeds through a coordinated-anionic mechanism and that the formation of units II is to be related to the reactions of I with $PdCl_2$ and $[Rh(CO)_2Cl]_2$.

Pinazzi and Brossas[1,2] reported on the polymerization of methylenecyclobutane (I) in the presence of Lewis acids and of Ziegler–Natta catalysts at low Al/transition metal molar ratios. Polymers constituted of different types of monomeric units have been generally obtained. However, the catalyst system $AlEt_2Cl$–$Cr(acac)_3$ furnished a polymer which was reported to be constituted only of structural units of type II.[1,2]


I


II


III

The mechanism of polymerization of I by transition metal catalysts appears to be rather intriguing. In fact, from the data available it is not clear whether the polymerization of I proceeds through a coordinated-anionic mechanism or is to be considered of a different type.

We have examined the polymerization of I by several transition metal catalysts, *i.e.*, by the $Al(i\text{-}Bu)_3$–$TiCl_3ARA$ system, which is a typical heterogeneous Ziegler–Natta catalyst; by $Ti(CH_2Ph)_4$, which is a homogeneous catalyst active for the polymerization of α-olefins;[3] and by $RhCl_3$ in ethanol, which is a system suitable for the polymerization of ring-strained cycloolefins.[4] Moreover, we have investigated the reactions between I and $[Rh(CO)_2Cl]_2$ and $PdCl_2$, which lead to π-allyl complexes *via* ring opening of I.

On the basis of the results obtained in the above investigation, we wish to examine here the mechanism of polymerization of I, by transition metal catalysts, to polymers consisting of structural units II.

## Experimental Section

Methylenecyclobutane (I), prepared according to Slabey,[5] was refluxed over Na-K alloy, then distilled and stored over molecular sieves under dry $N_2$. Isobutylene and ethylene were at least 99% pure. $Al(i\text{-}Bu)_3$ was 93–95% pure. $TiCl_3ARA$ purchased from Stauffer Chemical Co. was said to be made by reduction of $TiCl_4$ with aluminum and subsequently activated. It has an approximate composition $Ti_3Al_1Cl_{12}$.

$RhCl_3 \cdot 3H_2O$ and $PdCl_2$ were commercial products and were used without any treatment.

$Ti(CH_2Ph)_4$ was prepared according to Giannini, *et al.*[6]

Polymerizations were carried out as previously described.[7] The experimental details of the reactions between I and $[Rh(CO)_2Cl]_2$ and $PdCl_2$ are reported elsewhere.[8]

Ir spectra were obtained with a Perkin-Elmer spectrophotometer, Model 225. The nmr spectra were taken on a Jeolco instrument operating at 60 MHz at 25°, with TMS set at 0 ppm as internal standard. Intrinsic viscosities were obtained in benzene at 30°, using a Desreux-Bishoff viscometer. $\overline{M}_n$ values were determined in toluene at 37° by a Mechrolab vapor-pressure osmometer, Model 301 A.

## Results and Discussion

Some of the most significant data concerning the polymerization of I are reported in Table I. The results can be summarized as follows.

(a) In the presence of the $Al(i\text{-}Bu)_3$–$TiCl_3ARA$ system, I gives a solid polymer which has been found to be amorphous by ir and X-ray examination. When examined by ir analysis shortly after its preparation, the polymer is shown to be constituted of structural units of type II, as indicated by the characteristic bands at 3075, 1650, and 885 $cm^{-1}$ (Figure 1). The nmr spectrum (Figure 2) confirms the infrared data, showing three signals at 1.25 ($H^b$), 1.98 ($H^a$), and 4.75 ($H^c$) ppm. The percentage of II units evaluated by integration is at least 95%.

(b) $Ti(CH_2Ph)_4$ polymerizes I to an oily polymer much less regular than that described above. In fact, its ir spectrum shows not only bands attributable to II units (1650 and 885 $cm^{-1}$) but also bands attributable to 1,4-isoprene units (837 $cm^{-1}$) and to *cis*- and *trans*-1,4-pentadiene units (750 and 965 $cm^{-1}$, respectively) in noticeable amounts. Bands attributable to structural units of type III (1240 and 920 $cm^{-1}$) and to benzyl end groups (1490, 725, and 690 $cm^{-1}$) are also present. It is to be noted that $Ti(CH_2Ph_4)$ is not active, under the same conditions, for the polymerization of aliphatic vinylidene olefins, such as isobutylene.

(c) $RhCl_3 \cdot 3H_2O$ in ethanol polymerizes I to an oily polymer whose ir spectrum shows a complex pattern of structural units similar to that of the polymer derived from $Ti(CH_2Ph)_4$.

We have found that I can be copolymerized with $C_2H_4$ using $Ti(CH_2Ph)_4$ as the catalyst. A solid copolymer was obtained, sparingly soluble in $CS_2$, $CCl_4$, and $C_6H_6$, whose ir

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(1) C. P. Pinazzi and J. Brossas, *Makromol. Chem.*, **122**, 105 (1969).

(2) C. P. Pinazzi and J. Brossas, *ibid.*, **147**, 15 (1971).

(3) U. Giannini, U. Zucchini, and E. Albizzati, *J. Polym. Sci., Part B*, **8**, 405 (1970).

(4) G. Natta, G. Dall'Asta, and L. Porri, *Makromol. Chem.*, **81**, 253 (1965).

(5) V. A. Slabey, *J. Amer. Chem. Soc.*, **68**, 1335 (1946).

(6) U. Zucchini, E. Albizzati, and U. Giannini, *J. Organometal. Chem.*, **26**, 357 (1971).

(7) R. Rossi, G. Ingrosso, and L. Porri, 23rd International Congress of Pure and Applied Chemistry, Boston, Mass., 1971, Macromolecular Preprints, p 940.

(8) R. Rossi, P. Diversi, and L. Porri, *J. Organometal. Chem.*, **31**, C40 (1971).

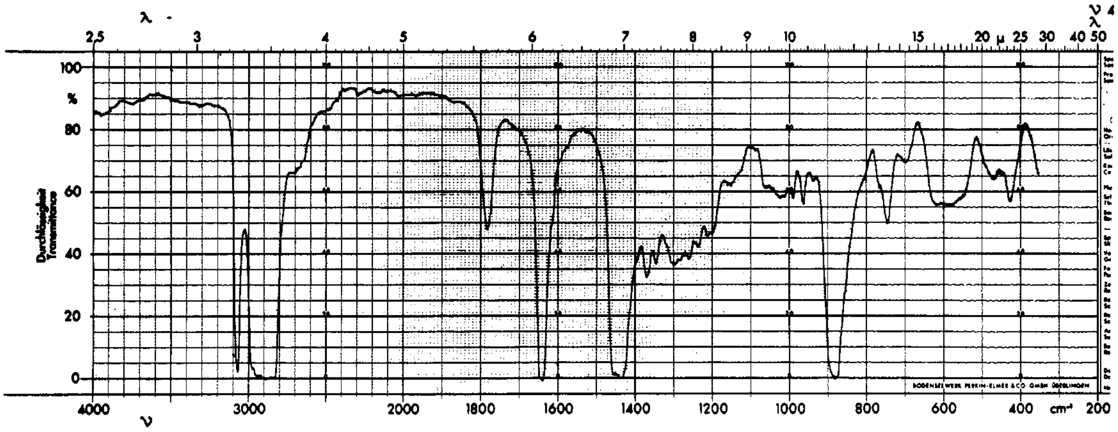

Figure 1. Infrared spectrum of methylenecyclobutane polymer obtained with the catalyst Al($i$-Bu)$_3$-TiCl$_3$ARA.

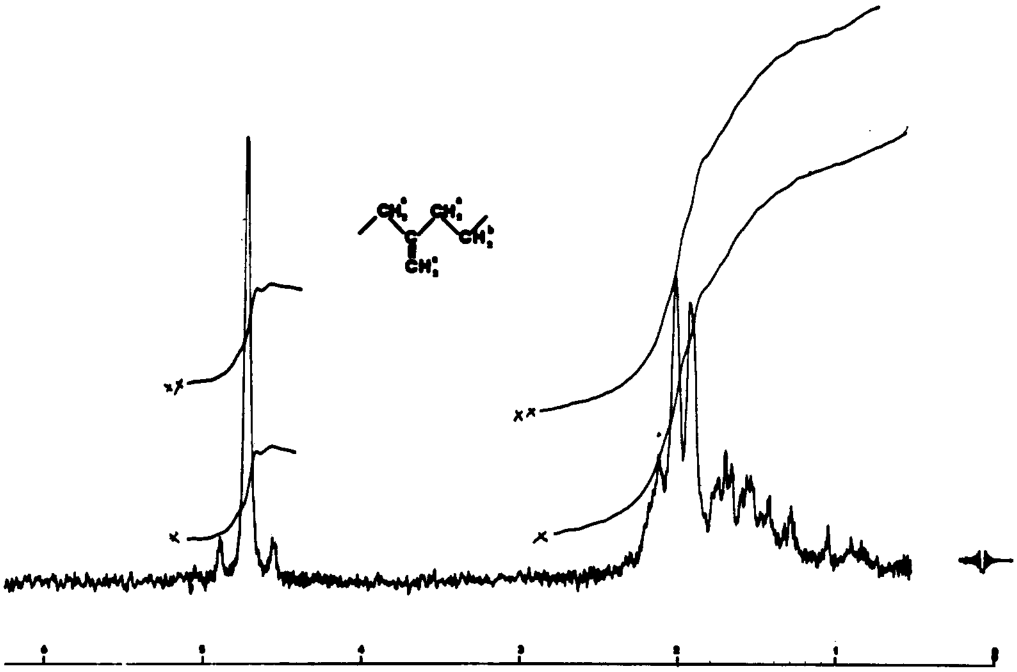

Figure 2. Nmr spectrum of methylenecyclobutane polymer obtained with the catalyst Al($i$-Bu)$_3$-TiCl$_3$ARA.

Table I
Polymerization of Methylenecyclobutane (I)

| Catalyst system | Molar ratio I/ transition metal | Solvent or diluent | Time, hr | Yield, % | Properties |
|---|---|---|---|---|---|
| TiCl$_3$ARA-Al-($i$-Bu)$_3$[a] | 52 | Isooctane | 250 | 16 | [$\eta$] = 0.48 dl g$^{-1}$ |
| Ti(CH$_2$Ph)$_4$[b] | 28.0 | Toluene | 336 | 10 | $\bar{M}_n$ = 567 |
| RhCl$_3\cdot$3H$_2$O[c] | 17.0 | Ethanol | 144 | 50 | Oil |

[a] Polymerization carried out at room temperature; molar ratio I/Al = 6.45. [b] Polymerization initiated at 0° during 48 hr and continued at room temperature. [c] Polymerization carried out at 70°.

spectrum shows the presence of structural units II in addition to 1,4-isoprene and 1,4-pentadiene units. The formation of a true copolymer is demonstrated by its insolubility (the homopolymers of I formed with catalysis by Ti(CH$_2$Ph)$_4$ are indeed oils soluble in C$_6$H$_6$ and CCl$_4$) and by the disappearance of the band at 745 cm$^{-1}$ present in the ir spectrum of the homopolymers of I constituted of structural units II. This band is presumably attributable to the rocking of three methylene groups.[9]

We have investigated the reaction of I with PdCl$_2$ and [Rh(CO)$_2$Cl]$_2$, and the results appear of some interest with regard to the polymerization mechanism. I reacts with PdCl$_2$ at 65° to give a mixture of two isomeric complexes, IV and V, in the ratio of about 1/1, and with [Rh(CO)$_2$Cl]$_2$ at 60° to yield complex VI.

From the nature of these $\pi$-allyl complexes it appears that the ring fission of (I) occurs at the C$_2$–C$_3$ bond.

On the basis of the above results, we are inclined to believe that the polymerization of I proceeds through a coordinated-

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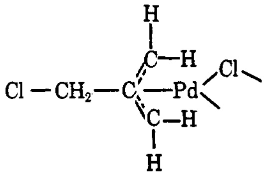
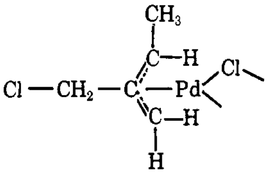
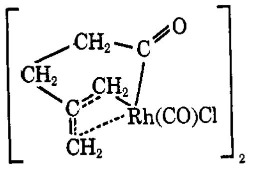
(9) While the bands attributable to the rocking vibrations of sequences of CH$_2$ groups have been recognized in paraffins [F. Ciampelli and C. Tosi, *Spectrochim. Acta, Part A*, **24**, 2157 (1968)] and saturated polymers [J. van Schooten and S. Mostert, *Polymer*, **4**, 135 (1963)], the bands of CH$_2$ groups near polar groups in structures such as $-C{=}C{-}CH_2-$, $-CO{-}CH_2-$, and $-O{-}CH_2-$ have not yet definitely assigned: A. Weissberger, "Chemical Applications of Spectroscopy," Interscience, New York, N. Y., 1956, p 346.



IV



V



VI

anionic mechanism; that is, it occurs by incorporation of the monomer on a polarized metal$^{\delta+}$–C$^{\delta-}$ bond between the transition metal and the last polymerized unit.

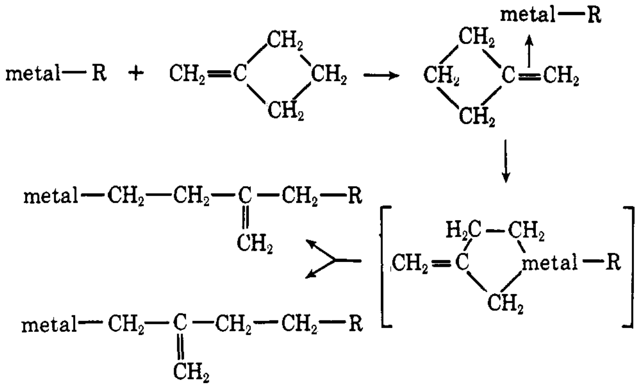
This mechanism easily accounts for the formation of a copolymer between I and ethylene. Furthermore, it is to be considered that both TiCl$_3$ARA–Al($i$-Bu)$_3$ and Ti(CH$_2$Ph)$_4$ are typical coordinated-anionic systems and are inactive for the oligomerization or polymerization of aliphatic vinylidene olefins such as isobutylene.

The formation of structural units of type II can be related to the analogous ring-opening reactions of I with PdCl$_2$ and [Rh(CO)$_2$Cl]$_2$ in which the organic moiety attributable to such units derives from the fission of I at the C$_2$–C$_3$ bond.

In the light of the above reactions the polymerization of I can tentatively be visualized as shown in Scheme I.

The strain of I is most probably the reason for the ring opening. Several analogous metal-promoted ring-opening reactions are reported in the literature.[10–12]

SCHEME I



The above mechanism is consistent with the fact that the homopolymer of I from TiCl$_3$ARA–Al($i$-Bu)$_3$ is amorphous. The lack of crystallinity in such a polymer could in fact be attributed to the presence of units II in head-to-head and head-to-tail arrangements. An irregular enchainment is foreseeable on the basis of the two above-represented modes of insertion of I into the metal$^{\delta+}$–C$^{\delta-}$ bond. On the other hand, the homopolymer of I from TiCl$_3$ARA–Al($i$-Bu)$_3$ shows three bands in the region of methylene rocking vibrations (700–800 cm$^{-1}$) which could be assigned to sequences of four, three, and two CH$_2$ groups (Figure 1).

The presence of 1,4-isoprene and 1,4-pentadiene units in the polymers obtained either by Ti(CH$_2$Ph)$_4$ or by the RhCl$_3$–EtOH system could be attributed to one or both of the following factors: (a) isomerization of the II units by the catalyst or a species derived from it; (b) possible isomerization of I to 1,3-pentadiene and isoprene.

It has been shown in fact that Ti(CH$_2$Ph)$_4$[6] and rhodium compounds[13,14] can promote isomerization of $\alpha$-olefins.

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(10) J. Wrister, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, **92**, 7499 (1970).

(11) K. G. Powell and F. J. McQuillin, *J. Chem. Soc. D*, 931 (1971).

(12) L. Cassar and J. Halpern, *ibid.*, 1089 (1970), and references therein.

(13) R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968).

(14) A. J. Hubert and H. Reimlinger, *Synthesis*, 405 (1970).

# Synthesis and Characterization of Dibenzothiophene–Formaldehyde Copolymers

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ABSTRACT: The structures of the polymeric products produced from a 1- to 24-hr condensation of paraformaldehyde with dibenzothiophene have been investigated by chemical and physical methods. It was shown that the polymers formed during the early stages of the condensation appear to have a linear structure with a degree of polymerization (DP) equivalent to *ca.* six repeat units. The polymers produced during the latter stages of the reaction (DP > 6) are branched and of different chemical composition than the early stage polymers. The polymer structures contain both methylene and oxymethylene bridges as well as hydroxymethyl end groups.

Under appropriate reaction conditions, formaldehyde condenses with a large number of organic compounds to yield derivatives ranging from simple methylol and methylated compounds to highly intractable resins.[1] The intermediates produced in many of these reactions have been identified and characterized, especially those low molecular weight products derived from pheolic condensations.[2–4] However,

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(1) J. F. Walker, "Formaldehyde," 3rd ed, Reinhold, New York, N. Y., 1969.

(2) D. Gould, "Phenolic Resins," Reinhold, New York, N. Y., 1959.

(3) R. Martin, "The Chemistry of Phenolic Resins," Wiley, New York, N. Y., 1958.

(4) N. Megson, "Phenolic Resin Chemistry," Butterworths, London, 1958.