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Cyclo- and Cyclized Diene Polymers. XIX. Polymerization of Butadiene with the $C_2H_5AlCl_2 + TiCl_4$ Catalyst

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SUMMARY

The polymerization of butadiene with an $EtAlCl_2$-$TiCl_4$ catalyst system yields cyclopolybutadiene with varying amounts of trans-1, 4 units, depending upon the Al/Ti ratio and the solvent. Apparently different active centers are produced at Ti > Al and Al > Ti ratios. When the catalyst system has Ti > Al, there is a rapid decrease in the initial polymerization rate and the cyclopolybutadiene contains large amounts of methyl groups, 10-12% of trans-1, 4 units, 2-3% of 1, 2 units, and, when the polymerization is carried out in aromatic solvents, aromatic moieties are incorporated in the structure. When the catalyst system has Al > Ti, there is a very slow decrease of the initial polymerization rate, and the cyclopolybutadiene contains up to 40% of trans-1, 4 units, less than 1% of 1, 2 units, and methyl groups and solvent moieties are essentially absent even when the polymerization is carried out in aromatic solvents. Cocatalytic amounts of iodine greatly increase the initial rate of polymerization. The Ti > Al catalyst may promote 1, 3-cation-radical propagation with transoid monomer to yield a perhydrophenanthrene structure while the Al > Ti catalyst may promote 1, 2 cation-radical propagation with cisoid monomer to yield a perhydroanthracene structure.

INTRODUCTION

The polymerization of butadiene, initiated with acidic catalysts such as Lewis acids, Friedel-Crafts catalysts, etc., has only been studied to a limited extent, undoubtedly because these reactions are, in most cases, difficulty reproducible, extremely sensitive to impurities in the reactants, and, as in all reactions involving carbonium ions, accompanied by undesirable side reactions. Another serious problem facing the investigators is the analysis of the microstructure of the "cationic" polymers.

In our earlier work [1-3] it was demonstrated that, in the presence of the cationic components of Ziegler-type catalysts as well as some other acids, butadiene and isoprene polymerized to cyclopolymers containing fused six-membered saturated rings in the polymer chain. Butadiene as well as isoprene [2] polymerized to cyclopolymer under the influence of the $EtAlCl_2 + TiCl_4$ catalyst system. In the polymerization of butadiene, in contrast to that of isoprene, the catalyst composition, i.e., molar ratio of Al to Ti, had an effect on the polymer structure.

EXPERIMENTAL

Materials

Butadiene of 99.6% purity was dried by passage through a column containing silica gel and by refluxing at elevated pressure over NaH. Dissolved gases were removed from the monomer by repeated freezing and evacuation. The butadiene was added as a gas in polymerization reactions. n-Heptane, thiophene-free benzene, and toluene were dried by prolonged refluxing over NaH and freed of gases by the same technique as used with the monomer. In these solvents butadiene did not polymerize when contacted with $EtAlCl_2$, $EtAlBr_2$, or $TiCl_4$ alone.

Polymerizations

Polymerizations were carried out at 20°C in a vacuum line system similar to that described earlier [1]. The total amount of the solvent was 30 ml. The catalyst components were charged from glass ampoules containing the desired amounts of the components, in the order solvent, $TiCl_4$, gaseous monomer, $EtAlCl_2$. The concentration of butadiene was held at a constant level of 1 mole/liter during the entire polymerization run. The reaction was stopped by the evacuation of unreacted butadiene and the addition of methanol. The resultant polymers were washed with methanol and dried in vacuo at elevated temperature. Unless otherwise indicated, the time of polymerization was 180 min.

Polymer Characterization

The microstructure of polybutadiene was analyzed by infrared spectroscopy using the KBr pellet technique [4]. The content of 1, 2 structural units was determined from the intensity of the absorption band at 910 cm^{-1}, the trans-1, 4 units using the band at 965 cm^{-1}, and the cis-1, 4 units from the bands at 742 and 3003 cm^{-1}. In addition, the content of phenyl and methyl groups in the cyclopolymer was determined on the basis of the absorption bands at 700 and 1378 cm^{-1}, respectively. The C=C double-bond content was determined, on the basis of the infrared analysis, from the sum of the 1, 4 and 1, 2 linkages, and, in the case of soluble polymers, by the iodine monochloride method [5].

RESULTS AND DISCUSSION

The polymerization of butadiene with a RMgX + $TiCl_4$ complex catalyst containing an excess of $TiCl_4$ has been shown to yield polybutadiene with a low content of 1, 4 and 1, 2 structural units [1]. These polymers, as well as polybutadiene cyclized by the action of acids [6], have essentially the structure of six-membered fused rings with linear connecting units in the chain.

Polymerization with an $EtAlCl_2$ + $TiCl_4$ catalyst gives cyclopolybutadiene in higher yields and, under proper conditions, with a higher level of 1, 4 content. Cyclopolybutadiene forms at molar ratios of $EtAlCl_2$ to $TiCl_4$ ranging from 20 : 1 to 1 : 20. The structure of cyclopolybutadiene changes according to the Al : Ti ratio in such a manner that the content of trans-1, 4 units ranges between 5 and 26% when the polymerization is carried out in heptane and reaches about 40% if the polymerization is carried out in aromatic solvents. The content of 1, 2 units is always lower than 4%.

The cis-1, 4 structure has not been detected by the infrared analysis. The absorption band at 742 cm^{-1}, which is assigned to cis-1, 4 in polybutadiene, has appeared in the spectra of some samples prepared in aromatic solvents, but the band at 3003 cm^{-1}, which should also appear if the cis-1, 4 structure is present, was absent in all cases. It follows that, in this case, the 742 cm^{-1} band was due to the aromatic fragments in the polymer.

The catalyst activity increases with increasing concentration of one of the catalyst components when the concentration of the other component is constant (Figs. 1 and 2).

The rate of polymerization at constant monomer pressure gradually decreases as the reaction proceeds and after a sufficiently long time drops practically to zero. At all Al/Ti ratios the catalyst is most effective at the beginning of the polymerization, i.e., immediately after the addition of the last component of the catalyst system.

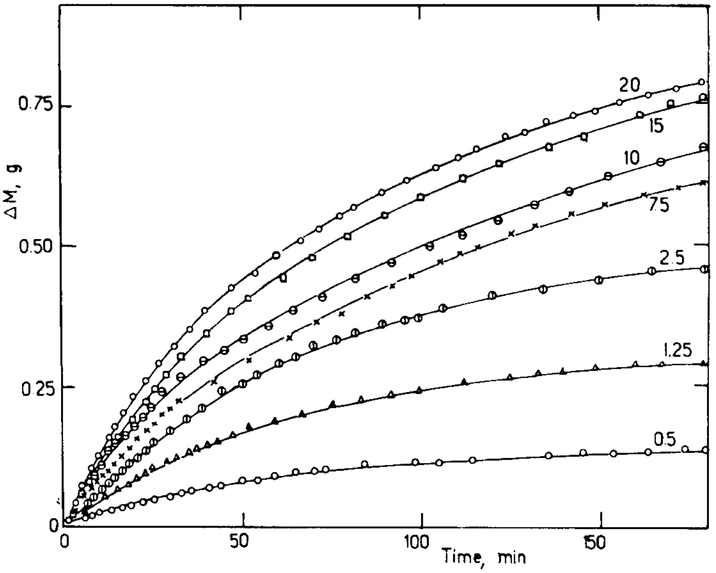


Fig. 1. Rate of polymerization of butadiene at 20°C as a function of Ti/Al ratio (numbers on curves) at constant $[EtAlCl_2] = 0.025$ mole/liter. [Butadiene] = 1 mole/liter during entire polymerization time.

The reaction between $EtAlCl_2$ and $TiCl_4$ in solution in the absence of monomer at 20°C is relatively slow. Solid $TiCl_3$ appears only after about 15 min. The appearance of the solid phase is related to the formation of the active centers. This catalyst system is active only when the solid is present [2]. However, a soluble complex which appears simultaneously with the solid is also catalytically active. It has been reported that although isoprene slightly accelerates the reaction [2], the maximum activity of the catalyst is achieved only after about 1 hr of polymerization. No such induction period has been observed with butadiene. By mixing $EtAlCl_2$ with $TiCl_4$ in the presence of butadiene a catalyst forms which is active almost immediately. The solid phase of $TiCl_3$ also appears within a few seconds after the addition of butadiene to a mixture of $EtAlCl_2$ and $TiCl_4$. It follows that butadiene somehow participates in the reduction of Ti^{4+} to Ti^{3+}.

With n-heptane as the reaction medium, the initial rate of polymerization increases with increasing concentration of any of the catalyst components. The structure of the polymers is practically unchanged when the Ti/Al ratio ranges from 1 : 1 to 20 : 1. The cyclopolymer contains 8-12% of trans-1, 4 and about 2% of 1, 2 units. The ratio of trans-1, 4 to 1, 2 is constant and equal to about 5 : 1

Table 1. Effect of Al/Ti Ratio on Polybutadiene Microstructure

	Ti/Al	trans-1,4	1,2	$\frac{\text{trans-1,4}}{1,2}$
[$EtAlCl_2$] = 0.025 mole/liter	1.25	12.4	2.6	4.7
	2.5	14.1	2.5	5.7
	2.5	11.8	2.0	5.9
	7.5	10.5	2.2	4.8
	10.0	11.1	2.2	5.0
	15.0	9.4	1.8	5.2
	18.7	10.7	2.2	4.9
	20.0	10.8	2.1	5.1

	Al/Ti	trans-1,4	1,2	$\frac{\text{trans-1,4}}{1,2}$
[$TiCl_4$] = 0.033 mole/liter	1.00	10.1	1.8	5.6
	1.56	17.2	3.0	5.7
	2.34	15.4	2.7	5.7
	3.12	15.6	1.9	8.2
	3.90	24.4	2.2	11.1
	6.0	24.3	1.3	18.7
	8.0	26.0	0.8	32.5
	20.0	23.6	<0.4	>60

(Table 1). It follows that one "linear" unit is present for each 8-9 monomer units without infrared-detectable double bonds, and approximately every sixth linear unit is in 1,2 position.

The presence of excess $EtAlCl_2$ in the initial mixture in n-heptane makes the situation quite different; e.g., at Al/Ti = 6 : 1 the catalyst is initially active and then loses its activity very rapidly, so that after about 60 min no polymerization occurs, but later activity is renewed (Fig. 2). The polymer isolated in the first period of the catalyst activity is of the same nature as that obtained with excess $TiCl_4$. Even the ratio of trans-1,4 to 1,2 structures is the

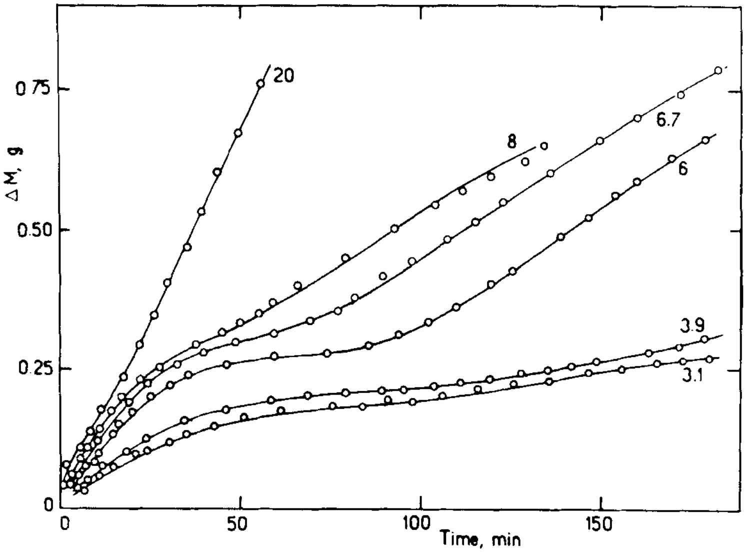


Fig. 2. Rate of polymerization of butadiene at 20°C as a function of Ti/Al ratio (numbers on curves) at constant $[TiCl_4] = 0.033$ mole/liter. [Butadiene] = 1 mole/liter during entire polymerization time.

same as with Ti > Al, which indicates that the polymer is formed from the same type of active species (Table 2).

The complex which forms in the second stage leads polymerization to a product with about 25% of trans-1,4 units and much less than 1% of 1,2 units (Table 1). The time after which this second type

Table 2. Effect of Al/Ti Ratio on Polymer Structure in the Early Stages of Polymerization

Al/Ti	Time of polymerization, min	$\frac{\text{trans-1,4}}{\text{1,2}}$
2.0	10	5.75
2.3	20	4.85
2.7	130	5.4
6.0	10	5.2
6.0	40	4.95

of active center becomes effective depends upon the molar ratio of Al/Ti. For example, with a 20-fold excess of the aluminum component, the reaction between $EtAlCl_2$ and $TiCl_4$ in the presence of monomer is very fast, and practically all of the polymer forms on the second type of active center. Under otherwise identical conditions, the rate of polymerization in the second stage is higher and the catalyst activity decreases at a much slower rate than with excess titanium. Further, with excess aluminum the polymer does not contain cis-1,4 units but every fourth monomer unit is linear trans-1,4.

Aging of the catalyst (Al/Ti = 0.8 : 1) before the introduction of the monomer has no influence on the polymer yield and structure (Table 3).

Table 3. Effect of Catalyst Aging on Structure of Polymers

Time of aging, hr	Yield, g	trans-1,4	1,2	$\frac{\text{trans-1,4}}{\text{1,2}}$
0	0.20	10.1	1.8	5.6
1	0.20	12.6	1.3	5.5
5	0.24	12.7	2.4	5.3
18	0.19	9.1	2.1	4.4

Both with fresh and aged catalyst the polymer yield corresponds to the consumption of monomer. This indicates that liquid oligomers, e.g., cyclic dimers and trimers, do not form under the conditions described in any appreciable amount.

Aromatic solvents have a positive effect on the rate of polymerization (Fig. 3), and at certain concentrations the polymers are soluble. In toluene and especially in xylene the products are not high polymers but oligomeric and telomeric oils which contain significant amounts of the solvent residues. The infrared spectra of polymers obtained in benzene clearly indicate monosubstitution of the aromatic rings, while polymers obtained in toluene show mainly para substitution of the toluene residue. The polymers prepared in benzene usually contain 7 to 9 phenyl groups per 100 monomer units [7].

The structure of the polymers obtained in aromatic solvents with the catalyst containing excess titanium is the same as that of polymers obtained in an aliphatic medium, except for the aromatic fragments. The ratio of trans-1,4 to 1,2 units is slightly different (Table 4).

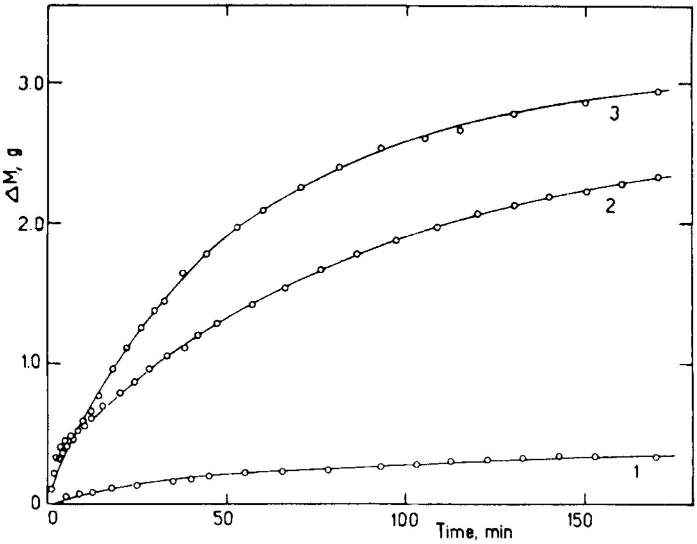


Fig. 3. Effect of reaction medium on rate of polymerization of butadiene at 20°C. [$TiCl_4$] = 0.033 mole/liter; Al/Ti = 1.5; [butadiene] = 1 mole/liter during entire polymerization time. (1) n-heptane, (2) benzene, (3) toluene.

The analysis of the C=C double-bond content by the ICI method shows good agreement with the determination by infrared spectroscopy (Table 5). Slightly higher values from the ICI method may indicate the presence of another type of double bond, different from that in 1,4 and 1,2 units. These bonds are probably of end cycles in polycyclic segments [7].

In aromatic solvents the differences between catalysts with excess Ti and excess Al are more evident. As discussed below, the

Table 4. Effect of Reaction Medium on trans-1,4/1,2 ratio

Medium	Ti/Al	trans-1,4 / 1,2
Heptane	7.5	4.9
Benzene	7.5	6.9
Toluene	7.5	8.0

Table 5. Unsaturation of Soluble Polymers

No.	$[EtAlCl_2]$, mmoles/30 ml	$[TiCl_4]$, mmoles/30 ml	Polymerization medium	C=C, % (infrared)	C=C, % (ICl)
1	0.8	6	Benzene	15.2	17
2	1.5	1	Benzene	17.8	22
3[a]	1	2	Benzene	9.8	14
4	8	1	Benzene	39	47
5[a]	1	2	Toluene	8.5	10

[a] + 0.5 mmole of I_2.

content of methyl groups in cyclopolybutadiene at Ti > Al ratios in aromatic solvents is higher than in aliphatic solvents. The differences between these two types of catalysts are shown in Table 6.

Table 6. Differences Between Catalysts with Excess Al and Ti

	Ti > Al	Al > Ti
Heptane	Rapid decrease of initial polymerization rate	Very slow decrease of initial polymerization rate
	Methyl groups in polymer	No methyl groups in polymer
	10-12% of trans-1,4 units	24-26% of trans-1,4 units
	2-3% of 1,2 units	Less than 0.4% of 1,2 units
	Infrared spectrum has no band at 1360 cm^{-1}	Infrared absorption band at 1360 cm^{-1}
Aromatic solvents	Fragments of solvent in polymer	Little aromatic structure in polymer
	About 12% of trans-1,4 units	Up to 40% of trans-1,4 units
	About 3% of 1,2 units	Less than 1% of 1,2 units
	Large amount of methyl groups in polymer	Practically no methyl groups in polymer

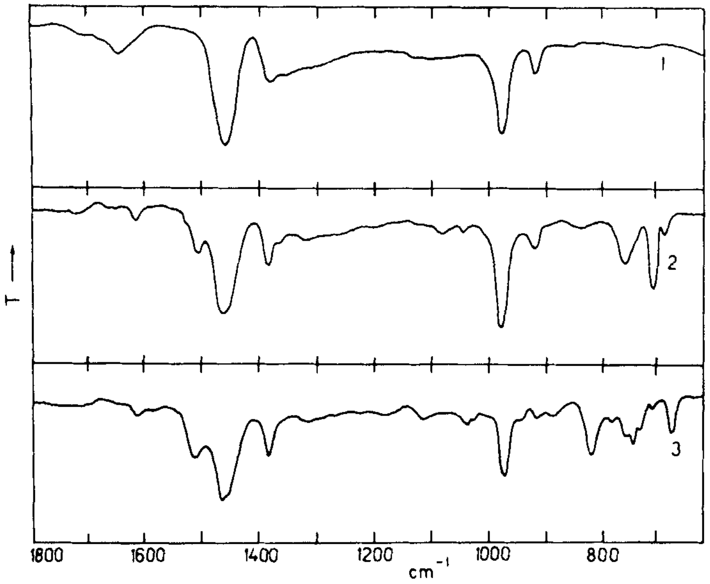


Fig. 4. Infrared spectrum of cyclopolybutadiene obtained at Ti > Al ratio in (1) n-heptane, (2) benzene, (3) toluene.

The infrared spectra of cyclopolybutadienes obtained with the $EtAlCl_2 + TiCl_4$ catalyst with excess Ti are shown in Fig. 4.

The content of linear structures depends to an extent upon the time of polymerization (Fig. 5). At very low conversions the polymer contains the lowest amount of linear structures.

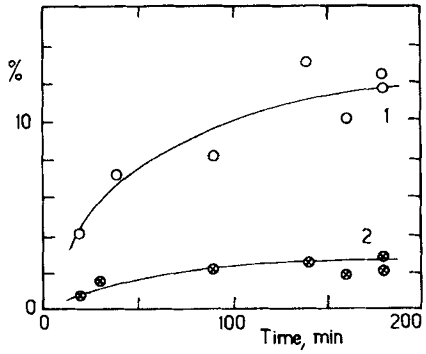
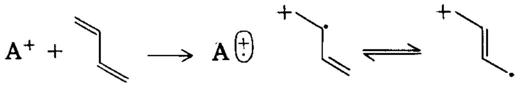


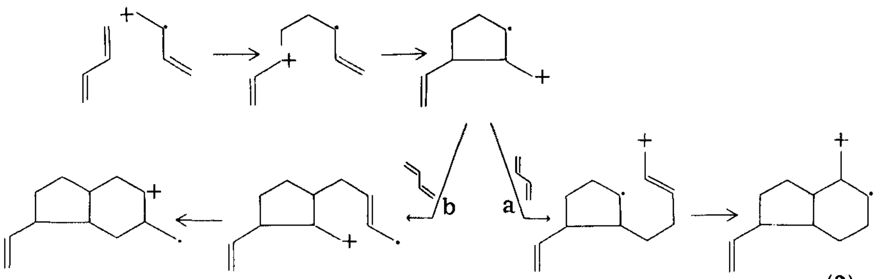
Fig. 5. Changes of structure with time of reaction in heptane. Al/Ti = 1. (1) trans-1,4, (2) 1,2.

An interesting feature in the cyclopolymerization of butadiene with the $EtAlCl_2 + TiCl_4$ and several other catalysts is the appearance of methyl groups in the polymer. According to some authors [8, 9], the methyl groups form by cyclization of 1, 2 units, which form initially as a result of linear polymerization. Assuming that cyclopolymerization proceeds through a cation-radical mechanism [7], which seems to be most probable for this type of polymerization, and considering that the content of 1, 2 units in the polymer is very low and the rate of cyclization of 1, 2-polybutadiene is expected to be rather low, as is the rate of cyclization of 3, 4-polyisoprene [10], the formation of methyl groups in cyclopolybutadiene follows from the nature of the cation radical.

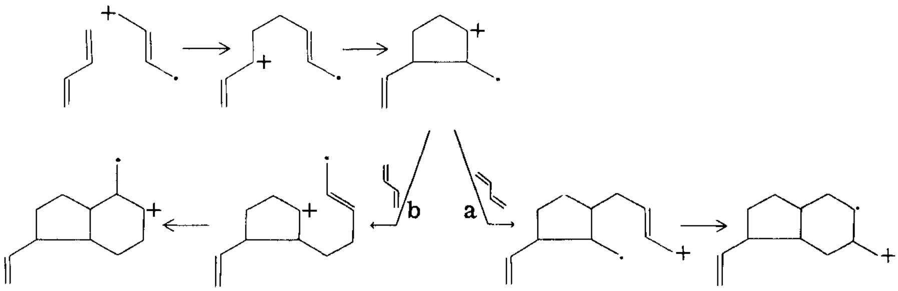
The observation that the $EtAlCl_2 + TiCl_4$ catalyst with Ti > Al in aliphatic solvents yields polymers with methyl groups while the same catalyst with Al > Ti yields cyclopolymers without methyl groups may be explained on the basis of different active centers resulting in different initiation or propagation processes.



(1)



(2)

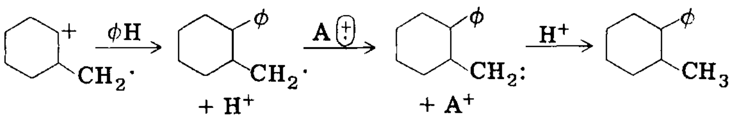


(3)

Irrespective of whether the monomer 1, 2 cation radical [Eq. (1)] or the 1, 4 cation radical [Eq. (1)] participates in the initial 1, 2 addition, an exocyclic primary carbonium ion results from subsequent 1, 4 cationic addition (path a), while an exocyclic primary methylene radical results from 1, 4 radical addition (path b). The 1, 3 cation radical undergoes an intramolecular hydride shift to convert the exocyclic primary carbonium ion to a methyl group:

(4)

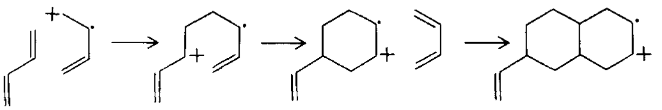
When aromatic solvents are present, the exocyclic primary radical may also be converted to a methyl group through the sequence in Eq. (5):



(5)

In the case of aliphatic solvents, the exocyclic primary radical may be converted to a methyl group by abstraction of a hydrogen atom from the solvent.

The absence of methyl groups and the high percentage of trans-1, 4 units when the catalyst is based on an Al > Ti ratio indicates that the active center in this case either promotes 1, 4 radical addition reactions [Eqs. (2) and (3), path b] or, more probably, 1, 2 cation-radical propagation.



(6)

As indicated, ring closure in the latter case requires that the incoming monomer have the cisoid configuration, while 1, 3 cation-radical propagation involves the transoid monomer.

It is of interest to note that the triisobutylaluminum-titanium tetrachloride catalyst system, at Al/Ti ratios above 2, yields a polybutadiene containing up to 50% cis-1, 4 and 50% trans-1, 4 structure, while at lower ratios the product is essentially an all-trans-1, 4 polybutadiene [11]. The presence of up to 40% trans-1, 4 units in the cyclopolybutadiene produced with the $EtAlCl_2$-$TiCl_4$ catalyst system at Al > Ti ratios indicates that the cisoid configuration of the monomer is formed in the presence of excess Al with both catalyst systems. Since the 1, 2 cation-radical reacts with cisoid monomer to form cyclic structures, the product from the $EtAlCl_2$-$TiCl_4$ system at high Al/Ti ratios should therefore contain fused cyclic units arising from cisoid monomer, accompanied by trans-1, 4 units arising from transoid monomer, with little or no 1, 2 units, as is actually observed.

The implication that the $EtAlCl_2$-$TiCl_4$ catalyst system promotes 1, 3 cation-radical propagation with transoid monomer at Ti > Al ratios and 1, 2 cation-radical propagation with cisoid monomer at Al > Ti ratios leads to the possibility that the cyclopolybutadiene in the former instance has a perhydrophenanthrene structure and in the latter instance a perhydroanthracene structure. The structures of the cyclopolybutadienes are presently under investigation.

The absolute content of methyl groups cannot be exactly determined by means of infrared analysis since the absorbance of the CH_3 band at 1380 cm^{-1} varies according to the structure of the hydrocarbon, and the model compounds are not available. Moreover, the 1380-cm^{-1} band coincides in some cases with a band at 1360 cm^{-1} (at higher contents of trans-1, 4 units). Nevertheless, the infrared spectra are quite informative (Fig. 6).

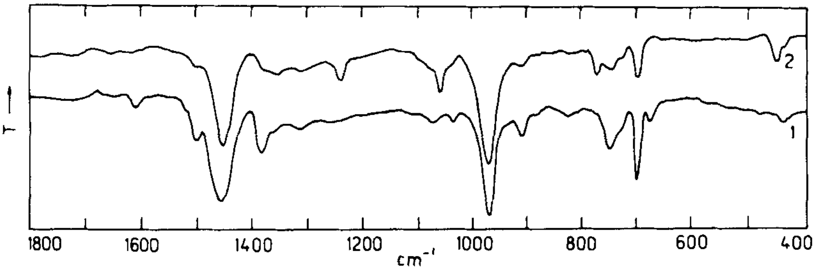


Fig. 6. Infrared spectra of cyclopolybutadiene obtained in benzene at Ti > Al, (2) Al > Ti.

Polymerizations with $EtAlBr_2 + TiCl_4$ and $AlBr_3 + TiCl_4$ give similar polymers of butadiene. The rates of polymerization with these catalysts are also comparable.

The initial rates of polymerization are strongly influenced by the addition of cocatalytic amounts of iodine. In equimolar proportions with respect to the catalyst, iodine increases the initial rate of polymerization in heptane almost 30 times (Fig. 7). However, the addition of more than about 3 moles of iodine per mole of the catalyst does not cause any further increase in the rate of polymerization.

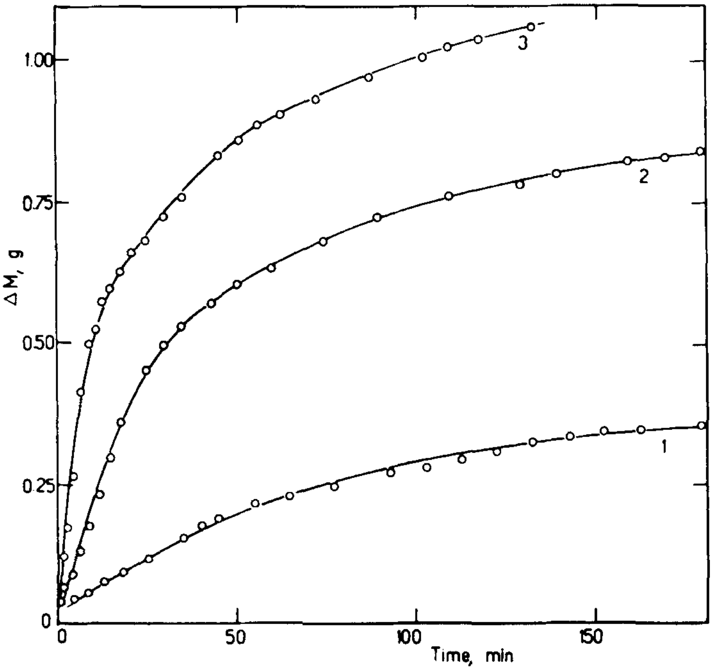


Fig. 7. Effect of iodine on rate of cyclopolymerization of butadiene in heptane. [$TiCl_4$] = 0.033 mole/liter, Al/Ti = 2. (1) No. I_2, (2) 0.5 mmole of I_2, (3) 3 mmoles of I_2.

The added iodine is quickly consumed by addition to or sorption on the polymer, and the rate of polymerization in the later stages is the same as in the absence of iodine. The iodine can be removed from the polymer at temperatures above 130°C. The resulting polymer has a structure similar to that obtained with the same catalyst without the halogen.

The maximum effect of iodine is noted when either of the catalyst components is present in excess. At equimolar proportions of Al/Ti, iodine has little effect.

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