CYCLOPOLYMERIZATION OF CONJUGATED DIENES

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ABSTRACT

The formation of essentially saturated polymers containing fused cyclo-hexane rings is a characteristic of the polymerization of conjugated dienes under the influence of all cationic or Lewis acid catalysts. The amount of cyclic structures and non-terminal linear unsaturation is dependent upon the electron accepting ability of the catalyst, which may be greatly influenced by the nature of the solvent. The cyclopolymerization generally proceeds to low conversion and then reaches a dormant state. Addition of monomer to the dormant mixture reinitiates polymerization which again attains a limiting equilibrium conversion. The molecular weight increases with conversion. Polymerization in aromatic solvents results in the incorporation of phenyl groups in the polymer structure. Polymers with low intrinsic viscosities have relatively high molecular weights as measured by light scattering. The proposed polymeriza-tion mechanism leading to a perhydrophenanthrene structure involves initia-tion by a 1,2 or 1,4 monomer cation-radical and propagation through a 1,3 polymer cation-radical.

INTRODUCTION

The polymerization of conjugated dienes with protonic or Lewis acids has been the subject of numerous investigations within the past 50 years. In general, the polymers from butadiene and isoprene were reported to be low molecular weight products, varying in appearance from viscous liquids to brittle solids. The microstructure consisted of predominantly *trans*-1,4 unsaturation, accompanied by 1,2 unsaturation, with little or no detectable *cis*-1,4 unsaturation. However, chemical analysis indicated that the total unsaturation was considerably lower than indicated by a normalized infrared analysis wherein the unsaturation was presumed to total 100 per cent. No identification of the structures responsible for the loss in unsaturation was made.

STRUCTURE OF CYCLOPOLYDIENES

In the course of an investigation of the polymerization of butadiene and isoprene with Ziegler-type catalysts consisting of alkyl or arylmagnesium bromide or triethyl aluminum with titanium tetrachloride, it was noted that the conversion and the nature of the polymer are dependent upon the Mg/Ti and Al/Ti molar ratios[1, 2]. The conversion curves contain two maxima (*Figure 1*), the first at an $RMgX/TiCl_4$ molar ratio of 0·5–1 or an $AlR_3/TiCl_4$ molar ratio below 1 and the second at an Mg/Ti ratio of 3–5 or Al/Ti ratio of about 1.
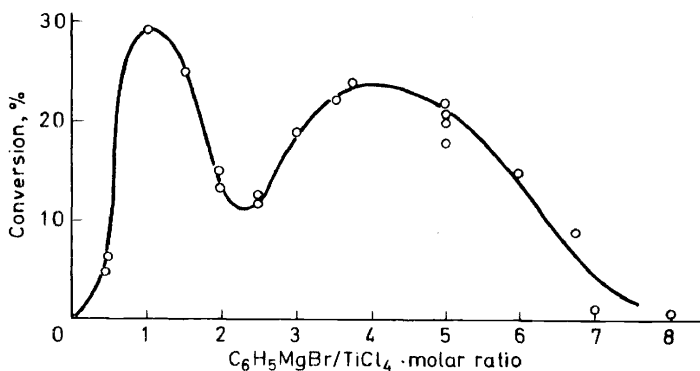
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Figure 1. Yield of polyisoprene as a function of catalyst composition. Catalyst: C_6H_5MgBr + $TiCl_4$: [Isoprene] = 140 g/l: [$TiCl_4$] = 20 mmoles/l; solvent benzene: temperature 20°C; ·reaction time 3 h.

The influence of temperature on yield is also dependent upon the Mg/Ti mole ratio. As shown in *Table 1*, at an Mg/Ti ratio of 0·3, in the range of the first maximum, the yield of polymer from butadiene decreases with increasing temperatures. At an Mg/Ti ratio of 2·0, entering the region of the second maximum, the polymer yield increases with increasing temperature. This is considered indicative of the operation of different polymerization mechanisms.

Table 1. Effect of temperature on polymerization of butadiene with $C_6H_5MgBr–TiCl_4$ catalyst (conversions after 1 h)

Molar ratio, $C_6H_5MgBr/TiCl_4$	Temperature, °C	Yield, g	trans-1.4 configuration %
0·3	54	0·05	7
	41	0·04	11
	27	0·10	15
	15	0·14	17
	5	0·16	26
2·0	87	2·7	
	75	0·6	
	66	0·5	
	27	0·15	

The infrared spectra of the polymers produced at the different ratios are distinctly different, as is the appearance of the polymers. The polymer formed at the first maximum is powdery and generally insoluble in common organic solvents and although its infrared spectrum may show some *trans*-1,4 content, it differs from those of 1,4 or 1,2-polydienes (*Figure 2b*). The polymer formed at the higher Mg/Ti or Al/Ti ratios is a soluble, non-resinous material whose infrared spectrum shows a preponderance of 1,4 units (*Figure 2a*).

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Very few differences exist between the infrared spectra of the insoluble, powdery polymers prepared from the conjugated diene monomers and cyclized polyisoprenes prepared by cyclization of linear *trans*-1,4- (balata), *cis*-1,4- (Hevea) and 3,4-polyisoprenes[3, 4]. The spectra of the powdery butadiene polymers have the same characteristics as those of the powdery isoprene polymers and cyclized polyisoprenes[3].

Treatment of the powdery polymers which still contain some linear structures with sulphuric acid results in the disappearance of the absorption bands assigned to the linear forms (*Figure 2c*). The powdery polymers obtained directly from the monomers revert irreversibly to liquids at elevated temperatures in air. The reversion temperatures are 370° for the non-linear polyisoprene, 405° for the non-linear polybutadiene and 420° for the non-linear polychloroprene. The infrared spectra of the liquids are the same as those of their solid precursors except that the 1,4-units are absent in the former[1, 2].
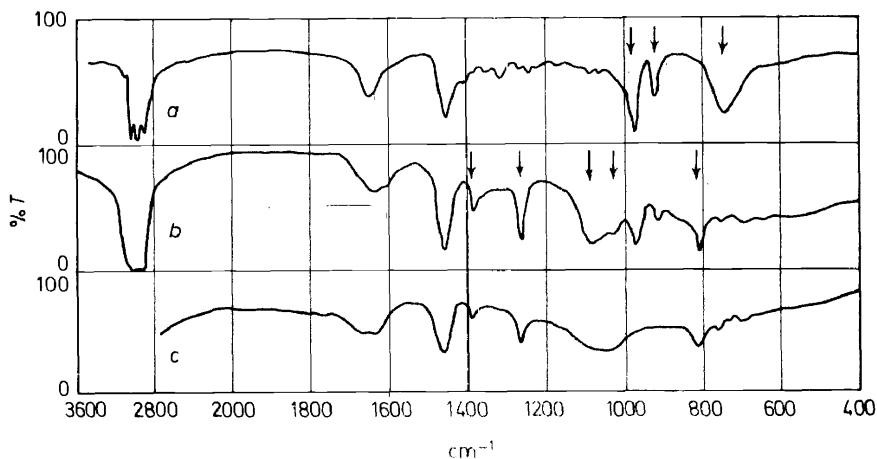

Figure 2. Infrared spectra of polybutadiene obtained with $C_6H_5MgBr/TiCl_4$ catalyst: (a) Mg/Ti = 5; (b) Mg/Ti = 0·5; (c) sample (b) cyclized by H_2SO_4.

The similarity between the spectra of the polymers prepared from the conjugated diene monomers by the use of the Ziegler-type catalysts and the spectra of the cyclized polymers indicates that both types of polymers have the same polycyclic structure. The failure to cyclize 3.4-polyisoprene or *cis*-1,4-polyisoprene with the individual catalyst components or with the two component catalyst system under the conditions which are effective in the polymerization of the diene monomers to cyclopolymers confirms that the latter are formed directly from monomer and not as a result of cyclization of initially formed linear polymers of these structures.

The exact structures of the cyclopolymers is not known. The infrared spectra are very simple and although structural assignments have been made to the various absorption bands which appear in the spectra[3], they

serve only as a basis for the postulation that the polymers contain fused cyclohexane rings. However, there is no direct evidence for the length of the blocks of fused rings. Examination of the spectra of cyclized polymers has led to the proposal that the blocks or segments contain 2–5 fused rings[1]. and are most probably tricyclic[5]. By comparison the cyclopolymers are considered more highly fused, i.e. at least 5 rings per segment[1].

Attempts to utilize nuclear magnetic resonance spectroscopy to confirm the cyclic character of the cyclopolymers have been unsuccessful. The assignment[6] of various peaks to the cyclic structure has been questioned[7].

The amount of cyclic structure but not the sequence length is obtained by difference after determining the absolute amount of unsaturation, i.e. the linear forms, by infrared analysis without the usual practice of normalizing so that the total unsaturation is 100 per cent and also, in the case of soluble polymers, by titration with iodine monochloride[8].

On the basis of spectral analyses and pyrolytic products[9], and particularly in consideration of the proposed mechanism of polymerization, which is discussed in a later section, the cyclopolymers are presumed to contain perhydrophenanthrene (I) and/or perhydroanthracene (II) units, e.g. from butadiene:

(I)   (II)
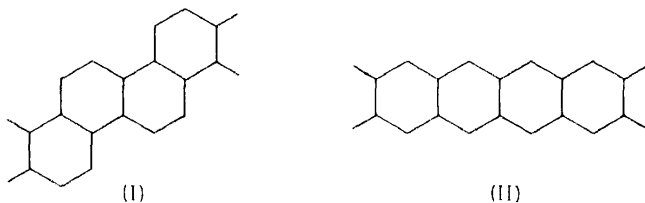
CYCLOPOLYMERIZATION AS A GENERAL CHARACTERISTIC OF DIENE POLYMERIZATION WITH CLASSICAL CATIONIC CATALYSTS

The discovery that Ziegler-type catalysts $RMgX–TiCl_4$ and $R_3Al–TiCl_4$ containing an excess of the transition metal compound, and therefore presumably cationic initiators, catalyze the polymerization of butadiene, isoprene and chloroprene to cyclopolymers, prompted an investigation of the extent of cyclopolymerization initiated by typical cationic catalysts. The probability of the occurrence of cyclic structures was enhanced by the low levels of unsaturation and the discrepancies between the infrared and chemical analyses of unsaturation reported in such polymers.

Lewis acid catalysts

The polymerization of isoprene to polymers with less than 20 per cent linear structures in the presence of ethyl aluminum dichloride[10] and classical cationic catalysts, i.e. Lewis acids[11], is clearly shown in *Tables 2* and *3*.

The course of the reaction depends strongly upon the type of solvent used as the polymerization medium. Polymerization in *n*-heptane is charac-

Table 2. Polymerization of isoprene in *n*-heptane medium[a]

Catalyst		Monomer conc., mole/l.	Time of Reaction min	Conversion %	Structure, %[b]			Note
Nature	Amount. mmole				1,4	3,4	1,2	
AlEtCl$_2$	0·7	0·8	180	5	12	2	1	
AlEtCl$_2$	0·7	1·7	180	21	27	5	n.d.	
AlCl$_3$	0·8	0·8	120	6	2	1	n.d.	Catalyst in suspension
AlBr$_3$	0·7	0·4	120	8	n.d.	n.d.	n.d.	
TiCl$_4$	0·8	0·8	180	0	—	—	—	
TiCl$_4$	0·8	0·8	180	6	2	1	n.d.	5 ml of moist *n*-heptane added
SnCl$_4$	2·7	1·7	60	24	2	1	n.d.	
H$_2$SO$_4$	0·8	0·8	60	28	0	0	0	Oligomers. *n* = 1–5

[a] 30 ml of solvent. 21 C.
[b] n. d. = not detectable.

terized by an extremely fast initial rate of polymerization followed by a period when the reaction practically stops. The conversion at that stage is very low and the polymers are powdery materials. insoluble in hydrocarbon and most common organic solvents. The infrared spectra generally do not indicate the presence of any absorption bands characteristic of common linear addition forms.

Although ethyl aluminum dichloride, aluminum bromide and stannic chloride behave in a similar manner. titanium tetrachloride is completely inactive unless moisture is introduced into the reaction mixture (*Table 2*). Nevertheless. the resultant cyclopolyisoprene contains less than 5 per cent residual unsaturation.
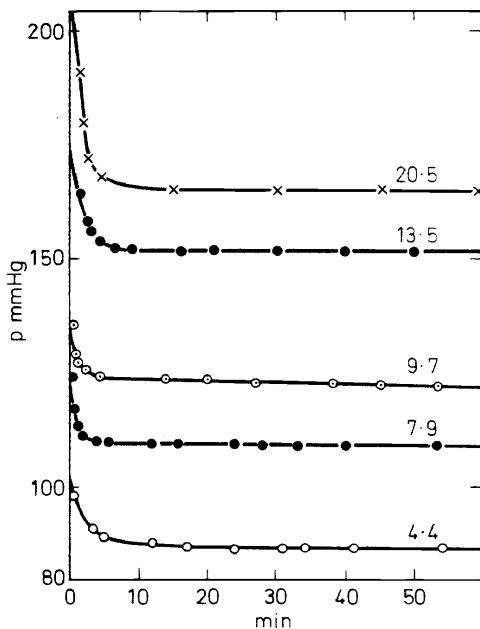
Table 3. Polymerization of isoprene in aromatic solvents at 21[a]

Catalyst	Solvent	Time min	Yield, %	Microstructure. %			Molecular weight[b]	Unsatur- ation, %
				cis-1,4	trans-1,4	3,4		
EtAlCl$_2$	Benzene	60	28·6	5	14	2	110,000	22
	Toluene	60	53·1	7	11	0·5		
	Xylene	60	73·5	—	13	2		
AlCl$_3$	Benzene	60	58·8	5	9	2	80,000	17
	Toluene	60	73·6	—	—	1		
AlBr$_3$	Benzene	60	79·5	7	14	3	60,000	25
	Toluene	60	91·3	4	8	0·5		26
CH$_3$TiCl$_3$	Toluene	60	20·6	7	14	0·5		
TiCl$_4$	Toluene	180	3·7	—	—	—		
EtAlCl$_2$– TiCl$_4$ (1:5)	Toluene	30	94·2	5	11	0·6	50,000	15
SnCl$_4$	Benzene	60	26·5	8	2	2		
SbCl$_3$	Toluene	60	11·8	8	10	2		

[a] [Isoprene] = 0·6–1·0 mole·l: 50 ml solvent: [catalyst] = 0·7–1·0 mmole except [SnCl$_4$] = 1·2 mmole and [SbCl$_3$] = 5 mmoles.
[b] Light scattering.

The low conversion is not indicative of the termination of polymerization. As shown in *Figure 3*, the introduction of additional amounts of monomer results in further polymerization until a new limiting conversion or equilibrium is established. This process may be repeated many times, increasing the conversion at each step. When an equilibrium mixture is sealed off and stored, nearly 100 per cent conversion is attained after several weeks.

Figure 3. Polymerization of isoprene in 30 ml *n*-heptane at 21°C with 0·7 mmole $C_2H_5AlCl_2$ as catalyst. Figures on curves indicate percent conversion at equilibrium stage. At this point isoprene pressure (concentration) increased to next highest level shown. Vapour pressure of pure *n*-heptane at 21°C = 38 mm Hg.

Polymerization rates in aromatic solvents are much higher than in *n*-heptane and the equilibrium conversion is also much higher (*Table 3*). The polymers are either white powders, tacky solids or oils depending upon the solvent and are very soluble in benzene. The molecular weight of the cyclopolyisoprenes produced in benzene range between 50,000 and 100,000 (light scattering).

The content of linear structures is higher than in cyclopolyisoprene prepared in heptane but does not exceed 30 per cent, independent of molecular weight (provided the product is not an oligomer). The use of aromatic solvents as reaction media results in the incorporation of high amounts of aromatic moieties, indicating that extensive chain transfer with the solvent takes place, a recognized characteristic of cationic polymerization. However, in contrast to conventional reactions of the latter type, wherein the transfer

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reaction results in chain termination and the incorporation of only one phenyl group per chain, the cyclopolymerization yields polymers of high molecular weight containing more than one phenyl group per chain.

Polymerization rates and limiting conversions are much higher in halogenated solvents than in aromatic solvents and a higher concentration of linear forms, predominantly *trans*-1,4, is present in the cyclopolymers. Although no solvent residues are detectable in cyclopolyisoprene prepared in chlorinated benzenes, some chlorine is present in polymers prepared in methylene chloride or carbon tetrachloride[11].

Ethyl aluminum halide–titanium tetrahalide catalysts

Cyclopolymerization of conjugated dienes is catalyzed not only by Lewis acids and $RMgX–TiCl_4$ and $R_3Al–TiCl_4$ combinations but also by Ziegler-type catalysts based on diethyl aluminum halides.

The polymerization of isoprene in n-heptane medium by the two component catalyst systems $(C_2H_5)_2 AlX–TiCl_4$ (where X is fluoride, chloride or bromide), while maintaining a constant monomer concentration, is characterized by a strong dependence of the reaction rate on the Al/Ti ratio, accompanied by changes in the microstructure of the polymers (*Tables 4* and 5).

Table 4. Polymerization of isoprene with $(C_2H_5)_2AlX + TiCl_4$ catalyst[a]

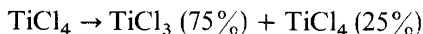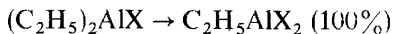| $(C_2H_5)_2AlCl$			$(C_2H_5)_2AlF$		
Al/Ti Mole Ratio	Yield, g	Cyclic Structure, %	Al/Ti Mole Ratio	Yield, g	Cyclic Structure, %
0·25	0·3	99	0·5	0·9	98
0·5	1·0	98	0·75	1·2	97
0·75	1·2	98	1·0	0·4	97
1·0	0·6	98	1·2	0·3	84
1·25	0·5	97	1·4	0·1	59
1·75	0·02	87	1·6	0·7	43
2·0	0·1	64	1·8	1·9[b]	33
2·5	0·2	49	2·0	2·3[b]	18
2·75	0·2	49	3·0	2·8[b]	14
3·0	0·3	42			
4·0	0·8	28			

[a] Catalyst components mixed for 60 min in heptane in absence of monomer at 21 C. Isoprene content maintained constant during 3 h reaction period.
[b] Yield after 2 h.

At certain ratios of the components of the catalyst the polymerization rate is practically zero, i.e. the catalyst is inactive. At ratios lower than these critical values, powdery, insoluble polymers are formed. Infrared analysis shows that these products are essentially all cyclic polyisoprenes. At Al/Ti ratios higher than the critical value, the polymerization rate rises again and the polymers obtained are a mixture of linear and cyclic structures.

The maximum activity for the formation of cyclopolyisoprene occurs at

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approximately the same Al/Ti molar ratio of 0·75, independent of the nature of the halogen. This corresponds to the reactions

$$(C_2H_5)_2AlX \rightarrow C_2H_5AlX_2 \ (100\%)$$

$$TiCl_4 \rightarrow TiCl_3 \ (75\%) + TiCl_4 \ (25\%)$$

The significantly lower activity of $C_2H_5AlCl_2$, β-$TiCl_3$, $AlCl_3$, β-$TiCl_3$–$C_2H_5AlCl_2$ and β-$TiCl_3$–$AlCl_3$ and the inactivity of $(C_2H_5)_2AlX$ indicate that the active catalytic species is derived from the reaction of ethyl aluminum dihalide with titanium tetrachloride. The most active catalysts are obtained when the reaction of diethyl aluminum halide with titanium tetrachloride yields a 4:1 mixture of $C_2H_5AlX_2 : TiCl_4$.

Table 5. Polymerization of isoprene with $(C_2H_5)_2AlX + TiCl_4$ catalyst[a]

$(C_2H_5)_2AlI$			$(C_2H_5)_2AlBr$		
Al/Ti Mole Ratio	Yield, g	Cyclic Structure, %	Al/Ti Mole Ratio	Yield g	Cyclic Structure, %
1	0·2	100	0·75	0·4	99
2	0·7	100	1·0	1·4	98
4	0·6	100	1·5	0·3	98
			2·0	0·1	94
			2·5	0·3	76
			4·0	0·4	40

[a] Catalyst components mixed for 60 min in heptane in absence of monomer at 21°. Isoprene content maintained constant during 3 h reaction period.

Polymerizations catalyzed by the diethyl aluminum iodide–titanium tetrachloride system (Table 5) are marked by a rapid consumption of monomer initially, cessation of the reaction at very low conversions and the formation of cyclopolyisoprenes at all Al/Ti ratios.

The very sharp minimum of polymerization rates at an Al/Ti ratio of 1·4 with the $(C_2H_5)_2AlF$–$TiCl_4$ system and the very broad region of minimum rates for systems containing the chloride and bromide are probably due to the decreasing reducing power and the increasing acidity of the complex in the series, F, Cl, Br.

The polymerization of isoprene with ethyl aluminum dichloride in heptane yields solid cyclopolyisoprene. The catalytic activity is markedly increased by the addition of titanium tetrachloride although the dry metal halide per se is not a catalyst for isoprene polymerization and titanium tetrachloride containing traces of moisture yields only small amounts of solid polymer.

Analogous to the observations described earlier with other catalyst systems, in polymerizations carried out while maintaining a constant isoprene partial pressure with a low concentration of catalyst components, the polymerization is characterized by a rapid initial stage, followed by a constant rate of monomer consumption and then a cessation of reaction[13].

Table 6. Polymerization of isoprene with EtAlCl$_2$ + TiCl$_4$ catalyst in heptane [EtAlCl$_2$] = 0·7 mmole

[TiCl$_4$] mmole	Al/Ti mole ratio	Yield, %	Cyclic structure, %
0	—	0·25	91
0·22	3·18	0·5	87
0·44	1·59	0·8	87
0·8	0·87	1·1	98
1·3	0·54	1·7	91
4·1	0·17	2·9	94
7·1	0·1	4·1	88
8·1	0·086	3·6	93
16·2	0·043	2·7	93

Catalyst components mixed for 60 min in 35 ml heptane in absence of monomer at 21. Isoprene concentration maintained constant at 0·87 mole/l during 3 h reaction period.

The rate is dependent upon the initial concentrations of the catalyst components. The polymer yield after a fixed reaction period depends upon the initial concentration of either of the two catalyst components (*Tables 6* and *7*). Since both components are cationic initiators, cyclopolymers are produced irrespective of which component is present in excess.

Table 7. Polymerization of isoprene with EtAlCl$_2$ + TiCl$_4$ catalyst in heptane [TiCl$_4$] = 0·44 mmole

[EtAlCl$_2$] mmole	Al/Ti mole ratio	Yield g	Cyclic structure, %
0	—	—	—
0·7	1·59	0·8	93
1·35	3·1	2·6	92
2·7	6·1	2·7	92
4·05	9·2	2·6	86
7·5	18·7	1·7	95

Catalyst components mixed for 60 min in 35 ml heptane in absence of monomer at. 21° Isoprene concentration maintained constant at 0·87 mole l during 3 h reaction period.

The yield and rate of polymerization in the initial stage depends upon the time during which the two catalyst components react before the addition of monomer (*Figure 4*). On increasing the catalyst aging or reaction time, the polymer yield after 3 hours first increases and after reaching a maximum decreases (*Figure 5*). The position of the maximum depends upon the initial Al/Ti ratio.

It is apparent that the reaction of the two catalyst components yields an intermediate whose catalytic activity is higher than that of either
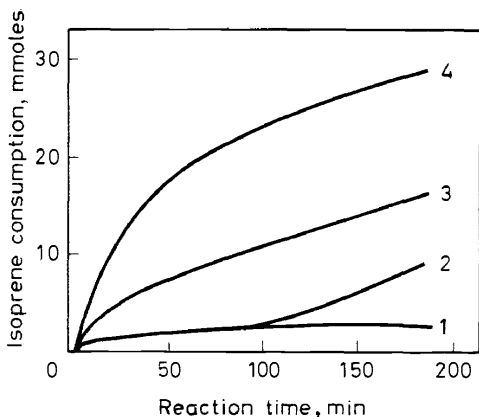
Figure 4. Effect of catalyst aging on isoprene polymerization in heptane at 21°C. [Isoprene] = 0·87 mole/l; [TiCl$_4$] = 0·023 mole/l; [C$_2$H$_5$AlCl$_2$] = 0·021 mole/l. (1) no TiCl$_4$; (2) no aging ; (3) 75 min aging ; (4) 690 min aging.

component. The cyclic structure of the polymers indicates that the active species are probably cations formed by dissociation of the reaction products. The concentration of the active species passes through a maximum in the course of the reaction between catalyst components indicating that the intermediate product is deactivated. The deactivation occurs in the absence of monomer, as shown by the effect of catalyst aging, as well as in the presence of monomer, as shown by the decrease in polymerization rate and finally cessation of polymerization. The electrical conductivity of the system after mixing the components first increases and after reaching a maximum decreases. The changes in conductivity parallel changes in polymerization activity.
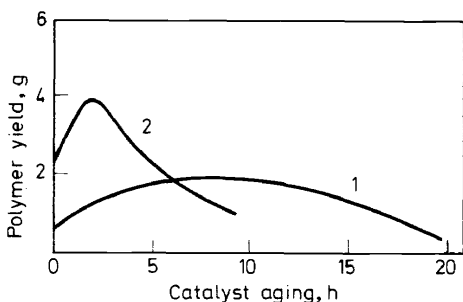

Figure 5. Effect of catalyst aging on isoprene polymerization in heptane at 21°C : reaction time 3 h. [Isoprene] = 0·87 mole/l : [C$_2$H$_5$AlCl$_2$] = 0·021 mole/l : [TiCl$_4$] : (1) 0·023. (2) 0·245 mole/l.

The conversion of isoprene to cyclopolymers increases with increasing temperature in *n*-heptane as well as in a mixture of *n*-heptane and benzene (*Table 8*)[15]. The apparent yield in benzene at times exceeds 100 per cent, owing to the chemically bonded solvent molecules. The cyclopolymers

prepared in benzene have a higher solubility than those prepared in *n*-heptane. The greater solubility cannot be explained by low molecular weight since cyclopolyisoprene with a molecular weight of 3,000,000 has been found to be soluble in benzene.

Table 8. Effect of temperature on polymerization of isoprene in benzene-heptane. $EtAlCl_2/TiCl_4/isoprene = 1/2/50$[a]

Benzene vol-%	Temp., °C	Yield, %	Benzene Soluble, %	$\phi/100$ m.u.[b]	Molecular weight[c]
100	72	94	87	2·1	100,000 L
	63	94	100	1·9	3,000,000 L
	43	94	90	1·9	
	25	91	90	3·0	
	10	88	78	2·5	3,000,000 L
22	68	81	54	0·8	2300
	25	53	62	1·0	7600
	5	36	57	0·9	
	−15	27	67	1·1	3500

[a] Total solvent 90 ml [isoprene] = 1·0 mole l; reaction time 1 h

[b] Phenyl groups per 100 monomer units.

[c] Ebulliometry except L = light scattering.

In conventional cationic polymerization, benzene acts as a chain transfer agent and terminates chain growth. In the cyclopolymerization of conjugated dienes with the $C_2H_5AlCl_2$–$TiCl_4$ catalyst, benzene is incorporated into the polymer chain without terminating chain growth. In cyclopolyisoprene two phenyl groups are incorporated into the polymer structure per 100 monomer units, independent of molecular weight from 1×10^4 to 2×10^6 (*Table 8*), while cyclopolybutadiene contains as many as 7–9 phenyl groups per 100 monomer units (*Table 9*). The concentration of phenyl groups in the cyclopolymers depends on the solvent composition (*Table 8*) and the catalyst composition (*Table 9*).

Table 9. Influence of catalyst composition on structure of cyclopoly-butadiene in benzene[a]

[EtAlCl₂] mole/l	[TiCl₄] mole/l	$\phi/100$ m.u.[b]	C=C/100 m u[b]	CH₃ groups Relative Amount
0·027	0·20	7	17	48
0·033	0·67	7	14	55
0·05	0·033	9	22	63
0·27	0·033	3	47	5

[a] 20°, 3 h; [Butadiene] = constant = 1 mole/l 300 ml benzene

[b] m. u. = monomer unit.

The concentration of double bonds in the cyclopolymers is essentially independent of temperature and benzene/heptane ratio. Cyclopolyisoprene contains one double bond per 3–5 monomer units, while cyclopolybutadiene

contains one double bond for 10 or more monomer units depending upon the ethyl aluminum dichloride concentration (*Table 9*). Infrared analysis shows that 10–40 per cent of the residual double bonds are not conventional 'linear' double bonds but are internal olefinic double bonds in a ring, i.e. cycloalkenyl.

Infrared analysis reveals the presence of methyl groups in the cyclopolymers. The content of methyl groups in cyclopolybutadiene is relatively high, increasing with increasing excess of titanium tetrachloride in the catalyst[15]. On the other hand, the methyl groups are almost absent when the catalyst contains a large excess of ethyl aluminum dichloride (*Table 9*).

Table 10. Cyclopolymerization of butadiene with ethyl aluminum dichloride-titanium tetrachloride catalyst system: 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 had 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

These and other differences in the polycyclobutadienes, prepared with an ethyl aluminum dichloride–titanium tetrachloride catalyst, which result from the use of catalysts containing either excess titanium or excess aluminum, are summarized in *Table 10*[16]. The differences may be explained on the basis of different active centres resulting in different initiation or propagation processes, as discussed in the mechanism section.

CHARACTERISTICS OF COPOLYMERIZATION

The characteristics generally observed in the cyclopolymerization of conjugated dienes are summarized in *Table 11*. The differences noted in butadiene polymerization with the $C_2H_5AlCl_2$–$TiCl_4$ catalyst system as a function of the Al/Ti ratio, i.e. the extent of incorporation of solvent moieties, only represent a minor deviation from the general characteristics.

Irrespective of the nature of the catalyst, the rate of polymerization of butadiene or isoprene at constant monomer pressure gradually decreases as the reaction proceeds. A rapid initial stage is followed by a constant rate of monomer consumption and then a cessation of reaction. Although in some cases, e.g. the polymerization of isoprene catalyzed by aluminum bromide in aromatic solvents[17], the stage of zero reaction rate is not reached for many hours, the reaction rate gradually decreases with time.

The reaction between ethyl aluminum dichloride and titanium tetra-chloride in solution in the absence of monomer is relatively slow. Solid titanium trichloride appears only after about 15 minutes at $20°$. The appearance of the solid phase is related to the formation of active centres. This catalyst system is active only when the solid is present[14]. However, a soluble complex which appears simultaneously with the solid is also catalytically active. Although isoprene slightly accelerates the reaction, the maximum activity of the catalyst is attained only after one hour of polymerization. No such induction period is observed with butadiene[16]. By mixing the catalyst components in the presence of butadiene an active catalyst forms almost immediately. The solid phase of titanium trichloride also appears within a few seconds after the addition of butadiene to a mixture of the catalyst components. It follows that butadiene somehow participates in the reduction of Ti^{4+} to Ti^{3+}.

Table 11 Characteristics of cyclopolymerization

(a) Effective catalytic species are cationic in nature
(b) Polymerization proceeds to a low conversion
(c) An equilibrium exists between monomer, catalyst and polymer
(d) Addition of monomer to the dormant equilibrium mixture reinitiates polymerization which again achieves a limiting equilibrium conversion
(e) The molecular weight increases with increased conversion
(f) The polymer contains non-terminal linear unsaturation as well as fused cyclic segments
(g) Polymerization in aromatic solvents results in the incorporation of phenyl groups in the polymer structure
(h) Polymers with low intrinsic or reduced viscosities have relatively high molecular weights as measured by light scattering

The polymerization of butadiene with ethyl aluminum dibromide–titanium tetrachloride and aluminum tribromide–titanium tetrachloride proceed in a comparable manner to the polymerization catalyzed by the ethyl aluminum dichloride–titanium tetrachloride system[16].

The initial rate of polymerization of butadiene with the latter catalyst is 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 (*Figure 6*). However, the addition of more than about 3 moles of iodine per mole of catalyst does not cause any further increase in the rate of polymerization. The added iodine is quickly consumed and the polymerization rate in the later stages is the same as in the absence of iodine. The iodine can be removed from the polymer at temperatures above $130°$. The resulting polymer has a structure similar to that obtained with the same catalyst without the iodine. The iodine has little effect when the catalyst components are present in equimolar amounts[16].

When the polymerization of isoprene is carried out in heptane with ethyl aluminum dichloride as catalyst at $20°$, and the isoprene concentration is maintained constant by the introduction of monomer at a rate equal to its consumption, the limiting conversion is soon attained. However, the addition of styrene monomer results in a renewed consumption of isoprene and
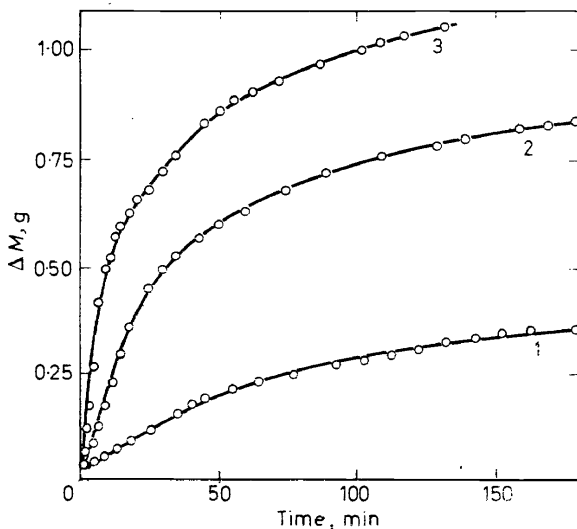
Figure 6. Effect of iodine on rate of cyclopolymerization of butadiene in heptane at 20° C. [TiCl$_4$] = 0·033 mole/l; [EtAlCl$_2$] = 0·066 mole/l. (1) no I$_2$; (2) 0·5 mmole I$_2$; (3) 3 mmole I$_2$.

additional isoprene must be added to maintain a constant concentration. The isoprene consumption curve duplicates the initial curve and an equilibrium is again established. This process may be repeated again and the final isoprene consumption is identical with that in a homopolymerization of isoprene under the same conditions (*Figure 7*). The re-establishment of the
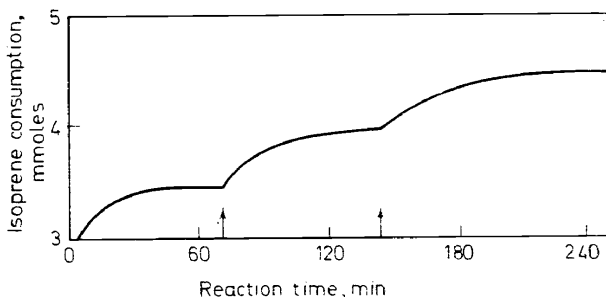

Figure 7. Effect of styrene addition on limiting conversion in isoprene polymerization in heptane at 20°C with C$_2$H$_5$AlCl$_2$ catalyst. Heptane 50 ml; [C$_2$H$_5$AlCl$_2$] = 2 mmoles. Isoprene concentration maintained constant at 0·88 mole/l. Isoprene initially polymerized to equilibrium, 20 mmoles styrene added at point indicated by arrow, isoprene introduced again to maintain constant concentration, 20 mmoles styrene added (arrow), isoprene again introduced to maintain constant concentration.

polymerization activity of isoprene after the addition of styrene is apparently due to the liberation of the catalyst from the monomer–catalyst complex which is in equilibrium with free monomer[18, 19]. The styrene is incorporated into the polymer chain in the form of a block copolymer in which the isoprene is present as saturated cyclic segments.

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SOLVENT EFFECT ON CYCLOPOLYMERIZATION

The cyclopolymerization of isoprene in hydrocarbon solvents is initiated to a limited extent by Lewis acids which are dimeric in nature, e.g. aluminum tribromide and aluminum trichloride, or by Lewis acids in the presence of cocatalysts, e.g. titanium tetrachloride–water[11]. However, the rate and extent of cyclopolymerization is greatly increased when Lewis acids such as antimony pentachloride, titanium tetrachloride, aluminum trichloride and phosphorus pentafluoride are used as catalysts in the absence of a cocatalyst with nitrobenzene as reaction medium[20].

Stable carbonium ion salts such as cycloheptatrienyl (tropylium) or triphenylmethyl (trityl) hexachloroantimonate have been shown to initiate the non-terminating cationic polymerization of cyclic ethers such as tetrahydrofuran and vinyl monomers such as alkyl vinyl ethers, N-vinylcarbazole and alkoxystyrenes, using methylene chloride or acetonitrile as reaction media[21–26].

Little or no polymerization occurs when tropylium hexachloroantimonate and trityl hexachloroantimonate are used as catalysts for the attempted polymerization of isoprene at 20° in n-heptane, benzene, toluene, acetonitrile, methylene chloride or nitromethane. The cyclopolymerization of isoprene is readily effected when nitrobenzene is used as the reaction medium. n-Heptane and methylene chloride may be mixed with the nitrobenzene, the yield of polymer increasing in direct proportion to the nitrobenzene content of the solvent mixture $(Table\ 12)$[27, 28].

Table 12. Influence of solvent composition on isoprene polymerization initiated by tropylium and trityl salts[a]

Catalyst	Solvent (vol/vol)	Temp., $^\circ$C	Conversion, %	$[\eta]$ dl/g[b]
$\phi_3CCl + SbCl_5$	CH_2Cl_2	0	2·0	—
	$CH_2Cl_2/\phi NO_2$			
	4/1	0	6·9	—
	ϕNO_2	20	51·5	0·057
$\phi_3C^+SbCl_6^-$	n-C_7H_{16}	20	0	—
	n-$C_7H_{16}/\phi NO_2$			
	4/1	20	0	—
	3/7	20	22·0	0·040
	ϕNO_2	20	44·0	0·056
$C_7H_7^+SbCl_6^-$	ϕNO_2	20	26·3	0·049
$SbCl_5$	ϕNO_2	20	33·8	0·055

[a] [Isoprene] = 10 ml = 1·6 moles/l: [catalyst] = 1 mmole 0·016 mole/l: solvents, 50 ml: temperature 20°: time 100 min.
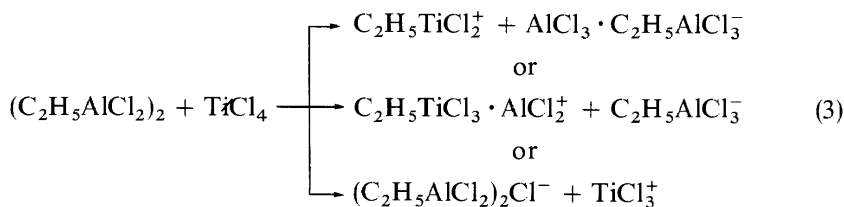[b] Benzene, 25°.

At constant isoprene concentration, a limiting conversion is reached, although polymerization resumes on the addition of monomer, analogous to the behaviour in the cyclopolymerization of isoprene in benzene or heptane with ethyl aluminum dichloride or ethyl aluminum dichloride–titanium tetrachloride catalysts.

Triphenylmethyl groups are detected in the cyclopolyisoprene prepared

with the trityl salt. However, no tropylium residues are detectable in polymers prepared with the tropylium salt catalyst. The content of triphenylmethyl groups in the cyclopolyisoprene is in inverse relation to the nitrobenzene content of the reaction medium.

The cyclopolymers contain 10–45 per cent of unsaturation (*trans*-1,4 and 3,4). The unsaturation decreases with increasing trityl ion concentration but is independent of the tropylium ion concentration.

MECHANISM OF CYCLOPOLYMERIZATION

Several qualitative mechanisms have been proposed to account for the formation of cyclopolymers from conjugated dienes. The earliest proposal[1,2] invoked the cationic polymerization of the diene to tactic 1,2 (butadiene) or 3,4 (isoprene) polymer. Cyclization resulted from the reversal of the direction of the polymerization reaction or the copolymerization of additional monomer or a growing chain with the pendant 1,2 (or 3,4) groups.

The second proposal[10] involved the dissociation of ethyl aluminum dichloride to the ion pair $Al(C_2H_5)_2^+ AlCl_4^-$ which reacted with the isoprene monomer to form a π-complex. Polymerization presumably proceeded in accordance with equation 1.

Neither of these proposals satisfactorily explains the various observed characteristics of cyclopolymerization. The latter and the proposed structure of the cyclopolymer are consistent with a Diels–Alder charge transfer mechanism. A mechanism which adequately incorporated the experimental observations was proposed[13] but modified[15] since it led to a perhydro-anthracene structure and did not account for the perhydrophenanthrene structure which is presently favoured.

The active initiating species in the case of $C_2H_5AlCl_2$ is the ion pair resulting from the dissociation of the dimer, as shown in equation 2.

$$(C_2H_5AlCl_2)_2 \begin{cases} \longrightarrow C_2H_5AlCl^+ + C_2H_5AlCl_3^- \\ \quad\quad\quad\text{or} \\ \longrightarrow (C_2H_5)_2Al^+ + AlCl_4^- \end{cases} \quad (2)$$

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In the case of $C_2H_5AlCl_2$–$TiCl_4$ or $(C_2H_5)_2AlCl$–$TiCl_4$ which produces the dichloride, the ion pair has the analogous structure shown in equation 3.

$$
(C_2H_5AlCl_2)_2 + TiCl_4 \longrightarrow
\begin{cases}
C_2H_5TiCl_2^+ + AlCl_3 \cdot C_2H_5AlCl_3^- \\
\text{or} \\
C_2H_5TiCl_3 \cdot AlCl_2^+ + C_2H_5AlCl_3^- \\
\text{or} \\
(C_2H_5AlCl_2)_2Cl^- + TiCl_3^+
\end{cases}
\quad (3)
$$

While these reactions adequately provide for the formation of an electron-deficient particle which is capable of initiating cyclopolymerization in hydrocarbon solvents, the failure to initiate polymerization in these solvents with tropylium and trityl ion salts indicates that dissociation alone does not necessarily provide an active particle. In the latter cases, the interaction of the trityl or tropylium cation or the salt with the strongly electron-accepting nitrobenzene apparently produces a charge-transfer complex which is a better electron acceptor than the original ions and is the actual active species in the initiation. The active species in the Lewis acid–nitrobenzene system, e.g. antimony pentachloride, may be $SbCl_4^+(C_6H_5NO_2)Cl^-$.

The formation of titanium trichloride in catalyst systems containing titanium tetrachloride may be indicative of the presence of $TiCl_3^+$ as the active initiating species.

Notwithstanding the actual nature of the initiating species it is sufficient to indicate that it is an electron-deficient particle which is thus an electron acceptor. For the sake of simplicity in the following discussion, the catalyst-derived electron acceptor is represented as A^+ with the understanding that, assuming it is part of an ion pair, there is a counteranion which is intentionally omitted from the equation. Butadiene is shown as the monomer with the understanding that analogous reactions are proposed for isoprene and other conjugated dienes.

Formation of active species

The active centre results from the formation of a donor–acceptor charge transfer complex through a one-electron transfer from the diene monomer to the catalyst cation.
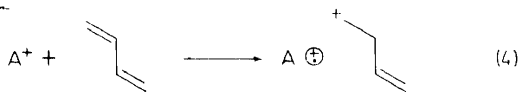

The monomer cation-radical may also exist in the allylic resonance form.
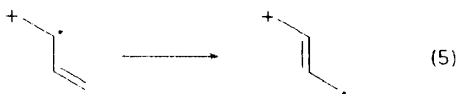
Initiation and ring formation

The 1,2 monomer cation-radical or its allylic resonance form, the 1,4 cation-radical, adds to one double bond of a diene monomer molecule, followed by addition to the residual double bond of the original monomer cation radical, resulting in ring closure and the generation of a 1,3 cation-radical, as shown in equations (6) and (7).


(6)

(7)
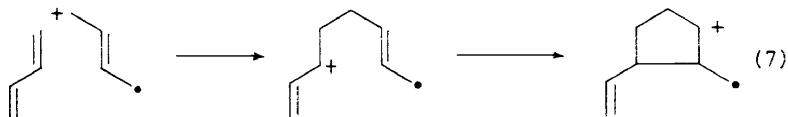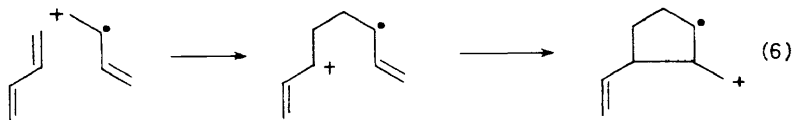
Propagation

The propagation step involves the 1,4 addition of the cation to the diene monomer followed by the 3,2 addition of the radical to the residual double bond. It is also possible that the radical undergoes the 1,4 addition while the cation undergoes the 3,2 addition. The resultant cyclodiene has a perhydrophenanthrene structure.

(8)
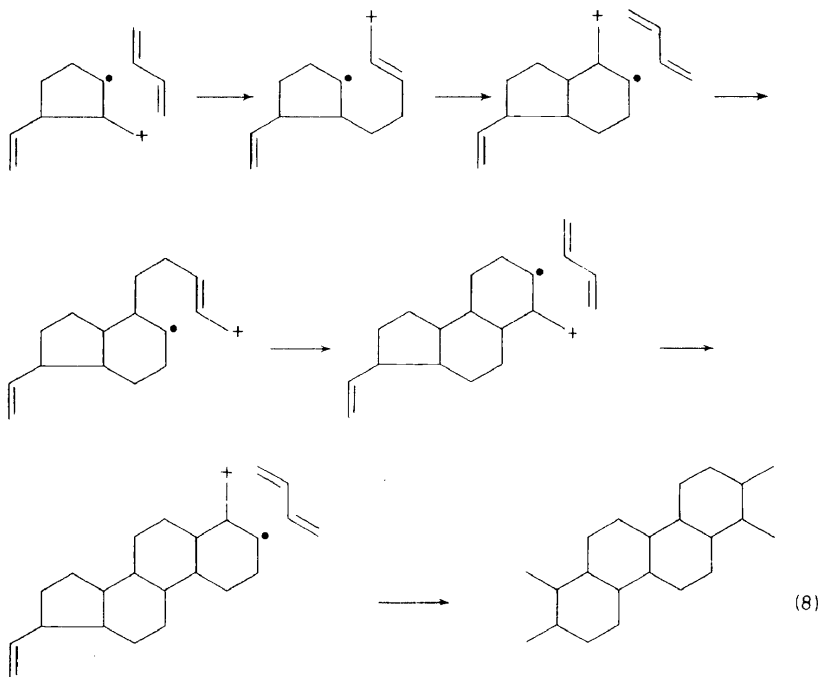
Residual unsaturation results from the 1,4 addition of monomer to the cation or radical species without the subsequent 3,2 addition step.

Phenyl groups are incorporated in the polymer when the reaction is carried out in aromatic solvents as a result of cationic alkylation and proton elimination. Methyl groups are formed when the 1,3 cation-radical undergoes intramolecular hydride transfer.


$$ (9) $$

$$ (10) $$
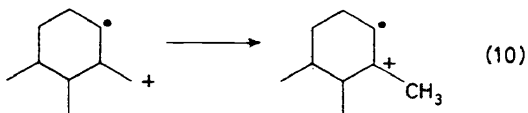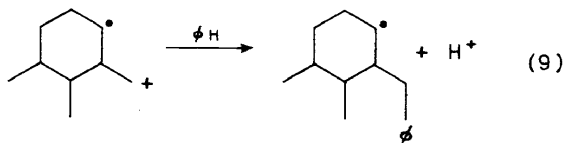
The internal or ring unsaturation, which accounts for 10–40 per cent of the residual double bonds in a cyclodiene polymer, results from deprotonation at the carbon adjacent to the cation, a step well known in the cyclization of diene polymers.


$$ (11) $$

$$ (12) $$
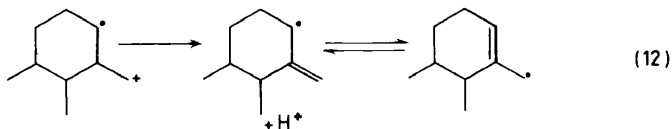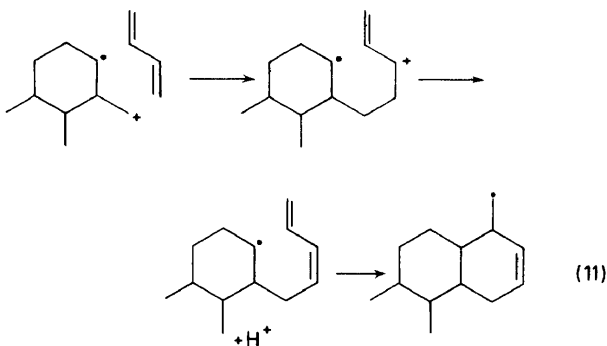
The residual linear or internal unsaturation in the polymer chain may react with activated monomer cation-radical in a reinitiation reaction. This results in the development of highly branched structures consistent with the brittleness of the cyclopolymers and the low intrinsic viscosities which are given by polymers whose molecular weights are quite high according to the light scattering measurements.

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In the cyclopolymerization of butadiene with the $C_2H_5AlCl_2$–$TiCl_4$ catalyst, when Ti > Al the cyclopolymer contains methyl groups and aromatic moieties when the reaction is carried out in an aromatic solvent. When Al > Ti methyl groups and solvent moieties are essentially absent. The Ti > Al catalyst is presumed to promote 1,3 cation-radical propagation with *transoid* monomer to yield the perhydrophenanthrene structure, as depicted in equations 6–8. The Al > Ti catalyst is presumed to promote 1,2 cation-radical propagation with *cisoid* monomer to yield a perhydro-anthracene structure, as shown in equation 13.


(13)
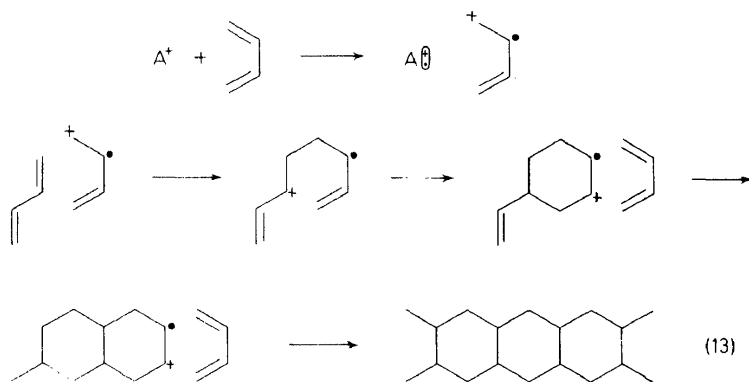
Although the reactions indicated in the above sequences imply that the sequence length of fused rings is infinite, the sequence is considered to be approximately five or six with connecting single bonds, due to reinitiation on the terminal vinyl groups shown in equations 8 and 13, or linear un-saturation.

The generation of active centres has been represented in equation 4 as a one-electron transfer to the catalyst-derived cation, producing a two-centre monomer cation-radical. The occurrence of a two-electron transfer, as in conventional cationic polymerization, would produce a conventional cationic species.

(14)
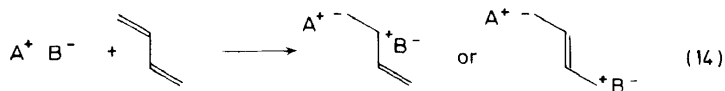
Monomer addition can take place in either a 1,2 and/or a 1,4 manner.
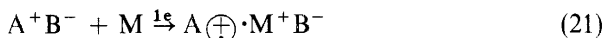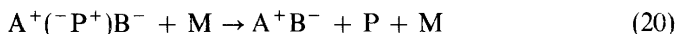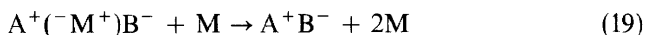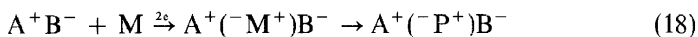

(15)

(16)

324
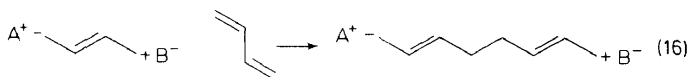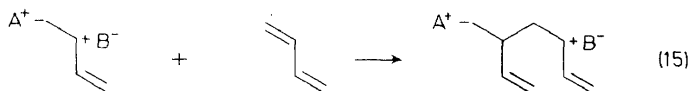
The carbonium ion at the end of the chain is a relatively stable allylic cation with reduced activity.

$$A^{+-} \diagdown\diagup\diagdown\diagup\diagdown\diagup\diagdown_{+\,B^-} \rightleftharpoons A^{+-}\diagdown\diagup\diagdown\diagup\diagdown\underset{B^-}{\overset{+}{\diagup}}\diagdown \qquad (17)$$

The resonance stabilization of the allylic cation accounts for the initial limiting conversion and the slow monomer addition over an extended period.

The reaction mixture, in the dormant state, contains monomer, polymer and catalyst. The low or negligible reactivity in this state is indicative of the tightness of the ion pairs $A^+(^-\text{monomer}^+)B^-$ and $A^+(^-\text{polymer}^+)B^-$ as compared to the catalyst, i.e. the reaction product of the catalyst components A^+B^-.

On the addition of new monomer, i.e. an increase in the concentration of monomer, the tight ion pairs are loosened, possibly through solvation, and the A^+B^- ion pair is made available for the one-electron transfer monomer activation.

$$A^+B^- + M \overset{2e}{\rightarrow} A^+(^-M^+)B^- \rightarrow A^+(^-P^+)B^- \qquad (18)$$

$$A^+(^-M^+)B^- + M \rightarrow A^+B^- + 2M \qquad (19)$$

$$A^+(^-P^+)B^- + M \rightarrow A^+B^- + P + M \qquad (20)$$

$$A^+B^- + M \overset{1e}{\rightarrow} A\overset{\cdot}{\oplus}\cdot M^+B^- \qquad (21)$$

$$A\overset{\cdot}{\oplus}\cdot M^+B^- + M \rightarrow A\overset{\cdot}{\oplus}\cdot P^+B^- \qquad (22)$$

The participation of both two-electron and one-electron transfer reactions in diene polymerization is highly probable although the stronger the electron acceptor the greater the contribution of the one-electron transfer reaction. The γ-ray initiated polymerization of butadiene and isoprene at $20°$ and at $-78°$ yields polymers which are linear and of mixed linear and cyclic structures, respectively[29].

Due to steric factors the polymerization of 2,3-dimethyl-1,3-butadiene yields polymer containing monocyclic units and reduced unsaturation when the catalyst is ethyl aluminum dichloride or $(\text{i-}C_4H_9)_3\text{Al–TiCl}_4$ with Ti > Al[30]. The monocyclic structure is also formed when the polymerization is initiated by γ-rays in bulk at $-78°$ or in a thiourea canal complex at $20°$ [29].

CONCLUSIONS

The formation of essentially saturated polymers containing fused cyclo-hexane rings is apparently a characteristic of the polymerization of conjugated dienes under the influence of all cationic catalysts. The amount of cyclic structures and linear unsaturation is dependent upon the electron accepting ability of the catalyst although the interaction of the catalyst with the solvent, where the latter is a strong electron acceptor such as nitrobenzene, may greatly enhance the electron accepting ability of the catalyst.

The inability to detect the cyclic structures by either infrared analysis or nuclear magnetic resonance spectroscopy emphasizes the importance of

chemical analysis as an adjunct to instrumental analysis in the determination of microstructure in diene polymers. The need to utilize absolute values rather than normalized values in the infrared analysis is strongly indicated by the 100 per cent linear unsaturation reported for polymers which may contain less than 10 per cent unsaturation.

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