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Cyclo- and Cyclized Diene Polymers. XVIII. Microstructure and Mechanism of Cyclopolymerization of Isoprene and Butadiene with $C_2H_5AlCl_2 + TiCl_4$ Catalyst

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Summary

The polymerization of isoprene and butadiene with an ethylaluminum dichloride–titanum tetrachloride catalyst system yields ladder polymers containing fused cyclic structures. Cyclopolymers prepared in n-heptane are generally insoluble powders, while cyclopolymers prepared in aromatic solvents are soluble even when the molecular weight exceeds 1×10^6. 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, while cyclopolybutadiene contains as many as 7–9 phenyl groups per 100 monomer units. The cyclopolymers contain residual unsaturation, 10–40% of which is cycloalkenyl, and methyl groups. Indirect evidence indicates that cyclopolyisoprene may have a perhydrophenanthrene structure. The proposed polymerization mechanism involves cation-radical initiation and propagation. An activated monomer cation radical results from a one-electron transfer from monomer to an electron acceptor species produced by the interaction of catalyst components. In the initiation step, a two-stage cationic addition results in ring closure and the formation of a cyclic 1,2 or 1,3 cation radical. Propagation involves simultaneous or consecutive addition of the radical cation to monomer to generate polymer with cyclic cation-radical end groups. Activated monomer cation radical may add to internal unsaturation to reinitiate cyclopolymerization and form highly branched cyclopolymers.

The polymerization of isoprene and butadiene with a ethylaluminum dichloride—titanium tetrachloride catalyst system yields cyclopolyisoprene [1, 2] and cyclopolybutadiene [3], respectively. The preparation of cyclopolymers from conjugated dienes by this as well as conventional Friedal-Crafts catalysts suggests simple cationic propagation [4]. However, the structure of the cyclopolymers and some unusual features of the polymerization reaction indicate that cyclopolymerization proceeds by a two-center mechanism, which has been proposed as involving Diels-Alder [5] or cation-radical [2] intermediates.

EXPERIMENTAL

Materials

All materials were reagent grade. Isoprene was distilled before use and dried over calcium hydride. Butadiene was dried over sodium hydride. Benzene and n-heptane were dried by refluxing over sodium hydride and outgassed by a freeze-thaw technique. Monomers were similarly outgassed before use. Ethylaluminum dichloride was added as a 1 M solution in n-heptane. $TiCl_4$ was used as received or in n-heptane solution. Di-t-butyl peroxide with a half-life of 218 hr at 100°C and t-butyl peroxypivalate (75% solution, Lupersol 11) with a half-life of 1 min at 117°C [6] were used as received from Lucidol.

Polymerization

A hypodermic-syringe technique was used in the polymerization of isoprene which was carried out in a three-necked flask provided with a reflux condenser, under an atmosphere of nitrogen which had been dried by passage through a column of Linde molecular sieves. The solvent, ethylaluminum dichloride and $TiCl_4$, were mixed in that order, the mixture was stirred for 0.5 hr at 25°C and monomeric isoprene was introduced by syringe at such a rate as to avoid any substantial increase of temperature. The reaction was terminated by the addition of methanol.

Butadiene was polymerized in an evacuated apparatus under constant monomer pressure [3]. The solvent and individual catalyst components were charged from glass ampoules containing the necessary amounts for each experiment. Solvent, gaseous monomer, $TiCl_4$, and $C_2H_5AlCl_2$ (or $AlBr_3$) were mixed in that order. The partial pressure was held constant during the entire reaction period by admission of gaseous monomer from the reservoir. Several blank runs proved that none of the catalyst components alone is a polymerization catalyst under these experimental conditions. Polymerization was terminated by rapid evacuation of the monomer and the catalyst destroyed by addition of methanol.

Polymer characterization

Infrared spectra were recorded on a Zeiss UR-10 instrument in the range 400–3200 cm^{-1} using the KBr pellet technique. The phenyl group content in the cyclopolymers obtained in benzene medium was determined from the absorption intensities of the bands at 700 and 758 cm^{-1}. The absorptivities were taken from the spectrum of polystyrene prepared by radical polymerization. The average value was used as a measure of the phenyl group content. Relative amounts of methyl groups in cyclopolybutadiene were calculated from the intensity of the methyl group band at 1380 cm^{-1}.

The content of carbon–carbon double bonds in the cyclopolymers was determined by the iodine monochloride method [7].

The molecular weights of the cyclopolymers were determined ebulliometrically [8] or by light scattering [9].

Fractionation of the cyclopolymers was carried out on a preparative scale from 8 g of polymer by the column technique [10].

RESULTS AND DISCUSSION

Incorporation of Phenyl Groups in Cyclopolymers

Polymerization of isoprene was carried out in n-heptane or benzene or mixtures thereof at temperatures ranging from −78 to 80°C (Tables 1 and 2). In view of the incorporation of solvent frag-

TABLE 1. Polymerization of Isoprene in Benzene–n-Heptane Mixture (90 ml of solvent, $[EtAlCl_2] = 0.02$ mole/liter, $[TiCl_4] = 0.04$ mole/liter, [isoprene] = 1.0 mole/liter, 25°C, 1 hr)

	Benzene, vol. %	Yield, %	Benzene solubility %	C=C[a] / 100 m.u.	C_6H_5[a] / 100 m.u.	Mol. wt.[b] × 10^{-3}
1	100	91	90	25	3.0	
2	50	78	82		1.6	
3	22	53	62		1.0	7.6
4	11	30	40		0.9	
5	5.5	33	51		0.3	3.85
6	3.2	31	48		0.3	2.10
7	1.1	16	34		0.3	1.63
8	0		0		0	

[a] m.u., monomer unit.
[b] Ebulliometrically.

TABLE 2. Influence of Temperature on Cyclopolymerization of Isoprene (90 ml of solvent. benzene–n-heptane mixture; $[EtAlCl_2] = 0.02$ mole/liter, $[TiCl_4] = 0.04$ mole/liter, $[TiCl_4] = 0.04$ mole/liter, [isoprene] = 1.0 mole/liter, 1 hr)

	Benzene, vol. %	Temp., °C	Yield %	Benzene solubility, %	C=C[a] / 100 m.u.	C_6H_5[a] / 100 m.u.	Mol. wt.[b] × 10^{-3}	Vinyl groups,[c] rel. amt.
1	100	72	94	87	20	2.1	100 L	0
2	100	63	94	100	22	1.9	3000 L	0
3	100	43	94	90	24	1.9		0
4	100	25	91	90	25	3.0		0
5	100	10	88	78	25	2.5	3000 L	0
6	100	65	102	10		2.0		
7	100	20	33	100	29			
8[d]	22	68	81	54		0.8	2.3 L	0
9[e]	22	25	53	62		1.0	7.6 E	6
10	22	5	36	57		0.9		8
11	22	–15	27	67		1.1	3.5 E	8
12	22	–33	1.1	28		1.1		13
13	0	25				0		0
14	0	4	19			0		Trace
15	0	–15	5			0		10
16	0	–78	1			0		17

[a] m.u., monomer unit. [b] L, light scattering; E, ebulliometry. [c] Absorbance at 910 cm^{-1} for 1 g and 1 cm^2. [d] $[EtAlCl_2] = 0.08$ mole/liter, $[TiCl_4] = 0.16$ mole/liter, [isoprene] = 4 moles/liter. [e] $[EtAlCl_2] = 0.008$ mole/liter, $[TiCl_4] = 0.016$ mole/liter, [isoprene] = 0.033 mole/liter.

ments into the polymer structure when benzene or other aromatic solvents are used [5], the phenyl group content and other changes in the polymer structure and properties were measured as a function of experimental conditions.

Polymerization of butadiene was carried out in n-heptane or benzene at 20°C, and the influence of catalyst composition on the methyl group, phenyl group, and carbon-carbon double bond content of cyclopolybutadiene was investigated (Table 3).

TABLE 3. Influence of Catalyst Composition on the Structure of Cyclopolybutadiene (20°C, 3 hr, [butadiene] = constant = 1 mole/liter, 30 ml of C_6H_6)

	$[EtAlCl_2]$, moles/liter	$[TiCl_4]$, moles/liter	$\frac{C_6H_5}{100\ \text{m.u.}}$	$\frac{C{=}C}{100\ \text{m.u.}}$	CH_3 groups,[a] rel. amt.
1	0.027	0.20	7	17	48
2	0.033	0.067	7	14	55
3	0.050	0.033	9	22	63
4	0.27	0.033	3	47	5
5	0.030[b]	0.030	4		53.5

[a] Absorbance at 1380 cm^{-1} for 1 g and 1 cm^2.

[b] $AlBr_3$.

Cyclopolymerization of isoprene and butadiene catalyzed with the $C_2H_5AlCl_2 + TiCl_4$ catalyst in n-heptane yields insoluble polymers while cyclopolymerization in aromatic solvents (except at high catalyst concentration) yields soluble polymers. Cyclopolymers prepared in n-heptane are insoluble in common solvents either because they are cross-linked or because they have a regular ladder-type structure with long sequences of fused rings. In cyclopolymers prepared in aromatic solvents, the regularity of the ladder structure is disturbed by substitution with solvent-derived moieties and by other side reactions which contribute to structure changes. Increased 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 2) [9].

Aromatic hydrocarbons also influence the rate of polymerization and conversion, probably due to their dielectric constant, basicity, and tendency to form complexes with aluminum compounds.

In conventional cationic polymerization, benzene acts as a chain transfer agent and terminates chain growth [11]. In the case of diene cyclopolymerization initiated with the $C_2H_5AlCl_2 + TiCl_4$

catalyst, benzene is incorporated into the polymer chain without terminating chain growth. Fractionation of cyclopolyisoprene indicates that there are about 2 phenyl groups per 100 monomer units, independent of molecular weight from 10,000 to 2,000,000. The number of phenyl groups in cyclopolybutadiene is even higher (Table 3) and is as much as 7–9 per 100 monomer units. The concentration of phenyl groups in the cyclopolymers depends on the benzene/heptane ratio and the catalyst composition (Tables 1 and 3). Figure 1 shows the almost linear relationship between the phenyl group content and the benzene concentration.

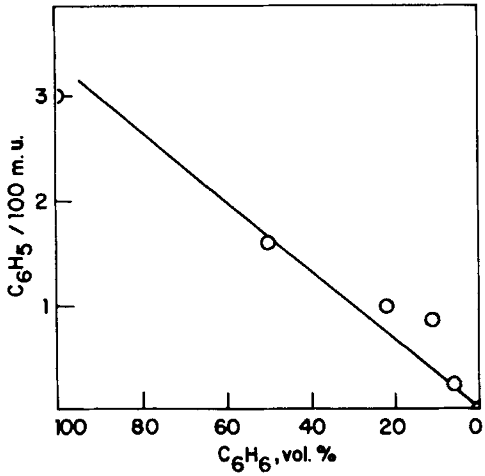


FIG. 1. Phenyl groups per 100 monomer units in cyclopolyisoprene as a function of volume% benzene in an n-heptane–benzene reaction medium.

Solubility and conversion to cyclopolyisoprene decrease with decreasing phenyl group content in the polymer. Table 3 shows that the incorporation of phenyl groups in cyclopolybutadiene is low when the catalyst contains excess aluminum and is relatively high with excess $TiCl_4$. The phenyl group content is practically independent of reaction temperature.

The conversion to cyclopolymers increases with increasing temperature in n-heptane as well as in heptane–benzene (Table 2). The apparent yield in benzene at times exceeds 100%, owing to the chemically bound solvent molecules.

The solubility of the cyclopolymers decreases with increasing catalyst and monomer concentrations. Cross-linking may occur through the phenyl groups as a result of further alkylation, analogous to the results in $C_2H_5AlCl_2$-catalyzed styrene–isoprene copolymerization [12]. Consistent with the expected very low concentration of such cross-links, it was not possible to detect disubstitution of the incorporated aromatic rings by infrared analysis. Cross-linking may also occur through unsaturated sites in polymer chain.

Carbon-Carbon Double Bond and Vinyl Group Concentrations

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 (Table 1), while cyclopolybutadiene contains one double bond for up to 10 monomer units [3]. The vinyl group content in cyclopolyisoprene depends on the catalyst composition and temperature. Below 0°C the vinyl group content increases slightly with decreasing temperature but is always very low, i.e., below 3% (Table 2).

The double-bond content in cyclopolybutadiene is relatively high at high $C_2H_5AlCl_2$ concentrations (Table 3). The vinyl group content depends on the catalyst composition but is always less than 5%.

The infrared analysis shows that 10-40% of the residual double bonds in a cyclopolymer are not conventional "linear" double bonds such as form in 1, 4, 1, 2, or 3, 4 addition but are internal olefinic double bonds in a ring.

Methyl Group Content in Cyclopolymers

The infrared examination indicates the presence of methyl groups in the cyclopolymers. Their appearance and concentration depend on the polymerization conditions.

In cyclopolyisoprene only the ratio of the intensity of the absorption band of (CH_2 + CH_3) groups at 1460 cm^{-1} to the intensity of the CH_3 group band at 1380 cm^{-1} can be determined. This ratio is lower in the cyclopolymer than in linear 1, 4-polyisoprene. However, the change in the ratio may be attributed to a change in the absorptivity.

In cyclopolybutadiene the intensity of the 1380-cm^{-1} band is a direct measure of the methyl group content. The methyl groups are detected when the polymerization is carried out in n-heptane as well as when the reaction medium contains benzene. The content of methyl groups is relatively high, with increasing excess of $TiCl_4$ in the catalyst (Fig. 2). On the other hand, the methyl groups are almost absent when the catalyst contains a large excess of the aluminum component (Fig. 3). The 1380-cm^{-1} band of the methyl group in the infrared spectrum is overlapped with a band at about 1360 cm^{-1}, probably that of the trans-1, 4 structures, and therefore quantitative determination of the methyl group content is approximate and only permits relative evaluation.

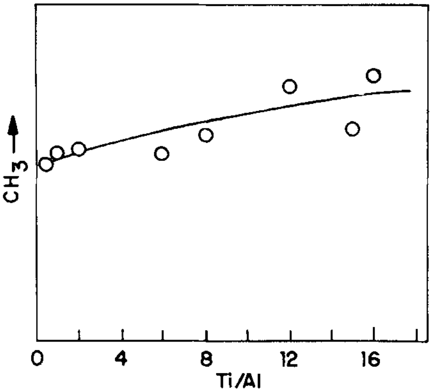


FIG. 2. Influence of $TiCl_4/EtAlCl_2$ ratio on the content of methyl groups in cyclopolybutadiene. $[EtAlCl_2]$ = constant = 0.027 mole/liter, [butadiene] = 1.0 mole/liter, 30 ml of n-heptane.

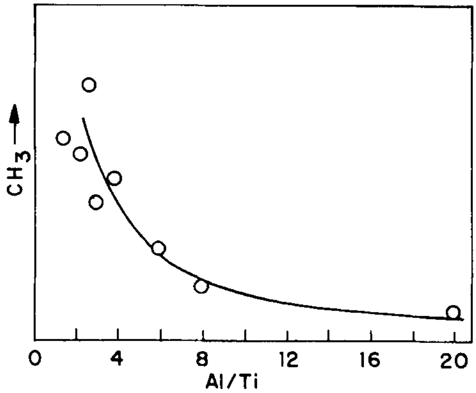


FIG. 3. Influence of $EtAlCl_2/TiCl_4$ ratio on the content of methyl groups in cyclopolybutadiene. $[TiCl_4]$ = constant = 0.033 mole/liter, [butadiene] = 1.0 mole/liter, 30 ml of n-heptane.

Fused-Ring Structure

The structure of the cyclopolymers has not yet been directly confirmed. The fused-ring character of the cyclopolymers from isoprene and butadiene was proposed in the initial reports on polymerization with catalysts such as $RMgX-TiCl_4$ and $R_3Al-TiCl_4$ at high $TiCl_4$ concentrations [4] as well as with $C_2H_5AlCl_2$ [5]. In the absence of direct chemical or spectral evidence, a fused-ring structure has been assumed based on the similarity of the infrared spectra of the cyclopolymers with that of cyclized 3,4-polyisoprene as well as cyclized cis-1,4 and trans-1,4-polyisoprene [13].

The nature of the fused-ring structure has not been elucidated and has been described as perhydroanthrancene or perhydrophenanthrene, without any attempt at differentiation. Work is in progress to more clearly identify the structure of the cyclopolymers. Some indirect evidence indicates that cyclopolyisoprene may have a perhydrophenanthrene structure.

The relatively high amount, i.e., 10–40% of internal ring unsaturation in cyclopolyisoprene is similar to the content of carbon–carbon double bonds in rings which are formed in the cyclization of cis-1,4- and trans-1,4-polyisoprene [13]. These cyclized polymers are presumed to have a perhydrophenanthrene structure. On the other hand, cyclized 3,4-polyisoprene which yields a perhydroanthracene structure has less than 5% of internal unsaturation.

A patent [14] describing the preparation of presumably similar cyclopolymers by the polymerization of isoprene and higher conjugated dienes with a vanadium oxychloride–methylaluminum sesquihalide catalyst assigns a perhydrophenanthrene structure to the cyclopolymers.

POLYMERIZATION MECHANISM

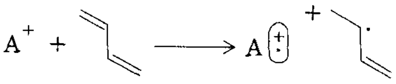
Earlier proposed mechanisms [4, 5] did not satisfactorily explain enough of the unusual aspects of the cyclopolymerization of conjugated dienes. A recent mechanism [2] which adequately incorporated the experimental observations proposed monomer activation by the catalyst cation via a one-electron transfer and addition of the activated monomer cation-radical to terminal or internal unsaturation, i.e., "living" polymerization by the addition of activated monomer to "dead" polymer.

Further consideration indicates that while the proposed mechanism adequately accounted for the cationic nature of effective catalysts, the initiation reaction, the incorporation of aromatic residues, the presence of methyl groups, and internal as well as ring unsaturation and the reinitiation of equilibrium polymerization, the resultant polymer structure was that of a perhydroanthracene. An alternative mechanism incorporates all these features while substituting a propagation step which involves the addition of monomer to a chain which contains a terminal cation radical. The resultant propagation mechanism can equally account for a perhydroanthracene structure through a 1,2 cation radical or a perhydrophenanthrene structure through a 1,3 cation radical. In view of the indirect evidence for the latter structure, emphasis will be placed thereon.

Formation of Active Species

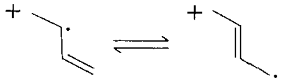
The reaction of $C_2H_5AlCl_2$ and $TiCl_4$ is extremely complex and the nature of the product has not been fully elucidated. For the present purpose, it is sufficient to indicate that it is an electron-deficient particle, probably the cationic part of an ion pair. Electron-deficient species are characterized as electron acceptors. The similarity of polymer structure and the polymerization characteristics suggest that cyclopolymerization of conjugated dienes with ethylaluminum dichloride and other cationic catalysts [5, 15, 16] involves analogous active species.

The active center results from the formation of a donor–acceptor charge transfer complex via a one-electron transfer:



(1)

The monomer cation radical may also exist in the allylic resonance form:



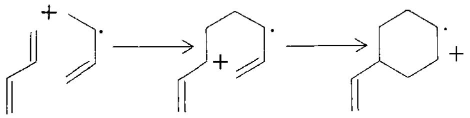
(2)

The catalyst-derived electron acceptor has been represented as A^+ with the understanding that, assuming it is part of an ion pair, there is a counteranion. The one-electron transfer from the diene would yield a cation radical which would have as a counterion the anion from the catalyst. The electron acceptor after the electron transfer may be represented as a neutral molecule A^0. However, since its exact nature is unknown, it is preferred to represent it as A$\left(\substack{+\\ \cdot}\right)$, for simplification of presentation.

The tendency for electron transfer is demonstrated by the observation that reduction of Ti^{4+} to Ti^{3+} in the $C_2H_5AlCl_2$ + $TiCl_4$ catalyst is very slow in the absence of monomer but is almost immediate when butadiene is added. Chlorine, probably eliminated as Cl^- from the $TiCl_4$ in reduction, is found in cyclopolymers as a result of reaction with a carbonium ion in the growing chain.

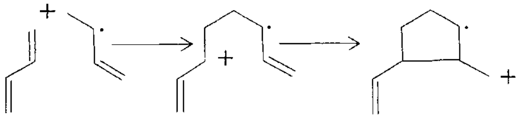
Initiation

There are two alternative initiation steps. The first alternative involves the reaction of the monomer cation radical with a monomer molecule, followed by ring closure to yield a 1, 2 cation radical:



The ring closure by the second cationic addition is well known from cyclization reactions. Reverse transfer of an electron from the catalyst-derived A⊕ gives a diradical which results in the formation of 4-vinylcyclohexene-1, the Diels–Alder adduct of butadiene.

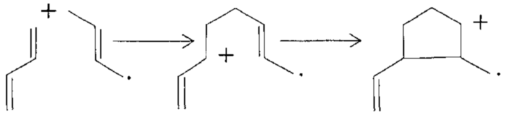
A second possible initiation step results in the formation of a five-membered ring and a 1, 3 cation radical:



(4)

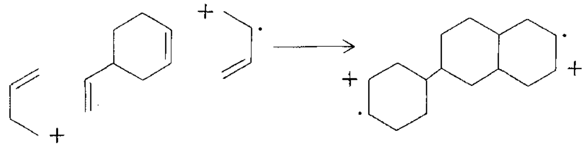
The initial five-membered ring is frequency observed in natural products such as steroids with basically cyclopolyisoprenic structure.

Analogous ring-closure reactions can be postulated with the mesomeric monomer cation radical

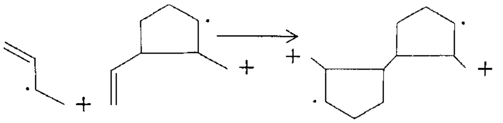


(5)

The diene monomer cation radical can react not only with a double bond in a diene monomer but also with any double bond in the system, e.g., with olefins. Thus the internal double bond in vinylcyclohexene or the residual vinyl group may react in a similar manner:



(6)



(7)

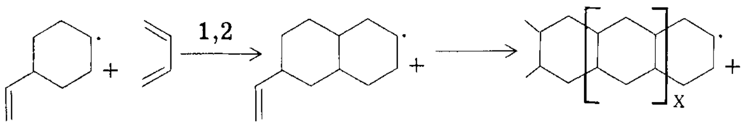
The polymerizability of internal bonds was demonstrated by carrying out the polymerization of isoprene in cyclohexene and 1-methylcyclohexene-1. The resultant reduction of the average molecular weight of the cyclopolyisoprene is indicative of the participation of the internal double bond of the solvent in the initiation [17]. This reaction is one cause for the formation of single bonds between double-chain or ladder structures. The extent to which this reaction occurs depends upon the reactivities of both double bonds in the diene. The isoprenyl group in isoprene reacts more readily than the vinyl group. The latter appears in cyclopolyisoprene prepared at low temperature (Table 2) and the concentration is always very low, most probably due to the location at the end of polymer chains.

If an olefinic double bond in the chain or an added olefin is capable of donating electrons to the catalyst, i.e., of acting as a reducing agent, its cation radical starts a new chain.

Propagation

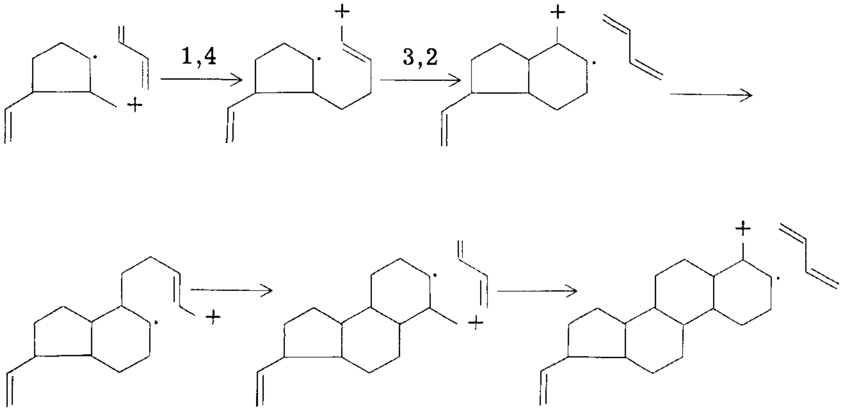
The propagation step involves the addition of diene monomer to polymer or oligomer cation radical.

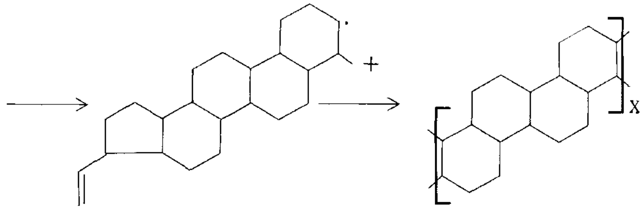
1,2 Cation Radical



(8)

1,3 Cation Radical

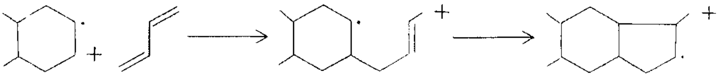




(9)

Whether the cationic or radical species reacts first by 1, 4 followed by 3, 2 addition is not clear, but both paths lead to the same structures. The only difference between the reactions is that the 1, 2 cation radical in sequence (8) leads to perhydroanthracene structures, while the 1, 3 cation radical in sequence (9) leads to perhydrophenanthrene structures. Since the structures of cyclopolyisoprene appears to be predominantly of the perhydrophenanthrene type, it is probable that the propagation step is as shown in sequence (9).

A 1, 2 cation radical, as shown in Eq. (3) or (8), may become a 1, 3 cation radical on the next or any subsequent monomer addition:

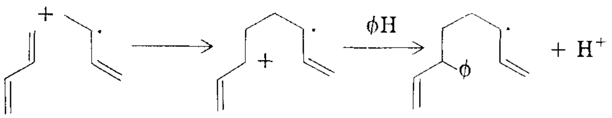


(10)

Thus the polymer structure may contain both perhydroanthracene and perhydrophenanthrene sequences.

Incorporation of Phenyl and Methyl Groups

The initiation and propagation steps involve both cations and radicals. When the reaction is carried out in an aromatic solvent, cationic alkylation results in the incorporation of phenyl groups in the polymer structure and proton elimination:



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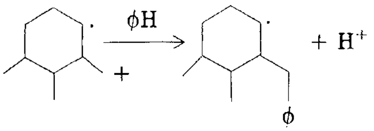
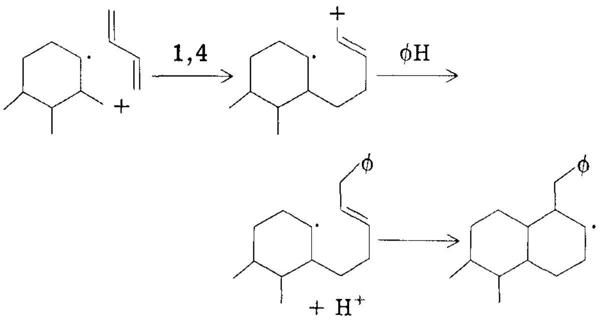
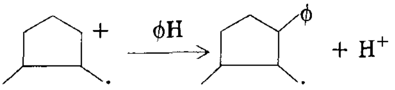


(12)



(13)



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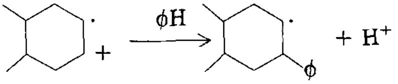
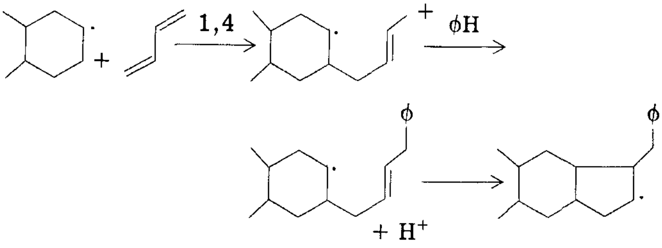
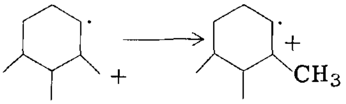


(15)



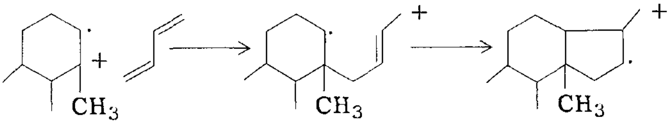
(16)

Methyl groups are formed when the 1, 3 cation radical undergoes an intramolecular hydride transfer to convert the primary cation to a tertiary cation:



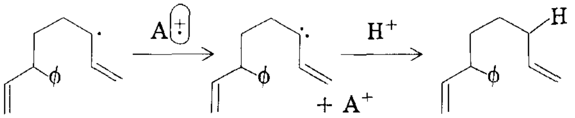
(17)

The resultant 1, 2 cation radical may react as in Eq. (8) or may become a 1, 3 cation radical on the next or a subsequent monomer addition:



(18)

The radicals remaining after the alkylation reactions shown in Eq. (11)–(16) may accept or abstract an electron from the "neutral" catalyst fragment $A\underset{\cdot}{\oplus}$ to form a carbanion which reacts with the proton eliminated by the alkylation to form a CH_2 or a CH_3 group and regenerates the catalyst cation A^+, e.g.,



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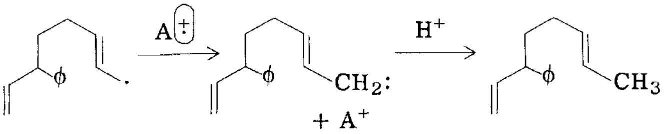

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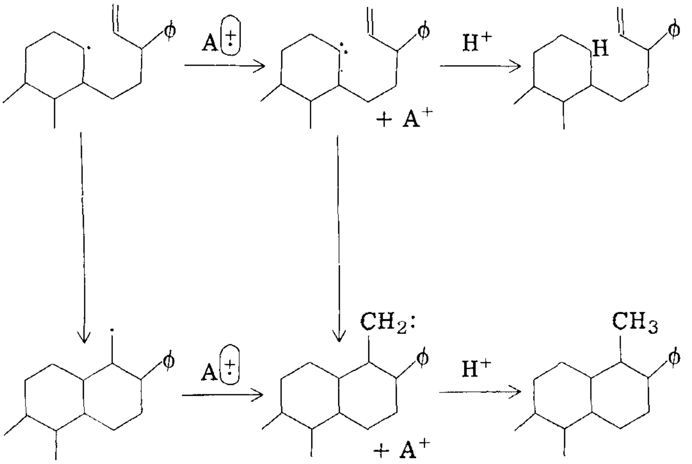

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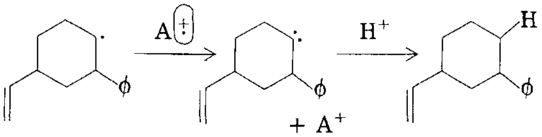
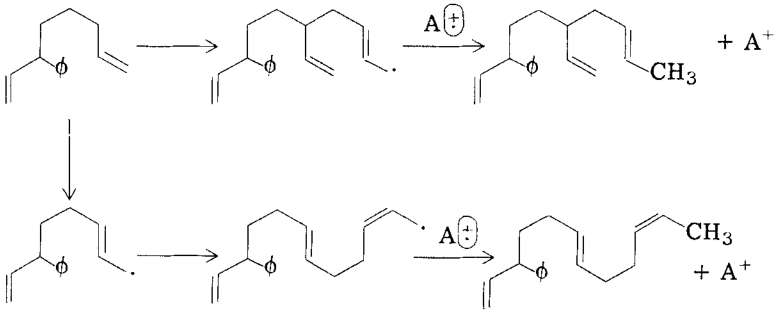
(22)



(23)

The radical species in Eq. (19)–(23) may react with one or more additional monomer molecules to produce linear segments, before the termination reaction, e.g.,



(24)

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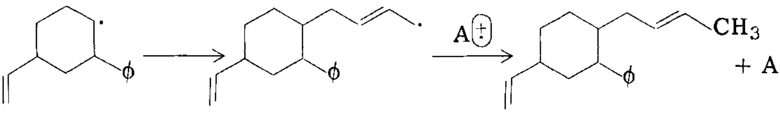


(26)

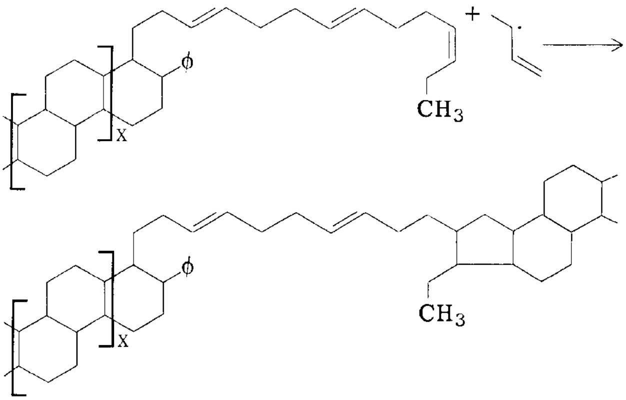
As shown in Eqs. (19)–(26), the reaction of the carbanion with the proton yields a methylene or a methyl group. Alternatively the proton may accept an electron from $A(\dot{+})$ and become a hydrogen radical which couples with the $CH_2\cdot$ to form a methyl group.

The concentration of methyl groups in cyclopolybutadiene obtained in benzene is higher than in the cyclopolymer obtained in n-heptane. However, in lieu of alkylation of the benzene ring, when the polymerization is carried out in n-heptane, hydride abstraction from the solvent by the polymer cation gives rise to new methylene or methyl groups (Figs. 2 and 3).

The formation of methyl groups in cyclopolybutadiene with a catalyst consisting of $AlBr_3 + TiCl_4$ (Table 3, No. 5) demonstrates that the alkyl groups are not derived from the catalyst but are a consequence of the reaction of the cation radicals generated during the polymerization.

Unsaturation in the Polymer Chain

Residual unsaturation in the polymer chain results from the addition of monomer to the radical species, as shown in Eqs. (24)–(26), or to the cation species in any cation radical. However, this nonterminal linear unsaturation may react with activated monomer cation radical in a reinitiation reaction, analogous to the reaction of the terminal or internal vinyl groups, as shown by the reactions in the presence of cyclohexene and 1-methylcyclohexene-1, and as shown in Eqs. (6) and (7).



(27)

The disruption of the fused-ring structure by the incorporation of phenyl groups or linear unsaturation and the production of a highly branched cyclopolymer contributes to the solubility of the polymer as well as the low viscosities related to high molecular weights.

The formation of fused rings is attributed to the concurrent or consecutive reactions of the cation and radical in the cation-radical species. If the reaction mixture contains a high concentration of free radicals from another source, these radicals should react with the radicals on a growing chain and either prevent or inhibit polymerization or disrupt the sequence of fused rings and produce a more soluble polymer.

To demonstrate this hypothesis isoprene was polymerized with a $C_2H_5AlCl_2$–$TiCl_4$ catalyst in the presence of radical initiators with different half-lives. As shown in Table 4, a blank experiment with di-t-butyl peroxide at 60°C, a temperature at which little radical generation would be expected, gave no polymer, whereas the reaction in the presence of the complex catalyst even at 25°C gave a very high conversion. In the presence of azobisisobutyronitrile at 70°C, the usual radical-generating temperature used with this catalyst in radical-catalyzed polymerization, a reduction in the conversion with

TABLE 4. Polymerization of Isoprene in the Presence of Radical Initiators[a] ([isoprene] = 1.0 mole/liter, 40 ml of n-heptane)

	$[EtAlCl_2]$, moles/liter	$[TiCl_4]$, moles/liter	Initiator[b]	Temp., °C	Time, hr.	Conversion
1	0	0	d—t—B 2 ml	60	0.5	0
2	0.02	0.12	d—t—B 2 ml[c]	25	1	Very high
3	0.02	0.04	t—b—P 2 ml[c]	70	1	0
4	0.02	0.04	t—b—P 2 ml	60	0.5	Low
5	0.02	0.12	t—b—P 2 ml	60	0.3	Low
6	0.02	0.04	AIBN 0.35 g	70	0.3	Medium
7	0.02	0.12	AIBN 0.6 g	70	1	Medium

[a] Radical initiator added with monomer.

[b] d—t—B, di-t-butyl peroxide; t—b—P, t-butyl peroxypivalate (75%); AIBN, azobisisobutyronitrile.

[c] Radical initiator added before monomer.

the $C_2H_5AlCl_2$–$TiCl_4$ catalyst was noted. When t-butyl peroxypivalate, a lower-temperature catalyst, was used as the radical source at 70°C, no polymerization occurred in the presence of the complex catalyst. At the slightly lower temperature of 60°C a low yield of polymer was obtained. The structure of the polymer was the same as that obtained with the $C_2H_5AlCl_2$–$TiCl_4$ catalyst at −78°C (Fig. 4). Thus, consistent with the proposed mechanism, a high concentration of free radicals interfered with the cation-radical propagation step.

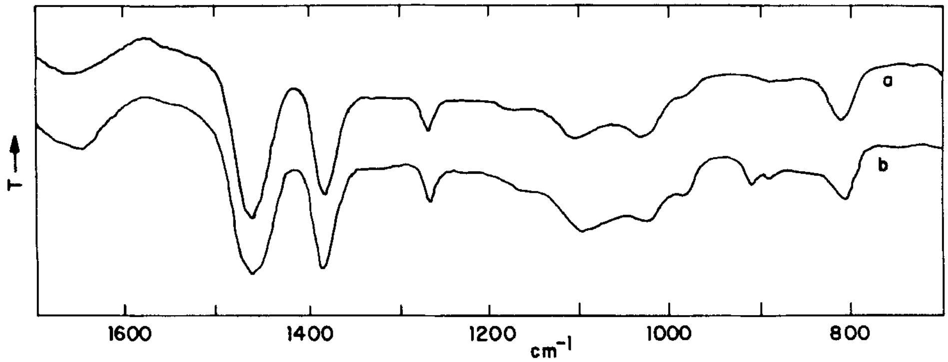
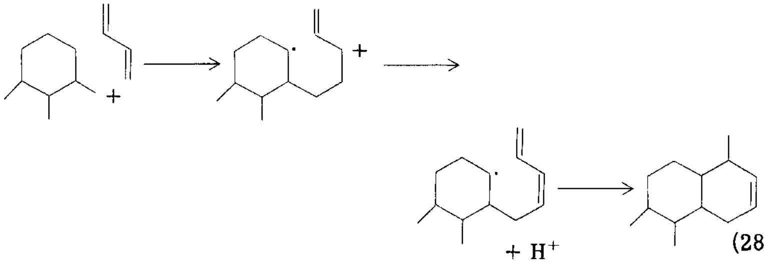


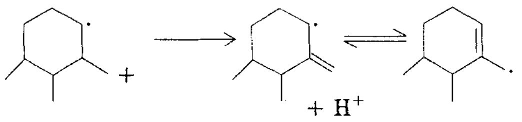
FIG. 4. Infrared spectrum of (a) cyclopolyisoprene No. 5 in Table 4, (b) cyclopolyisoprene No. 16 in Table 2.

The cyclopolyisoprene prepared in n-heptane in the presence of azobisisobutyronitrile and the complex catalyst had a somewhat higher content of isopropenyl groups than in the absence of the radical catalyst.

The internal or ring unsaturation, which accounts for 10–40% of the residual double bonds in a cyclopolymer, results from deprotonation at the carbon adjacent to the cation, a step well known in the cyclization of diene polymers.



(28)



(29)

The relatively high amount of internal ring unsaturation in cyclopolyisoprene is in accord with the ring unsaturation newly formed in the cyclization of cis-1, 4- and trans-1, 4-polyisoprene [13] and is apparently determined by the same probability factor which governs deprotonation in cyclization and limits the sequence of fused rings in the perhydrophenanthrene structure to the same extent.

In the case of isoprene–styrene copolymers obtained with analogous catalysts [12], the content of double bonds is low because the sequence of fused rings is broken by styrene units.

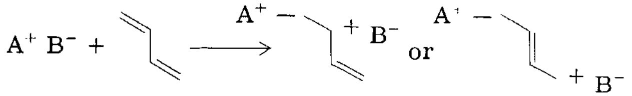
As shown in Eq. (27) reinitiation by addition of the monomer cation radical can occur at any site of unsaturation, e.g., after the addition of monomer units in a linear manner from the cation site on the polymer. Linear or 1, 4 addition may terminate by proton elimination to produce conjugated double bonds, as noted in the ultraviolet spectra of cyclopolymers:

$$\sim C{-}C{=}C{-}C^{+} \rightarrow \sim C{-}\overset{+}{C}{-}C{=}C \rightarrow \sim C{=}C{-}C{=}C \qquad (30)$$

Limiting Conversion, Dormancy, and Reinitiation

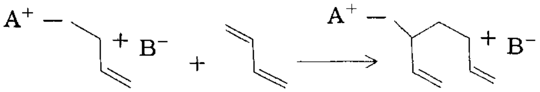
Cyclopolymerization is characterized by relatively low conversions and a dormant reaction mixture. Addition of new monomer to the dormant mixture reinitiates polymerization, which again achieves a limiting conversion. In the absence of additional monomer, the original unreacted monomer is slowly consumed over a long period of time.

The generation of active centers has been represented in Eq. (1) as a one-electron transfer to the catalyst-derived cation, presumably $C_2H_5AlCl^+$ in the $C_2H_5AlCl_2$ or $C_2H_5AlCl_2$-$TiCl_4$ complex catalyst system, producing a two-center monomer cation radical. The occurrence of a two-electron transfer, as in conventional cationic polymerization, would produce a conventional cationic species:

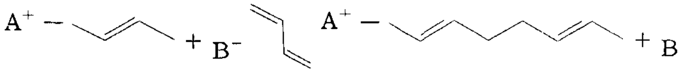


(31)

Monomer addition can take place in either a 1, 2 or 1, 4 manner:

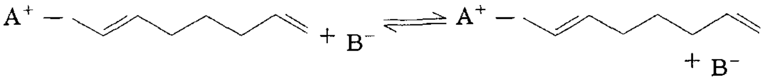


(32)


(33)

Mixed 1,2 and 1,4 structures are, of course possible.

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


(34)

The existence of such a resonance form is indicated by the formation of conjugated double bonds, as shown in Eq. (30). 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 ion pairs A^+ ($^-$monomer$^+$) B^- and A^+ ($^-$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:

$$A^+B^- + M \xrightarrow{2e} A^+(^-M^+)B^- \longrightarrow A^+(^-P^+)B^- \qquad (35)$$

$$A^+(^-M^+)B^- + M \longrightarrow A^+B^- + 2M \qquad (36)$$

$$A^+(^-P^+)B^- + M \longrightarrow A^+B^- + P + M \qquad (37)$$

$$A^+B^- + M \xrightarrow{1e} A\oplus \cdot M^+ B^- \qquad (38)$$

$$A\oplus \cdot M^+B^- + M \longrightarrow A\oplus \cdot P^+B^- \qquad (39)$$

Polymer structures arising from two-electron cationic polymerization, as shown in Eqs. (31)-(33) and (35), cannot be distinguished from those arising from one-electron cation radical polymerization, as shown in Eq. (39), since the unsaturation in the former may participate, by reaction with monomer cation radical, in the reinitiation reaction shown in Eq. (27).

ANALOGOUS ION-RADICAL MECHANISMS

A one-electron transfer from an electron donor to an electron acceptor to produce, via a charge transfer complex, a donor cation radical and an acceptor anion radical, followed by a second one-electron transfer from the donor cation radical to the monomer to regenerate the donor and yield a monomer cation radical has been proposed [18] in the polymeriation of isobutylene in the presence of vanadium oxychloride in n-heptane at –78 to 0°C. Isobutylene does not polymerize under these conditions until the addition of a small amount of either isoprene, butadiene, styrene, aromatic hydrocarbons such as naphthalene or anthracene, aromatic amines, ethers, or acids or carbon disulfide. The monomer cation radical produced by the indicated sequence of reactions undergoes radical coupling to yield a dicarbonium ion species which is the propagation center:

$$\underset{(\mathrm{VOCl_3})}{\mathrm{V}} + \mathrm{D(onor)} \rightarrow [\mathrm{VD}] \rightleftharpoons \mathrm{V}^{\cdot-} + \mathrm{D}^{\cdot+} \tag{40}$$

$$\mathrm{D}^{\cdot+} + \mathrm{M} \rightarrow \mathrm{D} + \mathrm{M}^{\cdot+} \tag{41}$$

$$2\mathrm{M}^{\cdot+} \rightarrow {}^{+}\mathrm{M{-}M}^{+} \tag{42}$$

$$ {}^{+}\mathrm{M{-}M}^{+} + (\mathrm{n} + \mathrm{m})\mathrm{M} \rightarrow {}^{+}\mathrm{M_n{-}M{-}M{-}M_m^{+}} \tag{43}$$

It is suggested [18] that the same scheme is applicable to the polymerization of styrene and isoprene as well as the copolymerization of isobutylene with isoprene, butadiene, and styrene initiated by $\mathrm{VOCl_3}$ in n-heptane. However, in the case of isobutylene, which does not readily polymerize by a free radical mechanism, the addition of monomer to the cation end of the monomer cation radical $\mathrm{M}^{\cdot+}$ results in separation of the radical and cation and the radical ends of two cation radicals can couple to yield a dicarbonium ion:

$$ {}^{+}\mathrm{M}^{\cdot} + \mathrm{M} \rightarrow {}^{+}\mathrm{M{-}M}\,\cdot \rightarrow {}^{+}\mathrm{M{-}M{-}M{-}M}^{+} \tag{44}$$

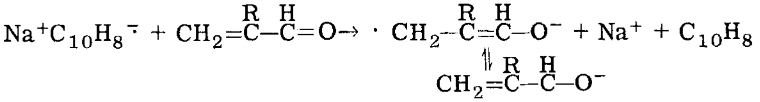
On the other hand, in the case of conjugated dienes, the radical and cation are resonance-stabilized species, and radical coupling appears to be unlikely:

$$\mathrm{D}^{\cdot+} + \mathrm{CH_2{=}CH{-}CH{=}CH_2} \rightarrow \mathrm{D} + {}^{+}\mathrm{CH_2{-}\dot{C}H{-}CH{=}CH_2} \tag{45}$$

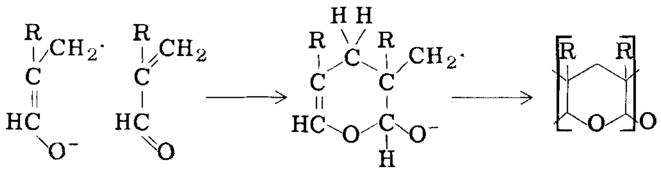
$$ {}^{+}\mathrm{CH_2{-}\dot{C}H{-}CH{=}CH_2} \rightleftharpoons {}^{+}\mathrm{CH_2{-}CH{=}CH{-}CH_2}\cdot \tag{46}$$

It will be of interest to determine whether the polymers from butadiene and isoprene as well as the copolymers with isobutylene are of predominantly linear or cyclic structure. As reported in this and previous papers, in the polymerization of conjugated dienes with cationic catalysts, i.e., with initiation by a monomer cation radical and propagation from a chain cation radical, as well as in the copolymerization of isoprene with styrene [12], the structural units derived from the diene are predominantly cyclic.

A close analogy to the presently proposed cation-radical mechanism, which yields fused cyclohexane rings, is the anion-radical mechanism, which has been proposed in the polymerization of methacrolein in tetrahydrofuran with a sodium naphthalene complex to yield fused tetrahydropyran rings [19]. A one-electron transfer from the naphthalene anion radical to the methacrolein yields a monomer anion radical which propagates by anion and radical addition reactions, in contrast to the radical dimerization and dicarbanion propagation proposed for other anion-radical polymerizations.



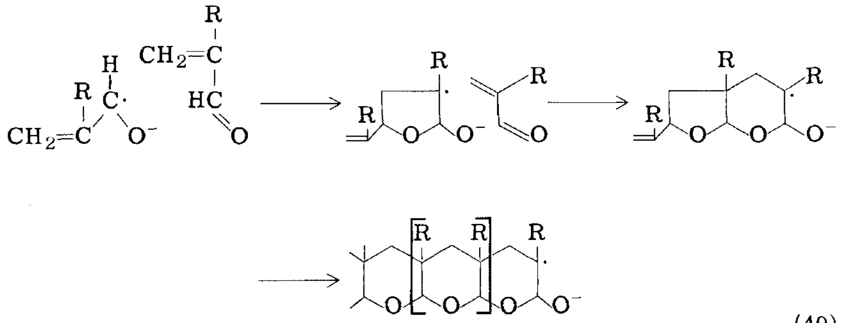
$$\mathrm{Na^+C_{10}H_8^{\cdot-} + CH_2{=}\overset{R}{C}{-}\overset{H}{C}{=}O \rightarrow \cdot\, CH_2{-}\overset{R}{C}{=}\overset{H}{C}{-}O^- + Na^+ + C_{10}H_8} \qquad (47)$$
$$\Updownarrow$$
$$\mathrm{CH_2{=}\overset{R}{C}{-}\overset{H}{C}{-}O^-}$$



(48)

The predominant structural feature is the fused tetrahydropyran rings, although acetal and vinyl groups (from alkoxide addition to monomer carbonyl group) as well as alkylene and carbonyl groups (from radical addition to monomer double bond) and lactone groups are also present. Although analogous structures are obtained when trityl sodium is used as catalyst, cyclic structures are absent in butyllithium-initiated polymerizations.

In lieu of the proposed 1, 4 anion radical and addition to the β-carbon of the double bond, a 1, 3 anion radical and the usual 1, 2 addition to the double bond is more likely:



(49)

The linear structure produced in this sequence is analogous to the perhydroanthracene structure of cyclopolydienes rather than the more probable perhydrophenanthrene structure. This results from the absence of the 1, 4 addition of the alkoxide anion to the monomer. Nevertheless, the formation of fused-ring systems in both anion-radical and cation-radical polymerizations, i.e., ion-radical initiatio and propagation, indicates the possibility of obtaining analogous ladder polymers from other monomers with conjugated unsaturation.

REFERENCES

[1] B. Matyska, K. Mach, J. Vodehnal, and I. Kössler, *Collection Czech. Chem. Commun.*, **30**, 2569 (1965).

[2] N. G. Gaylord, I. Kössler, B. Matyska, and K. Mach, paper presented at *153rd Meeting American Chemical Society, Miami Beach,* April 1967; *Polymer Preprints,* **8** (1), 174 (1967).

[3] M. Štolka et al., in preparation.

[4] N. G. Gaylord, I. Kössler, M. Štolka, and J. Vodehnal, *J. Am. Chem. Soc.*, **85**, 641 (1963); *J. Polymer Sci.*, **A2**, 3969 (1964).

[5] I. Kössler, M. Štolka, and K. Mach, *J. Polymer Sci.*, **C4**, 977 (1964).

[6] Lucidol Division, Wallace Tiernan Corp., *Tech. Bull. Lupersol 11.*

[7] L. Petrusová, V. Štěpan, and I. Kössler, *Collection Czech. Chem. Commun.*, **32**, (1967).

[8] J. Danhelka et al., in preparation.

[9] V. Boháčková, J Poláček, J. Vodehnal, and I. Kössler, in preparation.

[10] J. Poláček, L. Schulz, and I. Kössler, *J. Polymer Sci.*, in press.

[11] C.G Overberger and G. F. Endres, *J. Polymer Sci.*, **16**, 283 (1955).

[12] H. Krauserová, I. Kössler, B. Matyska, and N. G. Gaylord, *IUPAC International Symposium on Macromolecular Chemistry, Tokyo-Kyoto,* Sept. 1966, Preprint 3. 2. 07.

[13] M. Stolka, J. Vodehnal, and I. Kössler, *J. Polymer Sci.*, **A2**, 3987 (1964).

[14] V. L. Bell, Jr., to E. I. du Pont de Nemours & Co. Belg. Pat. 623, 940 (1962).

[15] B. Matyska, M. Švestka, and K. Mach, *Collection Czech. Chem. Commun.*, **31**, 659 (1966).

[16] N. G. Gaylord, B. Matyska, K. Mach, and J. Vodehnal, *J. Polymer Sci.*, **A-1**(4), 2493 (1966).

[17] E. Kunstová et al., in preparation.

[18] N. Yamada, K. Shimada, and T. Hayashi, *J. Polymer Sci.*, **B4**, 477 (1966).

[19] M. M. Koton, I. V. Andreeva, Yu. P. Getmanchuk, L. Ya. Madorskaya, E. I. Pokrovskii, A. I. Koltsov, and V. A. Filatova, *Vysokomolekul. Soedin.*, **7**, 2039 (1965).

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Zusammenfassung

Die Polymerisation von Isopren und Butadien mit Äthylaluminiumdichlorid-Titantetrachlorid als Katalysator ergibt leiterförmige Polymere, die kondensierte Ringstrukturen enthalten. In n-Heptan hergestellte Cyclopolymere sind gewöhnlich unlösliche weisse Pulver, während dagegen die in aromatischen Lösungsmitteln dargestellten Cyclopolymeren löslich sind, sogar wenn das Molekulargewicht grösser als 1 × 10^6 ist. Im Cyclopolyisopren sind zwei Phenyl gruppen pro 100 monomere Einheiten eingebaut, unabhängig vom Molekulargewicht im Bereich von 1 × 10^4 bis 2 × 10^6. Cyclopolybutadien dagegen enthält bis zu 7–9 Phenylgruppen pro 100 monomere Einheiten. Die Cyclopolymeren enthalten noch restliche ungesättigte Bestandteile, von denen 10–40% Cycloalkenyle sind, und auch Methylgruppen. Indirekte Befunde weisen darauf hin, dass Cyclopolyisopren möglicherweise eine Perhydrophenantren-Struktur hat. Der in Betracht gezogene Reaktionsmechanismus beruht auf einer kationischen Radikalstartreaktion und Fortplanzungsreaktion. Ein aktiviertes monomeres Kationenradikal entsteht durch Übertragung eines Elektrons von einem Monomeren an einen Elektronenacceptor, der durch Einwirkung der Katalysatorkomponenten enstanden ist. Während der Startreaktion ergibt eine zweistufige kationische Addition Ringbildung und Bildung eines cyklischen 1, 2 oder 1, 3 Kationradikals. Die Fortpflanzungsreaktion besteht aus gleichzeitiger oder konsekutiver Addition eines Radikalkations an das Monomere unter Bildung eines Polymers mit cyclischen Kationradikal-Endgruppen. Ein aktiviertes monomeres Kationradikal kann sich dann an die internen ungesättigten Bindungen addieren und so eine Cyclopolymerisation wiederauslösen und dadurch stark verzweigte Cyclopolymere bilden.

Résumé

La polymérisation de l'isoprène et du butadiène avec un système catalytique dichlorure d'éthyl aluminium-tétrachlorute de titane donne des polymères échelles, ayant des structures cycliques fusées. Les cyclopolyméres, preparés dans le n-heptane sont des poudres insolubles, tandisque les polymères obtenus dans des solvants aromatiques sont solubles même à masse moleculaire au-dessus de 1 × 10^6. Dans le cycloisoprene deux groupes phényles sont incorporés dans la structure polymérique per 100 unités monomères, independamment de la mass moléculaire entre 1 × 10^4 à 2 × 10^6, le

cyclopolybutadiène contient jusqu'à 7–9 groupes phényles per 100 unités monomeres. Les cyclopolymeres possedent une insaturation résiduèlle, dont 10–40% est cycloalcénylique, et des groupes méthyles. L'évidence indirecte montre que le cyclopolyisoprène peut avoir une structure perhydrophenanthrenique. Le mecanisme proposé de polymérisation implique l'initiation et propagation cation-radicalaire. Un monomère activé cation-radicalaire résulte du transfert d'un électron du monomère aux accepteurs d'électrons formés par l'interaction entre les composants du système catalytique. Dans le stade d'initiation, l'addition cationique en deux étapes resulte en ferméture du cycle et formation des cation-radicaire 1, 2 out 1, 3 cyclique. La propagation s'effectue par addition simultanée et consecutive du cation radicalaire au monomère pour former un polymère avec des groupes terminaux cycliques cation-radicalaires. Un monomère cation-radicalaire activé peut augmenter l'insaturation interne pour le reamorçage de la cyclopolymérisation et formation des copolymères très branchés.