Chemistry

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Abstract

Full Text

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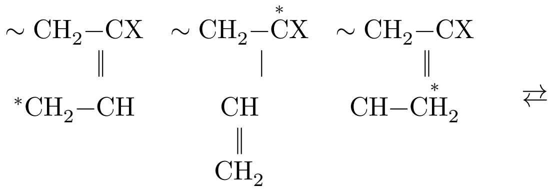
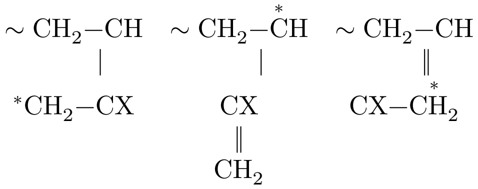
THE MECHANISM OF POLYMERIZATION OF DIENES AND THE STRUCTURE OF THE POLYMER CHAIN

As is known, in the polymerization of butadiene and its 2-substituted derivatives the monomer unit at the growing end of the chain may have the following configurations:



$$\begin{array}{ccc} \sim CH_2{-}CX & \sim CH_2{-}\overset{*}{C}X & \sim CH_2{-}CX \\ \| & | & \| \\ {}^{*}CH_2{-}CH & CH & CH{-}\overset{*}{C}H_2 \\ & \| & \\ & CH_2 & \end{array} \rightleftarrows$$

(1) (2) (3)



$$\begin{array}{ccc} \sim CH_2{-}CH & \sim CH_2{-}\overset{*}{C}H & \sim CH_2{-}CH \\ | & | & \| \\ {}^{*}CH_2{-}CX & CX & CX{-}\overset{*}{C}H_2 \\ & \| & \\ & CH_2 & \end{array}$$

(4) (5) (6)

Let us consider the most probable structure of the unit as a function of the nature of the active center. In the free-radical and free-ionic (cationic and anionic) mechanisms of chain growth, those structures are realized predominantly which correspond to the most stable state of the active center. It should be noted, however, that consideration of the question as applied to the free-ionic mechanism appears to be somewhat conditional, since in this case the role of the counterion in these processes is not taken into account.

In the polymerization of butadiene, isoprene, and chloroprene by radical and cationic mechanisms, trans structures 3 and 6 are formed predominantly ($^{1-4}$).

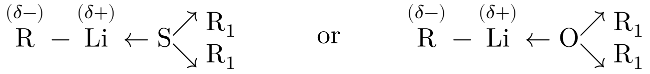
The amount of 1—4 trans units at a polymerization temperature of −20° is about 83% for polybutadiene, about 92% for polyisoprene, and 98% for polychloroprene. The remaining units have the 1—2 and 3—4 structure (structures 2 and 5). With increasing polymerization temperature, a tendency is observed toward an increase in the number of 1—4 cis units, with a corresponding decrease in the number of trans units. It follows from this that, in the cases under consideration, the trans configuration of the active center is the most stable.

In the polymerization of butadiene and isoprene under the influence of organometallic compounds of alkali metals, as the polarity of the bond increases (on going from RLi to RNa), an increase is observed in the number of 1—2 units (for butadiene) and 3—4 units (in the case of isoprene) ([5,6]). In the case of

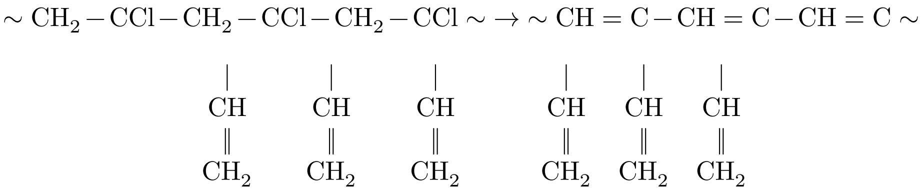
$$\overset{(\delta-)}{\mathrm{R}} - \overset{(\delta+)}{\mathrm{Na}}$$

these units are the principal structural unit of the chain. An analogous effect is exerted by impurities of electron-donor character,

which, by forming a complex with RLi, for example



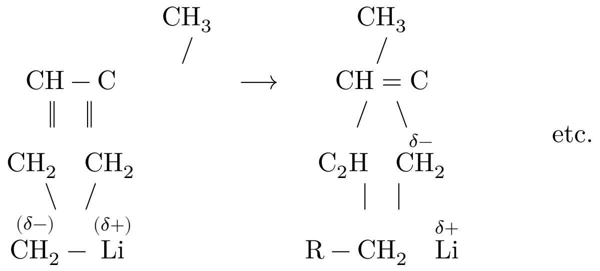
increase the polarity of the bond and the anionic activity of the system ([7–13]). Hence it follows that configurations of units 2 and 5 appear to be the most stable and probable for the hypothetical case of a free-anion mechanism of chain growth. In the polymerization of chloroprene the most probable structure proves to be 2, since in this state the active center (anion) is stabilized both by conjugation with the double bond and by the presence of a chlorine atom at the reaction center. One of us, together with N. M. Geller, showed that in the polymerization of chloroprene under the influence of R_3Al (in a complex with $R-Li$) a black polymer is formed and a considerable amount of HCl is evolved. This effect is evidently determined by the fact that the reaction leads to formation of a polymer with units of structure 2. Owing to the presence of a labile tertiary chlorine atom, HCl elimination takes place with the formation of segments with a conjugated system of double bonds:



$$\sim CH_2-\underset{\substack{|\\ CH\\ \|\\ CH_2}}{CCl}-CH_2-\underset{\substack{|\\ CH\\ \|\\ CH_2}}{CCl}-CH_2-\underset{\substack{|\\ CH\\ \|\\ CH_2}}{CCl}\sim\ \rightarrow\ \sim CH=\underset{\substack{|\\ CH\\ \|\\ CH_2}}{C}-CH=\underset{\substack{|\\ CH\\ \|\\ CH_2}}{C}-CH=\underset{\substack{|\\ CH\\ \|\\ CH_2}}{C}\sim$$

In contrast to free-radical and free-ionic polymerization, polymerization under the influence of various catalytic systems—which include Ziegler-type coordination-ionic systems, organometallic compounds, certain oxides of transition-valence metals, etc.—is characterized by the fact that each act of monomer addition occurs with the direct participation of the "catalyst." In this connection the microstructure of the chain is determined primarily by the nature of the "catalyst."

The formation of stereoregular polymers with a cis arrangement of units indicates above all that the act of monomer addition in these systems occurs without the participation of free ions, since in the latter cases the structures considered above are formed. The polymerization of isoprene under the influence of RLi, as is believed (^{14,15}), proceeds in the following manner:



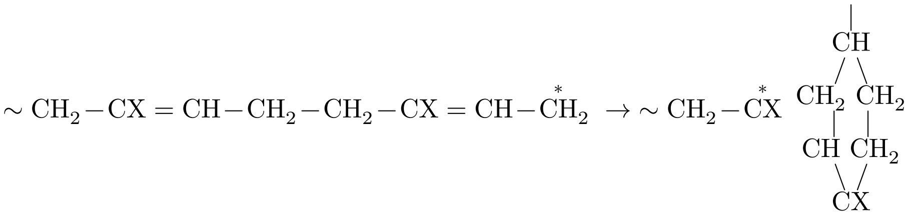
Analogously, a number of complex systems consisting of organoaluminum compounds and compounds of titanium or cobalt act in the same way. Alongside stereospecific systems leading to the formation only of 1-4 cis units, there are a number of stereospecific systems leading to the formation of polymers with unit structures only 1-4 trans or only 1-2 (or 3-4). Examples of systems of the first type are chromium oxide catalysts, systems of R_3Al and vanadium compounds, etc. (^{16,17}); examples of systems of the second type are systems of R_3Al and alkoxy compounds of titanium and other metals (^{18,19}). It may be assumed that formation of trans units in the first case is characteristic of systems acting by a coordination-cationic mechanism $(A)^{(-)}\overset{(+)}{CH_2}\sim$, in which

a certain "freedom" of the cation is observed, allowing the unit to assume the thermodynamically most stable state.

By the same considerations, systems leading to the formation of polymers with a 1-2 (or 3-4) arrangement of the units must be assigned to coordination-anionic systems $[A]^{(+)}\overset{(-)}{CH_2}\sim$, in which the anion possesses a certain freedom for transition to the most stable state. It follows from this that systems of the first type should be most suitable for the polymerization of cation-active monomers (vinyl alkyl ethers, isobutylene), and systems of the second type—for the polymerization of polar monomers (vinyl cyanide, vinyl chloride, etc.).

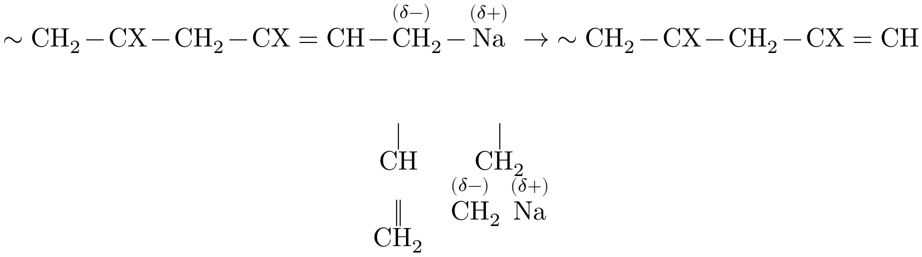
The deterioration of the stereospecificity of the action from the point of view considered is associated with those changes that the systems continuously undergo with respect to the degree of polarization of the bond, the degree of dissociation of ion pairs in coordination-ionic systems, etc.

It is also necessary to consider the question of certain secondary reactions in the chain of diene polymers as a function of the nature of the active centers. Upon interaction of the growing chain end with an internal double bond of its own chain, a decrease in the unsaturation of the polymer and, apparently, the formation of side cyclic groupings are observed:



The reaction of active centers with the double bonds of other molecules leads to the formation of branched and structured polymers. Reactions of this type proceed readily under the cationic mechanism of chain growth, especially in those cases where there is an X-alkyl group or hydrogen, since they lead to the formation of the most stable tertiary or secondary cations. The role of such reactions may be illustrated by the fact that, in the polymerization of butadiene and isoprene under the influence of dialkylaluminum chloride (in the presence of water as a cocatalyst) or other catalysts of cationic polymerization, soluble polymers are formed that contain in the chain only 50–60% of the theoretical number of double bonds ([20], [23]). The absence of high selectivity of the reaction in the interaction of the polymer cation with the monomer and with an internal double bond of the chain is indirect evidence that the stabilizing effect of conjugation in crotyl cations is considerably lower than in the corresponding free radicals. This is also indicated by the closeness of the constants of cationic copolymerization of isoprene and propylene ([25]).

The reaction given is less probable for chloroprene, since the presence of a chlorine atom at the reaction center should lead to an increase in the activity of the cation. According to the considerations indicated above, the reaction of an anionic active center with an internal double bond of the polymer chain appears improbable; it should lead to highly active tertiary or secondary anions. Indeed, in "anionic" polymerization of dienes, a substantial decrease in the unsaturation of the polymer is observed only in those cases where a considerable number of vinyl (isopropenyl) groups appear in the chain, for example, in polymerization under the influence of RNa

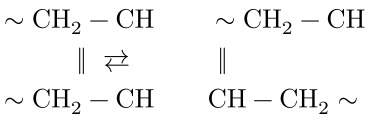


$$\sim \mathrm{CH_2-CX-CH_2-CX=CH-\overset{(\delta-)}{CH_2}-\overset{(\delta+)}{Na}} \rightarrow \sim \mathrm{CH_2-CX-CH_2-CX=CH}$$

$$\begin{array}{cc} | & | \\ \mathrm{CH} & \mathrm{CH_2} \\ \| & \overset{(\delta-)}{\mathrm{CH_2}}\ \overset{(\delta+)}{\mathrm{Na}} \\ \mathrm{CH_2} & \end{array}$$

The unsaturation of polybutadiene obtained under the influence of sodium is about 85% of theory ([21,22]).

In the radical mechanism of polymerization, as is known, chain transfer proceeds mainly through the α-methylene groups, which leads to the formation of branching without a decrease in the unsaturation of the chain. The role of these reactions increases substantially with increasing temperature. Reactions of cis-trans isomerization of units in the finished polymer chain also play an important role



$$\begin{array}{ccc} \sim \mathrm{CH_2-CH} & & \sim \mathrm{CH_2-CH} \\ \| & \rightleftarrows & \| \\ \sim \mathrm{CH_2-CH} & & \mathrm{CH-CH_2} \sim \end{array}$$

The act of isomerization is preceded by the formation of an intermediate complex compound of the active center with the double bond of the chain. Naturally, this reaction is most specific for the cationic mechanism of initiation ([24]).

In the case of an "anionic" mechanism of initiation, the cis-trans isomerization reactions of units are apparently possible in principle under the influence of the "cation" that is part of the organometallic compound or of the catalytic complex. The study of these questions as applied to organometallic compounds of alkali metals and to certain coordination-anionic systems of the Ziegler type appears to be very important.

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