ON THE MECHANISM OF UNIT FORMATION IN THE STEREOSPECIFIC POLYMERIZATION OF DIENES

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Abstract

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ON THE MECHANISM OF UNIT FORMATION IN THE STEREOSPECIFIC POLYMERIZATION OF DIENES

Recent studies have shown that π-allyl nickel complexes are catalysts for the stereospecific polymerization of butadiene (^{1}). Crotylnickel halides and analogous derivatives of a number of other transition metals may be regarded as compounds modeling the active end of a growing polymer chain. Starting from the indicated structure of the active centers, it appears possible to outline new approaches to consideration of the mechanism of unit formation in the course of polymerization.

In general form, the nature of the initial active center (I) and of the growing polymer chain (II) in the polymerization of butadiene may be represented as follows:

(I) and (II)

where X denotes halogen atoms or another element, and R is the polymer chain.

If the monomer (conjugated diene) enters the chain through the CH_2 ... Me bond (direction 1) with participation of the first and fourth carbon atoms, then in the chain being formed all units have the 1,4-cis or trans configuration:

[scheme: coordination of butadiene to the active center in direction 1, followed by formation of a $CH_2-CH_2-CH=CH-CH_2R$ fragment]

If entry of the monomer into the polymer chain likewise occurs in the 1–4 position, but from the side of the substituent (through the $>$ CH ... Me bond) (direction 2), then 1–2 units arise in the polymer chain.

[scheme: successive addition in direction 2, leading to a chain containing $CH_2=CH-CH-CH_2-CH-CH_2-CH$... fragments; "etc."]

In polymerization in direction 2, a spatially ordered 1-2-polybutadiene (syndiotactic or isotactic) may be formed, since in this case, in each elementary act of growth,

chain, the separating vinyl group is “attached”to the central atom of the complex (to the metal).

Let us consider, from this point of view, some experimentally established regularities in the polymerization of dienes under the influence of systems of the indicated type. It is known that the introduction of trialkylaluminum into the system $R_2AlCl + CoCl_2$ leads to an increase in the number of 1-2 units, and at a certain content of it only syndiotactic 1-2-polybutadiene is formed (^{2}).

Using crotyl nickel chloride as an example, it was shown that reaction with trialkylaluminum leads to replacement of the halide by an alkyl group and, ultimately, to the formation of more reduced forms of the metal (^{3}). Similar effects of increasing the number of 1-2 (and 3-4) units are observed when alkyl groups are introduced into the monomer. Thus, in the polymerization of alkyl-substituted butadienes under the influence of a “cobalt”system (^{3,4}), the number of units with isopropenyl side groups, corresponding to incorporation of the monomer along path (^{2}), increases in the series:

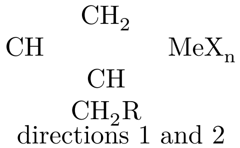
complex of unsubstituted diene < complex with one CH_3 substituent < complex with two CH_3 substituents

$(CH,\ CH_2,\ CH,\ CH_2R) - CoX_n < CH_3 - C(CH_2)(CH)(CH_2R) - CoX_n < CH_3 - C(CH_2)(C(CH_3)(CH_2R)) -$

coordination direction 2

It was established earlier that, in the joint polymerization of butadiene and isoprene, as well as of butadiene and 2-3-dimethylbutadiene under the influence of a cobalt system, a copolymer is formed in which the content of 3-4-isoprene or 1-2-dimethylbutadiene units is substantially lower than in the homopolymer of isoprene and 2-3-dimethylbutadiene, while the content of 1-2-butadiene units is correspondingly higher than in the homopolymer of butadiene. The results obtained served as the basis for the assumption that, at any given moment, the nature of the terminal unit of the chain determines the structure of the newly forming unit (^{4,5}). The meaning of this phenomenon may be considered as follows.

In contrast to π-allyl complexes, π-crotyl complexes, which model to a certain extent the structure of the active centers, must be characterized by nonequivalence of the carbon atoms bonded to the metal.



$$\begin{array}{ccc} & CH_2 & \\ CH & & MeX_n \\ & CH & \\ & CH_2R & \end{array}$$

directions 1 and 2

Proceeding from experimental data on the microstructure of the chain, it follows that the probability of coordination of the diene in direction 2 increases in going from butadiene to isoprene and 2-3-dimethylbutadiene, which coincides with the activity series of the monomers in cationic polymerization. In the indicated series, the number of 1-2 (and 3-4) units in the polymer chain increases ([4,5]). Butadiene is coordinated almost exclusively in direction 1. Therefore, if an isoprene or 2-3-dimethylbutadiene unit is present at the end of the chain (in the active center), then incorporation into the chain of a butadiene molecule causes an increase in the number of 1-4 units of isoprene and 2-3-dimethylbutadiene. If a butadiene unit is present at the end of the chain, then incorporation of isoprene and 2-3-dimethylbutadiene molecules along path 2 leads to a corresponding increase in the number of 1-2-butadiene units.

It is usually assumed that the structure of the units of the polymer chain is determined by the nature of the coordination of the diene with the catalytic complex—by one double bond (formation of 1-2 or 3-4 structures) or by two double bonds (formation of a 1-4 structure).

The schemes presented above provide that the entry of the monomer into the chain is preceded by a stage of coordination of the monomer with the catalytic complex, involving in all cases only the first and fourth atoms of the diene (i.e., in the 1-4 position). An indirect confirmation of this assumption is the fact that the cyclic dimers and trimers formed under certain conditions under the influence of the indicated systems contain, for the most part, respectively 8 and 12 carbon atoms in the ring, and not 6. The formation of a dimer with 6 carbon atoms in the ring would become possible in the case of coordination of the monomer in the 1,2 position.

The role of π-allylic systems in the process of polymerization is also illustrated by the fact that, in the stereospecific polymerization of dienes, it is not possible to carry out their copolymerization with such active monomers as styrene. The entry of styrene into the chain disrupts the π-allylic coordination, which apparently proves less favorable than the entry of the diene.

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