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**Cationic polymerization of isoprene using CF₃COOD/TiCl₄ initiating system:
a new view on the polymerization mechanism**

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Abstract

Cationic polymerization of isoprene with CF₃COOD/TiCl₄ initiating system has been studied under different experimental conditions. It was shown that *trans*-1,4 unit with different types of enchainment (regular head-to-tail and inverse head-to-head and tail-to tail) is a dominant structural unit of unsaturation part of polymer chain. The structure of head and end groups was established and mechanism of their formation was proposed. It was also demonstrated that initiation by deuterium ion occurs only at the very beginning of the polymerization followed by chain transfer to double bond of polymer with elimination of proton, which then initiates the growth of new chain. The synthesized polyisoprene is characterized by reduced unsaturation that is consistent with occurring of two side reactions: chain transfer to polymer and “polymerization” of olefinic double bonds of macromolecule.

KEYWORDS: Cationic polymerization, isoprene, deuterium-containing initiator, mechanism of polymerization.

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