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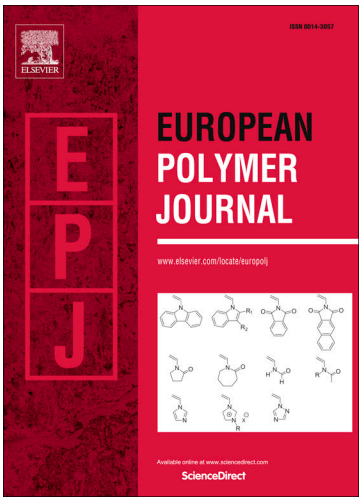

Cationic polymerization of isoprene using $CF_3COOD/TiCl_4$ initiating system: a new view on the polymerization mechanism

Victor A. Rozentsvet, Valery G. Kozlov, Olesya A. Stotskaya, Nelly A. Sablina, Frederic Peruch, Sergey V. Kostjuk

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Cationic polymerization of isoprene using $CF_3COOD/TiCl_4$ initiating system: a new view on the polymerization mechanism

Victor A. Rozentsvet [a] *, Valery G. Kozlov [a], Olesya A. Stotskaya [a], Nelly A. Sablina [a], Frederic Peruch [b], Sergey V. Kostjuk [c]

[a] *Institute of Ecology of the Volga River Basin, Russian Academy of Science, 10 Komzina St, Togliatti, 445003, Russia*

[b] *Laboratoire de Chimie des Polymères Organiques, UMR 5629, CNRS/Bordeaux University/Bordeaux INP, 16 avenue Pey Berland, Pessac Cedex, 33607, France*

[c] *Research Institute for Physical Chemical Problems of the Belarusian State University, 14 Leningradskaya St, Minsk, 220006, Belarus*

* *Corresponding author.*
E-mail: rozentsvet@mail.ru

Abstract

Cationic polymerization of isoprene with $CF_3COOD/TiCl_4$ 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.