

LETTERS
TO THE EDITOR

Organophosphorus Complexones as Catalysts for But-1-ene Polymerization

E. S. Petrov^a, T. E. Kron^a, O. I. Kudinova^b, and L. A. Novokshonova^b

^aKarpov Research Physicochemical Institute,
ul. Vorontsovo Pole 10, 105064 Moscow, Russia
e-mail: petrov@cc.nifhi.ac.ru

^bSemenov Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russia

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The isotacticity of the polymer prepared by olefin polymerization catalyzed by the $\text{TiCl}_4/\text{MgCl}_2/\text{AlEt}_3$ system depends significantly on the type of chelating complexones added to the catalyst (external donor D), the most common of which are dialkyldialkoxysilanes [1, 2]. However, the search for other type D compounds providing the required set of catalyst properties is being continued. Specifically, this problem is actual for the synthesis of isotactic polybut-1-ene (PB) which is of great practical importance [2]. Studying but-1-ene polymerization we found that the $\text{TiCl}_4/\text{MgCl}_2/\text{AlEt}_3$ /diisobutyl phthalate catalyst (internal donor) can be modified with polydentate phosphine oxides as external donors D. Such phosphine oxides were previously proposed as solvating agents and polar solvents [3, 4].

Thus, with $\text{D} = \text{Bu}_3\text{PO}$ (**I**) ($\text{Al/Ti} = 250$, $\text{Al/D} = 10$) the isotacticity index of polybut-1-ene is as low as 61%, with bidentate $\text{Bu}_2\text{P}(\text{O})\text{CH}_2\text{OMe}$ (**II**) which is capable of forming chelate complexes by the P=O and MeO oxygens, the isotacticity index of polybut-1-ene prepared under the same conditions is 88.2%. Still higher isotacticity index (92.4%) can be achieved with $\text{Me}_2\text{CHC}_2\text{H}_4\text{P}(\text{O})(\text{CH}_2\text{OMe})_2$ (**III**), and, therewith, the catalyst activity ($\text{Al/Ti} = 360$, $\text{Al/D} = 14$) is 8 kg of polybutene/(g Ti h mol⁻¹). The increase of the isotacticity index can be associated with the steric effect of the branched alkyl group at the phosphorus atom in **III**, but the possible involvement of the second MeO group into complex forma-

tion is also not excluded. Note that polybut-1-ene samples have high molecular weights: $(1.1\text{--}2) \times 10^6$.

Comparison shows that external donor **III** by the basic characteristics of the polymerization process approaches the currently used commercial donor $\text{C}_6\text{H}_{11}(\text{Me})\text{Si}(\text{OMe})_2$ (**IV**) with the following characteristics: isotacticity index 93.9%, activity 40 kg polybutene/(g Ti h mol⁻¹), molecular weight 1.5×10^6 (at $\text{Al/Ti} = 310$, $\text{Al/D} = 15$).

These preliminary results give us grounds to suggest a more detailed study of the properties of polydentate phosphines as external donors can lead to creation of new effective catalysts for stereospecific polymerization of but-1-ene.

Polymerization was conducted in *n*-heptane at 323 K with a constant monomer concentration of 1.7–1.8 M throughout the process. The isotacticity indices were determined by measuring the weight of the polybut-1-ene fraction insoluble in boiling diethyl ether. Compound **I** is a commercially available reagent, and compound **II** was synthesized according to [3]. Compound **III** was synthesized by analogy with the corresponding pentyl derivative [5], bp 112.5–113°C (1.5 mm Hg) [published data: bp 125–126°C (2 mm Hg)].

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