



Директор ИНЭОС РАН, д.х.н. Грифонов А.А.

W12111-6252/111

05 мая 2020

ЭКСПЕРТНОЕ ЗАКЛЮЧЕНИЕ О ВОЗМОЖНОСТИ ОПУБЛИКОВАНИЯ

Руководитель-эксперт Федерального государственного бюджетного учреждения науки Института элементоорганических соединений им. А.Н.Несмиянова Российской академии наук, рассмотрев статью В.А. Тускаева, С.Ч. Гагиевой, Д.А. Курмаева, С.В. Зубкевича, И.В. Федянина, М.И. Бузина, Г.Г. Никифоровой, В.Г. Васильева, Д. Сарачено, В.И. Привалова и Б.М. Булычева «MAO-Free Copolymerization of Ethylene and 1-Hexene with Ti (IV) Complexes Supported by Fluorinated 2-Hydroxymethylphenol Derivatives» в журнал Polymer Buletin подтверждает, что в материале не содержатся сведения, предусмотренные Постановлением Правительства РФ №1233 от 30.11.1994г. и на публикацию материала не следует получать разрешение Минобрнауки России и/или Президиума РАН

Заключение: статья может быть опубликована в открытой печати, т.к. она не содержит сведений, не подлежащих открытой публикации

Руководитель-эксперт Заместитель директора по научной работе

д.х.н. Серенко Ольга Анатольевна

(подпись)

Серенок

MAO-Free Copolymerization of Ethylene and 1-Hexene with Ti (IV) Complexes Supported by Fluorinated 2-Hydroxymethylphenol Derivatives

Vladislav A. Tuskaev^{a,b*}, Svetlana Ch. Gagieva^{a,b}, Dmitry A. Kurmaev^a, Sergey V. Zubkevich^a, Ivan V. Fedyanin^{b,c}, Mikhail I. Buzin^b, Galina G. Nikiforova^b, Viktor G. Vasil'ev^b, Daniele Saracheno^d, Viktor I. Privalov^e, Boris M. Bulychev^a

^a Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119992, Moscow, Russian Federation

^b A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991, Moscow, Russian Federation

^c Plekhanov Russian University of Economics, Stremyanny per. 36, Moscow, 117997, Russian Federation

^d Higher College of Chemistry of Russia, Dmitry Mendeleev University of Chemical Technology of Russia, Miusskaya sq. 9, 125047, Moscow, Russia

^e Kurnakov Institute of General and inorganic chemistry, Russian Academy of Sciences, 31 Leninsky prospect, 119991, Moscow, Russian Federation

KEYWORDS Titanium, OO-ligands, Copolymerization, Ethylene, 1-Hexene

Corresponding Author *E-mail: tuskaev@yandex.ru.

Additional Supporting Information may be found in the online version of this article.

ABSTRACT

Ethylene/1-hexene copolymerization was carried out with a new Ti (IV) complexes stabilized by fluorinated 2-hydroxymethylphenol derivatives and activated by MAO-free binary cocatalysts - {alkyl aluminum chloride + Bu_2Mg }. Structures and properties of the obtained copolymers were measured by DSC, GPC, and ^{13}C NMR. The effects of the ligand structure and the nature of organoaluminum activator on the polymer yield, comonomer incorporation, polymer composition, molecular weight, polydispersity index and stress-strain behavior have been investigated. The results indicated that the complex with adamantyl substituent was the most active in this series. The obtained copolymer exhibited the highest 1-hexene incorporation content of 20.8 mol %

INTRODUCTION

Ethylene copolymers with higher olefins, especially linear low-density polyethylene (LLDPE) and thermoplastic elastomers, are materials of great commercial significance [1]. Despite the fact that classic Ziegler-Natta catalysts are successfully used for their production, the number of technologies based on post-metallocene are being introduced every year [2]. One of the most important advantages of these types of catalysts is the ability to generate copolymers of uniform sequence and composition distributions, which makes it possible to obtain polymer products with a controlled density and degree of crystallinity.

In a large family of post-metallocene catalysts, transition metal complexes stabilized by alkoxide or phenoxide-alkoxide ligands are the least studied group. Previously, we proposed a new group of

Conclusion

In this work, the possibility of the successful use of MAO-free catalytic systems based on stable titanium alkoxo complexes, alkylaluminiumchlorides and di-butyl-magnesium for the synthesis of polyolefin elastomers – ethylene/1-hexene copolymers was demonstrated. As can be seen, the catalytic behavior of the adamantyl-substituted precatalyst **3c** differs from the other complexes. This complex not only gives the highest polymerization productivity but also shows the highest 1-hexene incorporation ratio (15-21 mol %). In all other cases, despite the structure of the pre-catalyst and the organoaluminum activator, the content of 1-hexene in the copolymers does not exceed 1.8–3%.

Acknowledgments

This work was financially supported by the Russian Science Foundation (Project No 18-13-00375). NMR and elemental analysis were performed with the financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition studies of INEOS RAS. DSC results were obtained on the equipment of the Educational and Scientific Centre of Functional and Nanomaterials, Moscow Pedagogical State University with the financial support from Ministry of Science and Higher Education of the Russian Federation.

References

1. Polymers and Copolymers of Higher Alpha-Olefins. Edited by B. A. Krentsel, Y. V. Kissin, V. J. Kleiner, L. L. Stotskaya, Carl Hanser Verlag: Munich, 1997: ISBN 3 446 17593 8 pp vii+374, [https://doi.org/10.1002/\(SICI\)1097-0126\(199907\)48:7<622::AID-PI190>3.0.CO;2-%23](https://doi.org/10.1002/(SICI)1097-0126(199907)48:7<622::AID-PI190>3.0.CO;2-%23)
2. M. C. Baier, M. A. Zuideveld and S. Mecking, *Angew. Chem. Int. Ed.*, 53, 9722 (2014). DOI: [10.1002/anie.201400799](https://doi.org/10.1002/anie.201400799).
3. M. V. Solov'ev, S. Ch. Gagieva, V. A. Tuskaev, N. M. Bravaya, O. E. Gadalo, V. N. Khrustalev, A. O. Borissova, and B. M. Bulychev, *Russ. Chem. Bull.*, 60, 2227 (2011). DOI: [10.1007/s11172-011-0342-1](https://doi.org/10.1007/s11172-011-0342-1).
4. S. Ch. Gagieva, N. A. Kolosov, D. A. Kurmaev, I. V. Fedyanin, V. A. Tuskaev, B. M. Bulychev, *Russ. Chem. Bull.* 63, 2748 (2014). DOI: [10.1007/s11172-014-0810-5](https://doi.org/10.1007/s11172-014-0810-5).
5. S.Ch. Gagieva, D.A. Kurmaev, V.A. Tuskaev, S.V. Zubkevich, A.O. Borissova, I.V. Fedyanin, B.M. Bulychev, *Polyhedron* 98, 131 (2015). DOI:[10.1016/j.poly.2015.06.024](https://doi.org/10.1016/j.poly.2015.06.024).
6. S. Ch. Gagieva, I. V. Fedyanin, V. A. Tuskaev, T. M. Zvukova, B. M. Bulychev *J. Organomet. Chem.* 802, 9 (2016). DOI:[10.1016/j.jorganchem.2015.11.007](https://doi.org/10.1016/j.jorganchem.2015.11.007).
7. S. Ch. Gagieva, V. A. Tuskaev, I. V. Fedyanin, A. I. Sizov, E. S. Mikhaylik, E. K. Golubev, B M. Bulychev, *Polyhedron* 122, 179 (2017). <http://dx.doi.org/10.1016/j.poly.2016.11.007>.
8. V. A. Tuskaev, S. Ch. Gagieva, D. A. Kurmaev, I. V. Fedyanin, S. V. Zubkevich, B. M. Bulychev, *Russ. Chem. Bull.* 67, 377 (2018). <https://doi.org/10.1007/s11172-018-2084-9>.
9. V. A. Tuskaev, S. Ch. Gagieva, D. A. Kurmaev, S. V. Zubkevich, N. A. Kolosov, E. K. Golubev, G. G. Nikiforova, V. N. Khrustalev, B. M. Bulychev *J. Organomet. Chem.* 867, 266(2018). <https://doi.org/10.1016/j.jorganchem.2017.12.027>.
10. V. A. Tuskaev, S. Ch. Gagieva, D. A. Kurmaev, S.V. Zubkevich, P.V. Dorovatovskii, V. N. Khrustalev, E. S. Mikhaylik, E. K. Golubev, M. I. Buzin, G. G. Nikiforova, V. G. Vasil'ev, T. M. Zvukova, B. M. Bulychev, *Inorg. Chim. Acta* 498, 119159 (2019). <https://doi.org/10.1016/j.ica.2019.119159>.
11. L. A. Rishina, N. M. Galashina, S. Ch. Gagieva, V. A. Tuskaev, B. M. Bulychev, Yu. N.Belokon' *Polymer Science, Ser. A*, 50, 110 (2008). <https://doi.org/10.1007/s11498-008-2003-1>.