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| D:\Rinat\Rinat\доки\журнал\статьи\logo.jpg | RING-OPENING METATHESIS POLYMERIZATION OF 5-ETHYL-2-NORBORNENE IN THE PRESENCE OF DIMETHYL MALEATE AS A CHAIN-TRANSFER AGENT | | |
| Cite this: *INEOS OPEN*,  **2025**, *8 (1–3)*, XX–XX  DOI: 10.32931/ioXXXXx  *Received XX Month 20XX,*  *Accepted 8 February 2025*  http://ineosopen.org | | V. R. Nazemutdinova, K. S. Sadovnikov, A. I. Wozniak,\* A. A. Morontsev,\* and M. V. Bermeshev | |
| Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninskii pr. 29, Moscow, 119991 Russia | |
| Abstract  This work deals with the synthesis of a telehelic metathesis poly(5-ethyl-2-norbornene) (poly(EtNB)) obtained under the action of the second-generation Grubbs catalyst in the presence of dimethyl maleate acting as a chain-transfer agent. The structures of the products were confirmed by NMR and IR spectroscopy. The effect of the conditions for synthesis of poly(EtNB) on the molecular weight (*M*n) and thermal properties was shown. | | | D:\TIPS\YandexDisk\НИР\Documents\Articles\22 PolyEtNB with DMM for INEOS Open\Безымянный5.tiff |
| **Key words:** ring-opening metathesis polymerization, telechelic poly(5-ethyl-2-norbornene), second-generation Grubbs catalyst, dimethyl maleate. | | | |

**Introduction**

The synthesis of polymers by the ring-opening metathesis polymerization (ROMP) of cycloolefins is a powerful tool of polymer science, allowing for obtaining the products of various architectures. Different ruthenium carbene complexes [1], capable of promoting living or pseudo-living polymerization [2, 3], are widely used as initiators for this polymerization. The control of *M*n values of polymers obtained by ROMP can easily be accomplished by adding acyclic alkenes acting as chain-transfer agents. The prediction of *M*n can be carried out utilizing the Mayo equation [4]. The use of functionalized alkenes enables the preparation of telechelics, which was demonstrated by the polymerization of cyclooctene [5–10], unsubstituted norbornene [8], 5-*n*-butyl-2-norbornene [10], a copolymerization of cyclooctene and unsubstituted norbornene [8, 9], and cyclooctene and methyl ester of 5-norbornene-2-carboxylic acid [9]. Telechelics can be used as adhesives, cross-linking agents, coatings, *etc.* [9, 11]. Despite the fact that this method for the preparation of telechelics is simple in experimental terms, it remains poorly studied. In particular, there are no data on the effect of the length of the alkyl substituent of a norbornene on its ROMP in the presence of dimethyl maleate (DMM). Since the first studies in this area devoted to the polymerization of 5-*n*-butyl-2-norbornene have already been reported [10], at the next stage it was decided to reduce the length of the alkyl substituent and evaluate the effect of this reduction on the ability of the substituted norbornene to form a telechelic. Therefore, the goals of this work were to study the possibility of synthesizing a telechelic as a result of the polymerization of 5-ethyl-2-norbornene (EtNB) under the action of the second-generation Grubbs catalyst in the presence of DMM as well as to establish the effect of the polymerization conditions on the value of *M*n and thermal properties of the resulting product.

Results and discussion

The synthesis of poly(5-ethyl-2-norbornene) was carried out by the ROMP of the initial cycloolefin under the action of the second-generation Grubbs catalyst in the presence of dimethyl maleate (DMM) at different ratios of the raw reagents in THF (Scheme 1).

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Scheme 1. Synthesis of poly(EtNB) by ROMP in the presence of DMM.

The ratio of the initial reagents was selected based on the solution of the Mayo equation [4]. The reaction was stopped by adding ethyl vinyl ether. The product was precipitated in an alcohol, the unreacted components were removed by the repeated precipitation in an alcohol. The structures of the products were confirmed by 1H, 13C NMR and IR spectroscopy, 1H–13C HSQC, 1H–13C HMBC, 1H–13C H2BC, and 1H–1H COSY two-dimensional correlation spectroscopy (Fig. 1 and Figs. S1–S6 in the Electronic supplementary information (ESI), respectively), as well as 1H NMR spectroscopy of the metathesis polymers obtained in the presence of DMM [5]. The presence of the signals from protons of double bonds connected with ester group indicated the formation of a telechelic. Based on the integral intensity of protons of the double bond connected with the ester group (*I*7.01–6.89 and *I*5.83–5.75) and the double bond of the main chain (*I*5.43–5.04), the values of *M*nNMR were calculated for all the poly(EtNB) telechelics:

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where *M*(EtNB) is the molar mass of 5-ethyl-2-norbornene, equal to 122.2 g/mol, *M*(DMM) is the molar mass of dimethyl maleate, equal to 144.1 g/mol.

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Figure 1. 1H–13C HSQC spectrum of poly(EtNB) characterized by *M*nGPC = 6.6 kDa, *Ɖ* = 2.7.

A decrease in the ([EtNB]+[DMM])/([Gr2]) ratio at equimolar amounts of EtNB and DMM in the reaction mixture led to a decrease in *M*nGPC of the product (Table 1, entries 1–4). It should be noted that low concentrations of Gr2 are sufficient for intense polymerization of the cycloolefin and insufficient for cross-metathesis between poly(EtNB) and DMM. A decrease in the concentration of EtNB also contributed to the intensification of the cross-metathesis reaction between resulting poly(EtNB) and DMM (entries 5, 6, 2, 7), which is probably due to an increase in the solubility of poly(EtNB), facilitating accessibility of the double bonds of the polymer backbone. Increasing the amount of DMM (Table 1, entries 8–10, 3) appeared to contribute to a slight decrease in *M*nGPC. However, excess DMM promotes the precipitation of poly(EtNB), which may lead to broadening of *Ð*. For example, the products with high *M*nGPC were characterized by a broad dispersion (entries 1 and 5).

Table 1. Polymerization conditions and characteristics of the resulting poly(EtNB) telechelics

| Entry | *C*M(EtNB), mol/l | [ЕtNB]/  [DMM] | ([ЕtNB]+[DMM])/  [Gr2], ×10–3 | *M*nNMR, kDa | *M*nGPC, kDa | *Ð* |
| --- | --- | --- | --- | --- | --- | --- |
| 1 | 2.4 | 1.9 | 5.1 | 9.5 | 12.3 | 5.6 |
| 2 | 2.4 | 1.9 | 4.5 | 5.8 | 8.0 | 2.1 |
| 3 | 2.5 | 2.0 | 3.7 | 4.6***a*** | 6.6 | 2.7 |
| 4 | 2.5 | 2.0 | 3.0 | 3.9*b* | 6.2 | 2.7 |
| 5 | 3.4 | 1.8 | 4.5 | 13.6 | 13.8 | 5.2 |
| 6 | 2.9 | 1.9 | 4.2 | 7.7 | 8.4 | 3.0 |
| 7 | 1.9 | 1.9 | 4.4 | 6.0 | 8.1 | 2.4 |
| 8 | 2.4 | 4.5 | 3.6 | 7.3 | 9.0 | 2.5 |
| 9 | 2.4 | 4.0 | 3.5 | 6.2 | 7.9 | 2.7 |
| 10 | 2.4 | 2.8 | 3.9 | 7.1 | 8.0 | 3.1 |

reaction conditions: the second-generation Grubbs catalyst, CHCl3, 6 h, 60 °C, stirring in a shaker; yields: 79–97%; ***a*** yield: 24%; ***b***yield: 40%; *Td* = 237 °C.

The values of *M*nNMR were usually lower than those of *M*nGPC, which may be due to the resolution of the GPC device, which does not take into account the molecular fraction below 1 kDa. Nevertheless, the results are comparable. It should be noted that a decrease in *M*nGPC can lead to the partial loss of the poly(EtNB) telechelic during its isolation (Table 1, entries 3 and 4). In addition, all products were characterized by GPC, DSC, and TGA. All the polymers obtained were characterized by the

glass transition temperatures ranging within 31–35 °C, *i.e.*, the polymers are in a glassy state at room temperature. The data presented here are in good agreement with the results of the metathesis polymerization of 5-butyl-2-norbornene (BNB) [10]. However, to obtain a poly(BNB) telechelic similar to poly(EtNB) in *M*n, a lower concentration of BNB than for EtNB was required.

**Conclusions**

Telechelate poly(EtNB) was obtained by ROMP under the action of the second-generation Grubbs catalyst using dimethyl maleate as a chain-transfer agent for the first time. The structure of the product was confirmed by NMR and IR spectroscopy. It was shown that DMM can act as an efficient chain-transfer agent. A decrease in the concentration of the initial monomer or DMM and an increase in the loading of Gr2 led to low-molecular-weight products.

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Corresponding author

\* E-mail: morontsev@ips.ac.ru. Tel: +7(495)647-5927 (ext. 193) (A. A. Morontsev).

\* E-mail: wozniak@ips.ac.ru. Tel: +7(495)647-5927 (ext. 301) (A. I. Wozniak).

Electronic supplementary information

Electronic supplementary information (ESI) available online: the experimental details, NMR spectra, DSC curves. For ESI, see DOI: 10.32931/ioXXXXx.

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