



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/ioXXXXXx

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*

Received XX Month 20XX

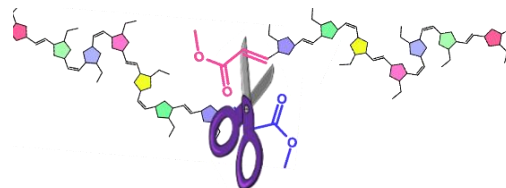
Accepted 8 February 2025

<http://ineosopen.org>

Abstract

This work deals with the synthesis of a telechelic 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.

Key words: ring-opening metathesis polymerization, telechelic poly(5-ethyl-2-norbornene), second-generation Grubbs catalyst, dimethyl maleate.

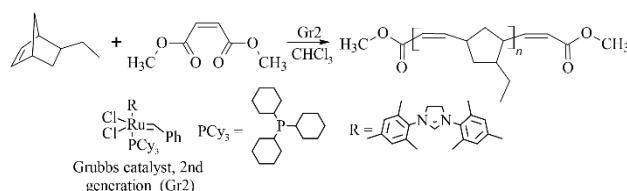


Introduction

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).



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 , ^{13}C NMR and IR spectroscopy, ^1H – ^{13}C HSQC, ^1H – ^{13}C HMBC, ^1H – ^{13}C 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_n^{NMR} were calculated for all the poly(EtNB) telechelics:

$$M_n^{\text{NMR}} = \frac{M(\text{EtNB}) \times (2 \times I_{5.43-5.04} + I_{7.01-6.89} + I_{5.83-5.75})}{(I_{7.01-6.89} + I_{5.83-5.75})} + M(\text{DMM}),$$

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

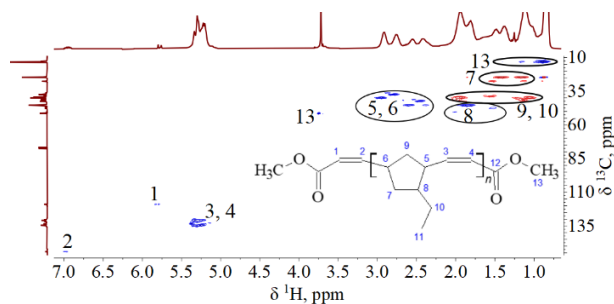


Figure 1. ^1H – ^{13}C HSQC spectrum of poly(EtNB) characterized by $M_n^{\text{GPC}} = 6.6$ kDa, $D = 2.7$.

A decrease in the $([\text{EtNB}] + [\text{DMM}]) / ([\text{Gr2}])$ ratio at equimolar amounts of EtNB and DMM in the reaction mixture led to a decrease in M_n^{GPC} 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_n^{GPC} . However, excess DMM promotes the precipitation of poly(EtNB), which may lead to broadening of D . For example, the products with high M_n^{GPC} were characterized by a broad dispersion (entries 1 and 5).

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

Entry	$C_M(\text{EtNB})$, mol/l	$[\text{EtNB}] / [\text{DMM}]$	$([\text{EtNB}] + [\text{DMM}]) / [\text{Gr2}] \times 10^{-3}$	M_n^{NMR} , kDa	M_n^{GPC} , kDa	D
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, CHCl_3 , 6 h, 60 °C, stirring in a shaker; yields: 79–97%; ^a yield: 24%; ^b yield: 40%; $T_d = 237$ °C.

The values of M_n^{NMR} were usually lower than those of M_n^{GPC} , 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_n^{GPC} 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

Telechelte 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.

Acknowledgements

This work was supported by the Russian Science Foundation (project no. 23-73-00126). The work was performed using the equipment of the Collaborative Access Center "Center for Polymer Research" of ISPM RAS. The authors are grateful to G. A. Shandryuk for DSC analysis and S. A. Legkov for recording the IR spectra.

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.

References

- O. M. Ogba, N. C. Warner, D. J. O'Leary, R. h. Grubbs, *Chem. Soc. Rev.*, **2018**, 47, 4510–4544. DOI: 10.1039/C8CS00027A
- J. Qui, B. Charleux, K. Matyjaszewski, *Polimery*, **2001**, 46, 453–460.
- C. W. Bielawski, R. H. Grubbs, *Prog. Polym. Sci.*, **2007**, 32, 1–29. DOI: 10.1016/j.progpolymsci.2006.08.006
- I. Mandal, A. F. M. Kilbinger, *JACS Au*, **2022**, 2, 2800–2808. DOI: 10.1021/jacsau.2c00566
- G. Si, C. Tan, M. Chen, C. Chen, *Angew. Chem., Int. Ed.*, **2022**, 61, e202203796. DOI: 10.1002/anie.202203796
- L. M. Pitet, M. A. Hillmyer, *Macromolecules*, **2011**, 44, 2378–2381. DOI: 10.1021/ma102975r
- A. K. Diallo, L. Annunziata, S. Fouquay, G. Michaud, F. Simon, J.-M. Brusson, S. M. Guillaume, J.-F. Carpentier, *Polym. Chem.*, **2014**, 5, 2583–2591. DOI: 10.1039/C3PY01639K
- X. Wang, L. Dai, S. Jie, Z. Bu, B.-G. Li, *ChemistrySelect*, **2020**, 5, 8512–8517. DOI: 10.1002/slct.202002441

9. E. Vanbiervliet, S. Fouquay, G. Michaud, F. Simon, J.-F. Carpentier, S. M. Guillaume, *Polymers*, **2018**, *10*, 1241. DOI: 10.3390/polym10111241
10. V. R. Stepanyants, V. R. Nazemutdinova, *Polym. Sci., Ser. B*, **2023**, *65*, 760–772. DOI: 10.1134/S1560090423600249
11. C. Chauveau, S. Fouquay, G. Michaud, F. Simon, J.-F. Carpentier, S. M. Guillaume, *ACS Appl. Polym. Mater.*, **2020**, *2*, 5135–5146. DOI: 10.1021/acsapm.0c00912

This article is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License.

