



# Addition polymerization of functionalized norbornenes as a powerful tool for assembling molecular moieties of new polymers with versatile properties

M.V. Bermeshev\*, P.P. Chapala

A.V. Topchiev Institute of Petrochemical Synthesis, RAS, 29 Leninsky pr., 119991, Moscow, Russia



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This manuscript is dedicated to the 80th birthday of Professor Eugene Finkelshtein for his life-long achievement in research.

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Pervaporation

## ABSTRACT

This comprehensive review surveys recent research trends in the addition polymerization of functionalized norbornenes for the macromolecular design of high performance materials in terms of catalyst activity, monomer reactivity, modifications and potential applications of addition polynorbornenes bearing functional groups. The structure of addition polynorbornene backbones is responsible for their high thermal resistance and chemical stability. In order to impart desired properties to the polymers, various functional side groups can be incorporated into the monomer units by the Ti-, Ni-, or Pd-catalyzed polymerization of norbornenes, which are available via cycloaddition reactions or norbornadiene-2,5 modifications. Based on the use of different substituents in the norbornene monomer units and different polymer compositions, the addition polynorbornenes have been successfully developed for the preparation of pervaporation, gas-separation, and proton-conducting membranes, sensors, catalyst supports, and for applications as photoresist, electrooptical, and dielectric materials etc.

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**Abbreviations:** AP, addition polymerization; <sup>Ac</sup>Fe, acetyl ferrocenium; BARF, [3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>4</sub>B<sup>-</sup>; COD, cyclooctadiene-1,5; crotyl, MeC(H)=C(H)CH<sub>2</sub>-; CTA, chain transfer agent; DANFABA, PhNHMe<sub>2</sub><sup>+</sup>[(BC<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>; dba, dibenzylideneacetone; DNQ-PACS, diazonaphthoquinone photoactive compounds; ITO, indium-tin oxide; LiFABA, Li<sup>+</sup>[(BC<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>; MAO, methylaluminoxane; mCPBA, *meta*-chloroperoxybenzoic acid; NaBARF, Na<sup>+</sup>[3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>4</sub>B<sup>-</sup>; NaFABA, Na<sup>+</sup>[(BC<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>; Naph, naphthyl; NB, norbornene; NBOMe, 5-methoxynorbornenyl; NiNph<sub>2</sub>, nickel naphthenate; Ni(COD)<sub>2</sub>, bis(1,5-cyclooctadiene)nickel(0); OTf, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>; Pd(OAc)<sub>2</sub>, palladium acetate; Pd(acac)<sub>2</sub>, palladium acetyl acetonate; PEM, proton exchange membrane; SDS, sodium dodecyl sulfate; TIBA, tri(*i*-butyl)aluminium; Tr, Ph<sub>3</sub>C; TrFABA, Ph<sub>3</sub>C<sup>+</sup>[(BC<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>; *t*-Boc, *t*-butyloxycarbonyl group; TBPDS, *t*-butyldiphenylsilyl; T<sub>g</sub>, glass transition temperature; TMAH, tetramethyl ammonium hydroxide; Me, methyl; Et, ethyl; *n*-Pr, *n*-propyl; *i*-Pr, *i*-propyl; *n*-Bu, *n*-butyl; *i*-Bu, *i*-butyl; *n*-Pen, *n*-pentyl; *n*-Hex, *n*-hexyl; *n*-Dec, *n*-decyl; Ph, phenyl.

\* Corresponding author.

E-mail address: [bmvm@ips.ac.ru](mailto:bmvm@ips.ac.ru) (M.V. Bermeshev).

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## 1. Introduction

Norbornene (bicyclo[2.2.1]heptene-2) and its derivatives are of considerable current interest as reactive cyclic olefin monomers due to an opportunity of synthesizing very different norbornenes and their ability to participate in various polymerization reactions for the macromolecular design of new polymers with desired properties. Functionalized norbornenes can be easily obtained by cycloaddition reactions or norbornadiene-2,5 modifications (Fig. 1). The most convenient and simple method of their synthesis is a [4π+2π]-cycloaddition (Diels–Alder) reaction (Fig. 1a) [1,2]. As a rule, it affords a mixture of *exo* and *endo* isomers with the predominance of the latter, which is less reactive in polymerizations [3,4]. Other ways of norbornene synthesis like catalytic [2π+2π]-[5–8] or thermal [2σ+2σ+2π]-cycloaddition reaction [9–11] and norbornadiene-2,5 modifications [12,13] are less commonly used (Fig. 1b–d). However, some of them are stereo- and regioselective

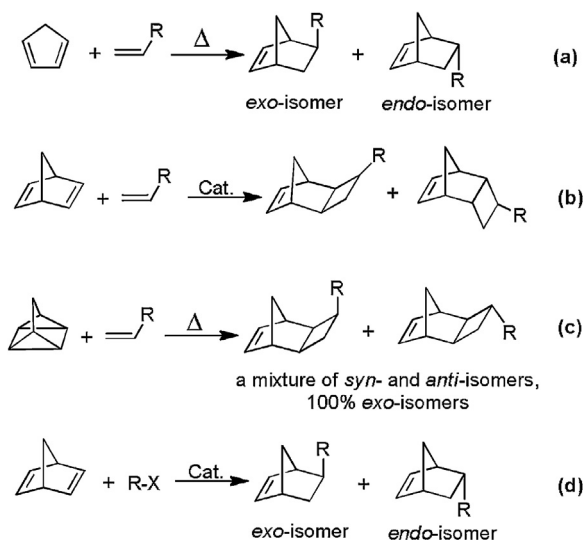


Fig. 1. Norbornenes synthesis methods.

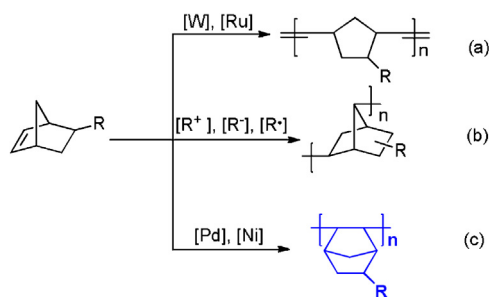


Fig. 2. Polymerization of norbornenes.

[10,14–16]. For instance, the [2σ+2σ+2π]-cycloaddition reaction of quadricyclane with alkenes/alkynes results in more preferable *exo* isomers (Fig. 1c) [10,17–19], and this approach has become actively applied [20–23].

The polymerization of norbornenes can be performed via three ways depending on the catalyst to form polymers with different main chain structures and, hence, versatile properties (Fig. 2). Usually, an *exo* isomer is consumed in polymerization much more rapidly than its *endo* analogue [24]. Ring-opening metathesis polymerization (ROMP) is the best-known pathway to convert norbornenes into polymers (Fig. 2a) [25,26]. Highly active and tolerant catalysts were developed for the ROMP of norbornene derivatives [27–30] in order to obtain polymers with controlled topology and desired microstructure and composition. Thus, the metathesis of norbornenes is applicable to the polymer synthesis of commercial products (Norsorex<sup>®</sup>, Telene<sup>®</sup>, Zeonex<sup>®</sup> (hydrogenated metathesis polymer), etc.) [31,32].

The radical, cationic, or anionic polymerization of norbornene derivatives is scantily known (Fig. 2b). In most cases, low-molecular-weight polymers or oligomers are formed under these conditions [33–40], and only few examples were published where high-molecular-weight polymers were obtained [41–44].

Another way to convert norbornenes is addition polymerization (AP) (Fig. 2c), which is occasionally referred to as vinyl or vinyl/addition polymerization. Here, we will use the term «addition polymerization». This route leads to a saturated structure of main

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