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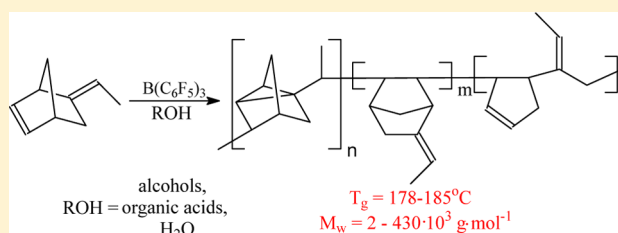
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Cationic Polymerization of Norbornene Derivatives in the Presence of Boranes

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Supporting Information

ABSTRACT: Cationic polymerization of 5-methylene-2-norbornene, 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene, dicyclopentadiene, and norbornadiene-2,5 in the presence of boranes was systematically studied. It was found that $B(C_6F_5)_3$ in combination with caprylic acid, 1-phenylethanol or water was a highly active catalyst for the polymerization of 5-alkylidene-2-norbornenes. The corresponding cationic polymers were obtained with up to yields 95% and with high molecular weights ($M_w \leq 430\,000$). The activity of 5-alkylidene-2-norbornenes in the polymerization using $B(C_6F_5)_3$ containing systems was the highest among the other monomers (5-vinyl-2-norbornene, dicyclopentadiene, and norbornadiene-2,5). $BF_3 \cdot O(C_2H_5)_2$ based catalysts turned out to be not so active for cationic polymerization of monomers compared with the systems containing $B(C_6F_5)_3$. They produced polymers predominantly containing the addition (vinyl) units instead of isomerization units. The structure of the polymer main chain units depended on the nature of the monomers: in the case of norbornadiene-2,5, 5-methylene-2-norbornene, and 5-ethylidene-2-norbornene the transannular polymerization proceeded, while dicyclopentadiene and 5-vinyl-2-norbornene formed the addition type polymers under the studied conditions.



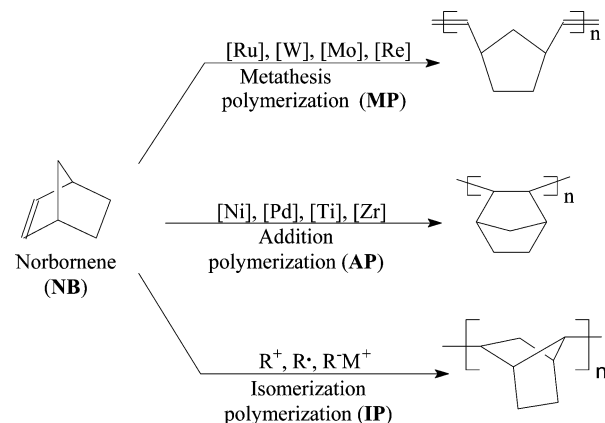
INTRODUCTION

Norbornene and its derivatives are unique monomers due to the capability to polymerize according to three different schemes: metathesis, addition and isomerization mechanisms (Scheme 1).^{1–4} It is also very important that often they are accessible compounds in synthetic and technological aspects. Polynorbornenes possess good mechanical strength, heat resistance, low birefringence, good membrane properties, and

optical transparency.^{5,6} These features make norbornenes very attractive monomers for macromolecular design of polymers with required properties. So at present there are several commercial polymer materials (TOPAS, TELENE, ZEONEX etc.) based on the most available norbornene derivatives.^{7,8} The synthesis of norbornenes to be used for polymerization is usually based on $[4\pi + 2\pi]$ -Diels–Alder reaction of cyclopentadiene with substituted ethylenes/acetylenes⁹ or on $[2\sigma + 2\sigma + 2\pi]$ -cycloaddition reaction between quadricyclane and an ethylene or acetylene derivative.^{10,11}

At the present time, a lot of catalyst systems have been developed for metathesis polymerization (MP) of norbornenes. This allowed the synthesis of polymers containing desired side groups with controlled topology and molecular weights.¹ Addition polymerization^{2,12} (AP) of norbornenes was studied less than MP because of the lower reaction driving force than in MP. In the case of AP some two and three component catalytic systems were suggested.^{2,12–17} These systems made it possible to obtain high molecular weight polymers containing even bulky^{13–15} or electro-withdrawing groups.^{16,17} Isomerization polymerization (IP) of norbornenes was studied poorly and the

Scheme 1. Pathways of Norbornene Polymerization



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number of dedicated publications was very limited. In attempts to perform this IP radical,³ cationic^{18–29} and anionic^{18,29} initiators were used. Usually, only oligomers or low molecular weight polymers were formed during IP. Therefore, physicochemical properties of this class of polymers have not been sufficiently studied.

Radical polymerization of unsubstituted norbornene was investigated in works^{3,30,31} but only oligomers were obtained as a result. Radical polymerization of norbornadiene-2,5 (NBD) was studied in greater detail: the first work was published in 1959,³² while in later studies, different conditions were applied but molecular weights remained low ($M_w \leq 17\,000$).^{30,33–35} The higher activity of monomers in the polymerization was achieved when an electron-withdrawing substituent (COOR) was incorporated into the norbornadiene moiety.^{36–39} The behavior of norbornene derivatives using anionic initiators (*n*-BuLi, Et₃Al) was discussed in several works^{18,29} but the weight-average molecular weights (M_w s) of the obtained polymers did not exceed 52 000.

Cationic polymerization of norbornene derivatives was studied more intensely than their radical or anionic polymerization. The polymerization of NB in the presence of different initiating systems was described in.^{3,20,22,25} The highest number-average molecular weights (M_n s) of polynorbornene of about 2000 was when EtAlCl₂ was used as a component of the catalytic system.²² 5-Alkylnorbornenes also demonstrated low activities in cationic polymerization.¹⁹ The polymerization degree of such monomers was not higher than 4–6 when *tert*-BuCl/EtAlCl₂ was applied for the initiation. The cationic polymerization of NBD was explored significantly more than polymerization of NB. In this case, a wide series of co-initiators was applied (AlCl₃,^{18,29,40–42} EtAlCl₂,^{18,23} TiCl₄,⁴ MoCl₅¹⁸) producing the corresponding polymers with M_w s up to 56 000. Cationic polymerization of dicyclopentadiene (DCPD), the most available norbornene derivative, was also studied in the presence of different Lewis acids: AlCl₃,²⁴ EtAlCl₂,²⁴ BF₃,²⁴ BF₃·OEt₂,^{24,26,27} TiCl₄, SnCl₄, Et₂AlCl, and SbCl₅.²⁴ The formed polymers were low molecular weight products ($M_n \leq 4450$). Cationic polymerization of another easily accessible hydrocarbon norbornene-type monomer, 5-vinyl-2-norbornene (VNB), was performed in the presence of EtCl/EtAlCl₂ initiating system. As a result, the polymers with M_n s lower than 4300 were obtained.²² This work also showed that cationic polymerization of 5-isopropenyl-2-norbornene would produce only oligomers like viscous oils or low molecular weight products.²² 5-Ethylidene-2-norbornene (ENB) was widely used as a component in terpolymerization of ethylene/propylene/diene.⁴³ In the papers^{44–46} for ENB addition homo- and copolymerization some Lewis acids as activators for transition metals complexes were used. In spite of this, the behavior of ENB in the presence of cationic co-initiators was studied less than VNB. Cationic polymerization of ENB using EtAlCl₂ and Et₂AlCl as co-initiators activated by tetraalkylammonium borates was only recently published in Japan patent.⁴⁷ It appears that at the present time this patent could be considered as only one example of successful isomerization polymerization of norbornene derivatives without electron-withdrawing substituents yielding high molecular weight products ($M_w \leq 314\,000$). Polymerization of 5-methylene-2-norbornene (MNB) in the presence of different cationic co-initiators has been studied previously (EtAlCl₂,^{21,22,48} VCl₄, AlBr₃,⁴⁸ WCl₆, MoCl₅, and TiCl₄²¹). However, there were no data available regarding molecular weights and properties of the obtained polymers. Therefore, it becomes clear that IP of

norbornene derivatives is still a poorly studied type of polymerization. A search for the appropriate active catalysts for this process, as well as study of properties of the corresponding polymers, remains a challenging task.

In our earlier work, we have investigated the addition copolymerization of 5-trimethylsilylnorbornene-2 with ENB using Nf₂Ni/MAO/B(C₆F₅)₃ catalyst system.⁴⁹ It was found that boranes could catalyze the homopolymerization of ENB according to the transannular scheme.⁵⁰ In this work we have synthesized high molecular weight polynorbornenes in the presence of boranes and have studied the structure of the obtained polymers. Different norbornene derivatives (Figure 1)

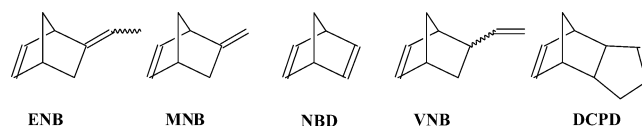



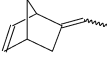
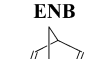

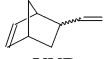

Figure 1. Monomers studied in this work.

were chosen for the polymerization as monomers. B(C₆F₅)₃ and BF₃·O(C₂H₅)₂ in combination with an organic acid, an alcohol or water were used as catalysts. Currently, there are only few works that describe the use of organoboron compounds for IP of norbornenes.^{24,26,27} It should be noted that systems based on Lewis acids such as B(C₆F₅)₃ and BF₃·O(C₂H₅)₂ recently were developed for cationic polymerization of some industrial important olefins (isobutylene,⁵¹ cyclopentadiene,⁵² styrene and its derivatives,^{53–61} isoprene,⁶² isobutyl vinyl ether⁶³). Thus, Sawamoto's group developed a number of initiating systems^{58–61} based on BF₃·O(C₂H₅)₂ for controlling the cationic polymerization of styrene and its derivatives in the presence of water. Kostjuk with co-workers^{53–57,62,63} suggested new initiating systems based on aromatic alcohols as initiators and B(C₆F₅)₃ or BF₃·O(C₂H₅)₂ as co-initiators. They succeeded to perform the living cationic polymerization of *p*-methoxystyrene, styrene and cyclopentadiene under mild reaction conditions, in open air and in the presence of fairly large amounts of water. Moreover, it was shown that under certain conditions, B(C₆F₅)₃-based initiating system allowed to synthesize high molecular weight polymers at elevated temperatures due to the generation of so-called weakly coordinating counterions.^{51,54} Therefore, B-containing systems look like as attractive initiating systems for the investigation of cationic polymerization of norbornene derivatives into high molecular weight polymers.

EXPERIMENTAL SECTION

Materials. Toluene, 5-ethylidene-2-norbornene (ENB), norbornadiene-2,5 (NBD), dicyclopentadiene (DCPD), 5-vinyl-2-norbornene (VNB), BF₃·O(C₂H₅)₂, C₇H₁₅COOH, PhCH(OH)CH₃, the first generation Grubbs catalyst were received from Aldrich. B(C₆F₅)₃ and B(C₆H₅)₃ were purchased from Alfa Aesar. Toluene, 5-ethylidene-2-norbornene (ENB), and norbornadiene-2,5 (NBD) were distilled over sodium metal in an inert atmosphere before use. Dicyclopentadiene (DCPD), 5-vinyl-2-norbornene (VNB) were distilled over CaH₂ under reduced pressure before use. 5-Methylene-2-norbornene (MNB) was synthesized according to the procedure described in ref 64 and distilled over sodium metal in an inert atmosphere before use. B(C₆F₅)₃ was sublimated twice before use. BF₃·O(C₂H₅)₂ was distilled under reduced pressure before use. C₇H₁₅COOH and PhCH(OH)CH₃ were distilled in an inert atmosphere. (η^6 -Toluene)Ni(C₆F₅)₂ was synthesized according to the method described in ref 65. All manipulations involving air- and moisture sensitive compounds were carried out under dried purified argon using standard Schlenk and vacuum-line techniques. All monomers were stored in an inert atmosphere.

Table 1. Cationic Polymerization of Norbornene Derivatives Using B(C₆F₅)₃-Containing Systems (B) at 20 °C^a

Monomer (M)	Initiator (I)	Mol. ratio		Time, h	Yield, %	M _w ·10 ⁻³	M _n ·10 ⁻³	M _w /M _n	T _g , °C	Olefinic protons content, ^a %
		M/B	I/B							
 MNB	H ₂ O	400/1	1/1	1/4	21	77.0	26.5	2.9	100	0
 ENB	H ₂ O	400/1	1/1	1/4	6	66.4	20.1	3.3	178	2.2
 ENB	H ₂ O	400/1	1/1	120	23	200	22.5	8.9	—	—
 NBD	<i>n</i> -C ₇ H ₁₅ COOH	50/1	1/2	120	4	1.37	1.14	1.20	240	0
 VNB	<i>n</i> -C ₇ H ₁₅ COOH	50/1	1/2	120	5	1.77	1.26	1.40	125	12
 DCPD	<i>n</i> -C ₇ H ₁₅ COOH	50/1	1/2	120	27	1.32	0.90	1.46	n.d. ^b	13

^aKey: (a) The content (%) of olefinic protons in cationic polymers was determined as a ratio of the integral at 4.9–6.0 ppm to the sum of all integrals in ¹H NMR spectra according to the following equation $I_{6.0-4.9\text{ppm}}/(I_{6.0-4.9\text{ppm}} + I_{3.0-0.5\text{ppm}}) \times 100\%$. (b) Not observed until decomposition starts.

Methods of Polymer Characterization. NMR spectra were recorded on a Bruker MSL-300 spectrometer operating at 300 MHz for ¹H and on a Varian Unity Inova AS500 spectrometer operating at 125 MHz for ¹³C. Each polymer sample was dissolved in CDCl₃ up to a concentration of 10%. For high-resolution solid-state ¹³C measurements, conventional CP/MAS ¹³C NMR was performed at 125 MHz and at 25 °C using a Varian Unity Inova AS500 spectrometer equipped with a solid-state high-resolution apparatus. The rotors that contained the polymer samples were spun at B15 kHz and the 90° pulse, the contact and repetition times were 3.5 ms, 2 ms, and 2 s. The calibration of chemical shift scales was based on adamantane spectra. Gel permeation chromatography analysis of the polymers was performed on a Waters system with a differential refractometer (Chromatopack Microgel-5, toluene as the eluent, flow rate of 1 mL/min). The molecular weight and polydispersity were calculated using the standard procedure relative to monodispersed polystyrene standards. Differential scanning calorimetry was performed on a Mettler TA4000 system with a heating rate of 20 K per minute. Thermal gravimetric measurements (TGA) were carried out using a PerkinElmer TGA-7 instrument. A wide-angle X-ray scattering (WAXS) study was carried out using an instrument with a two-coordinate AXS detector (Bruker) and the Cu KR line (wavelength of 0.154 nm). The transparency of polymer films was measured on a Specord-40 UV spectrometer (Bruker, Germany).

Film Casting. The films of studied polymers were cast from the 1.5–2 wt % solution in toluene. The solution was poured into a steel cylinder with a stretched cellophane base. The solvent was allowed to evaporate slowly to yield the desired polymer films. After the films' formation the cellophane was wetted to detach the films from it. Before testing, the films were kept under reduced pressure until a constant weight (for about 24 h). The thickness of the films was in the range of 80–100 μm.

General Cationic Polymerization Procedure. A solution of borane in toluene (0.15 M) was placed in a preheated argon-filled ampule, followed by the addition of calculated amount of an initiator using a microsyringe. The mixture had been mixed for 2–3 min, after which a monomer was added. Polymerization was stopped at the given time (15 min) by the addition of ethanol which caused precipitation of polymer. The product was filtered, washed with ethanol and dried. After that the polymer was dissolved in toluene again, precipitated in ethanol, and dried in vacuum (0.05 mmHg) at 80–90 °C to the constant weight. The procedure was repeated twice.

The Polymerization of ENB in the Presence of B(C₆F₅)₃/H₂O at 20 °C. The solution of B(C₆F₅)₃ in toluene (0.67 mL, 0.1 mmol, 0.15 M) was placed in a preheated, argon-filled ampule. Bidistilled water (1.8 μL, 0.1 mmol) was then added using a microsyringe. The mixture had been mixed for 2–3 min. After that, ENB (4.8 g, 40 mmol)

was added. Polymerization was stopped after 15 min by the addition of ethanol which caused precipitation of polymer. The product was filtered, washed with ethanol and dried. After that the polymer was dissolved in toluene again, precipitated into ethanol and dried under reduced pressure (0.05 mmHg) at 80–90 °C to the constant weight. The procedure was repeated twice.

$$\text{yield } 6\%, \quad M_w = 6.6 \times 10^4, \quad M_w/M_n = 3.3$$

The Polymerization of ENB in the Presence of B(C₆F₅)₃/*n*-C₇H₁₅COOH at –20 °C. The solution of B(C₆F₅)₃ in toluene (0.28 mL, 4.2 × 10⁻² mmol, 0.15 M) was placed in a preheated, argon-filled ampule. *n*-C₇H₁₅COOH (3.4 μL, 2.1 × 10⁻² mmol) was added using a microsyringe. The mixture had been mixed for 2–3 min and cooled at –20 °C. After that, precooled at –25 °C ENB (7.6 g, 63.3 mmol) was added. The mixture was stirred at –20 °C in 5, 10, 15, and 20 min increments, the aliquots (1–1.5 mL) were taken and precipitated with cold ethanol (–20 °C). The product was filtered, washed with ethanol, and dried. After that, the polymer was dissolved in toluene again, precipitated into ethanol, and dried under reduced pressure (0.05 mmHg) at 80–90 °C to the constant weight. The procedure was repeated twice. The results are given in Table 4.

Poly(5-ethylidene-2-norbornene). ¹H NMR (CDCl₃; δ, ppm): 5.87–5.54 m (0.6H), 5.33–5.10 m (0.4H), 2.80–0.44 m (43H).

¹³C NMR (CDCl₃; δ, ppm): 147.72–146.92 m (weak), 136.30–132.92 m, 123.32–122.65 m, 111.90–111.00 m (weak), 53.3–50.1 m, 45.5 m, 39.9–26.8 m, 23.0–12.7 m.

IR (ATR, cm⁻¹): 3048, 2934, 2867, 1454, 1371, 853.

Anal. Calcd (C₉H₁₂): C, 89.94; H, 10.06. Found: C, 89.70; H, 10.05%.

Poly(norbornadiene-2,5). ¹H NMR (CDCl₃; δ, ppm): 2.80–0.62 m (8H).

¹³C NMR (CP/MAS, δ): 60.08–23.34 m, 21.39–7.71 m.

IR (KBr, cm⁻¹): 3052, 2938, 1466, 1304, 802.

Poly(5-methylene-2-norbornene). ¹H NMR (CDCl₃; δ, ppm): 1.74–1.60 (m, 2H), 1.40–1.08 (m, 6H), 0.74 (br.s, 2H).

IR (ATR, cm⁻¹): 3047, 2935, 2866, 1467, 1449, 1326, 1300, 862.

Poly(5-vinyl-2-norbornene). ¹H NMR (CDCl₃; δ, ppm): 6.01–4.77 m (1H), 2.92–0.48 m (7.3H).

¹³C NMR (CP/MAS, δ): 149.12–109.80 m, 60.46–17.48 m.

IR (KBr, cm⁻¹): 2948, 2868, 1637, 1449, 991, 908, 738.

Poly(dicyclopentadiene). ¹H NMR (CDCl₃; δ, ppm): 6.12–4.98 m (2H), 3.13–0.55 m (13.5H).

¹³C NMR (CP/MAS, δ): 141.55–122.99 m, 62.42–15.28 m.

IR (KBr, cm⁻¹): 3043, 2940, 2887, 1619, 1445, 1354, 1034, 946, 837, 703.

Metathesis Polymerization of ENB. ENB (1.2 g, 10.0 mmol), toluene (20.0 mL) and the first generation Grubbs catalyst as a toluene

solution (0.67 mL, 2.0×10^{-3} mmol, 3×10^{-3} M) were charged into a round-bottom glass ampule (40 mL) equipped with a magnetic stirrer under an inert atmosphere at 20 °C. After 20 min an additional 10 mL of toluene was added. Polymerization was stopped by addition of 0.05 mL of ethylvinyl ether after 1 h. The polymer was precipitated into 0.1% ethanol solution of antioxidant (2,2'-methylene-bis(6-*tert*-butyl-4-methylphenol)), decanted, washed with several portions of the same solution and dried under reduced pressure. It was reprecipitated twice from toluene solution into ethanol and dried under reduced pressure at 50 °C until a constant weight.

yield 90%, $M_w = 2.2 \times 10^5$, $M_w/M_n = 1.4$, $T_g = 113^\circ\text{C}$

^1H NMR (CDCl_3 ; δ , ppm): 5.48–5.03 m (3H), 3.46–2.68 m (1H), 2.57–1.78 m (3.85H), 1.62–1.45 m (3H, CH_3), 1.30–1.06 m (1.15H).

^{13}C NMR (CP/MAS, δ): 148.88–141.80 m ($\text{C}=\text{C}(\text{H})\text{CH}_3$), 139.11–127.63 m ($\text{C}(\text{H})=\text{C}(\text{H})$), 120.30–112.00 m ($\text{C}=\text{C}(\text{H})\text{CH}_3$), 52.89–28.71 m, 19.43–11.62 m (CH_3).

Addition Polymerization of ENB. A solution of (η^6 -toluene) $\text{Ni}(\text{C}_6\text{F}_5)_2$ in toluene (0.5 mL, 2×10^{-2} mmol, 4×10^{-2} M) was added to ENB (1.2 g, 10 mmol) at 20 °C. The reaction mixture was stirred for 24 h. Then the polymerization mixture was precipitated into ethanol. The product was filtered, washed with ethanol and dried under reduced pressure. After that the polymer was dissolved in toluene again, reprecipitated into ethanol and dried under reduced pressure (0.05 mmHg) at 80–90 °C to the constant weight. The procedure was repeated twice.

yield 45%, $M_w = 1.6 \times 10^4$, $M_w/M_n = 2.3$, $T_g > T_d$

^1H NMR (CDCl_3 ; δ , ppm): 5.47–4.85 m (1H, $\text{C}=\text{C}(\text{H})\text{CH}_3$), 3.07–0.71 m (11H).

^{13}C NMR (CDCl_3 ; δ , ppm): 149.11–144.88 m ($\text{C}=\text{C}(\text{H})\text{CH}_3$), 113.70–108.59 m ($\text{C}=\text{C}(\text{H})\text{CH}_3$), 55.29–34.26, 15.87–12.51.

RESULTS AND DISCUSSION

Polymerization of Norbornadiene-2,5. The cationic polymerization of norbornadiene-2,5 (NBD) was well investigated in the presence of different co-initiators.^{4,18,23,29,40–42} However, to the best of our knowledge, the polymerization of NBD using boranes as co-initiators was not yet described. Therefore, in this work we also studied its cationic polymerization using $\text{B}(\text{C}_6\text{F}_5)_3$. As it was found in the presence of caprylic acid/ $\text{B}(\text{C}_6\text{F}_5)_3$ initiating system, NBD slowly polymerized with formation of a product with low molecular weights (Table 1) having a glass transition temperature at about 240 °C. According to NMR spectroscopy (Figure S1), the obtained polymer was fully saturated, and so it can be suggested that there are two possible structures of monomer units in the polymer (Figure 2).

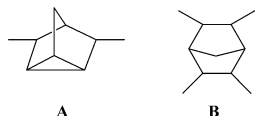


Figure 2. Possible structure of monomer units in the cationic PNBD.

In ^{13}C NMR spectrum, there was a multiplet in the region of 10–18 ppm (Figure 3A) which corresponds to cyclopropane rings,⁴⁰ i.e. this confirmed the presence of A-type monomer units (Figure 2). The same was also confirmed with help of IR data: the strong 800 cm^{-1} band was attributed to the 2,6-disubstituted nortricyclene structure (Figure S2).^{23,40} The formation of B-type monomer units should more likely result in a cross-linked or high-molecular weight polymer due to the bifunctional nature of

NBD in this case. The weak peak between $\delta = 50$ and 55 ppm (Figure 3A) indicates the presence of B-units.⁴⁰ The overall intensity of this signal from these branching units was small which, together with relatively low M_w (1.4×10^3 , Table 1), explained the absence of gelation.

Looking at the structure of the monomer unit A of PNBD, one could expect well-resolved NMR spectra as it is observed for PMNB (see the part: polymerization of 5-methylene-2-norbornene). However, PNBD spectra were complicated, and it can be explained by the formation of *exo/exo*- and *endo/endo*-linkages in the polymer (Figure 4). The formation of *endo/endo*-linkages was sterically unfavorable as it was demonstrated in literature.^{23,40} The idea of the formation of an isomer linkage of monomer units was in agreement with the fact that the obtained PNBD was amorphous according to WAXD data (Figure S3).

So cationic polymerization of NBD in the presence of caprylic acid/ $\text{B}(\text{C}_6\text{F}_5)_3$ could be presented as follow (Scheme 2).

Polymerization of 5-Methylene-2-norbornene. It was found that 5-methylene-2-norbornene (MNB) was a very active monomer in cationic polymerization in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ -containing systems (Table 1). As well as in the case of ENB, it was possible to obtain high molecular weight products with $\text{B}(\text{C}_6\text{F}_5)_3$ -systems from MNB. Furthermore, the activity of MNB was higher than ENB at the same conditions (Table 1) that could be explained by an easier access to the *exo* cyclic double bond in MNB. The obtained polymer was fully saturated, according to NMR and IR data. ^1H NMR spectrum of the poly(5-methylene-2-norbornene) (PMNB) was well resolved and consists of three signals (Figure S4). On the basis of NMR and IR spectral data, the following scheme of cationic polymerization of MNB could be suggested (Scheme 3).

The proposed mechanism for MNB polymerization catalyzed by $\text{H}_2\text{O}/\text{B}(\text{C}_6\text{F}_5)_3$ initiating system is presented in Scheme 4. Initiation occurred by the addition of proton, which is generated upon interaction of $\text{B}(\text{C}_6\text{F}_5)_3$ with H_2O ,^{53,54,65} to *exo* methylene double bond with a formation of a stable tertiary carbocation (A). This suggestion is confirmed by the competitive experiments performed by Kennedy et al.,^{22,66} who studied the polymerization of the mixture of 5-methylenenorbornane and norbornene using $\text{EtCl}/\text{EtAlCl}_2$ initiating system. The results of these experiments shown that 5-methylenenorbornane was largely consumed while substantial amounts of norbornene remained unreacted; i.e., the *exo* (methylene) double bond had a greater reactivity to protonation than *endo* (norbornene) one. The similar results were also obtained later when the isomerization of MNB cations (which were obtained by reaction of various protonic acids with MNB) was studied.⁶⁷ Since the propagation through the *exo* methylene group is inhibited due to a high steric hindrance, the transannular rearrangement of carbocation A into a less sterically hindered secondary carbocation (B) took place.²² The propagation occurred through the repetitive addition of *exo* methylene double bond of monomer to carbocation B followed by the rearrangement of the obtained tertiary carbocation as it is depicted in Scheme 4. So $\text{H}_2\text{O}/\text{B}(\text{C}_6\text{F}_5)_3$ initiating system involved in cyclopolymerization a cyclic diene (MNB), double bonds of which become involved in new cyclic structures. Thus, so-called transannular polymerization was realized.⁶⁸ The termination of polymerization may occur through the further rearrangement of carbocation B into more stable (but sterically hindered) tertiary cations via hydride shifts or via β -proton abstraction⁵² with the formation of an inactive *endo* olefin double bond.

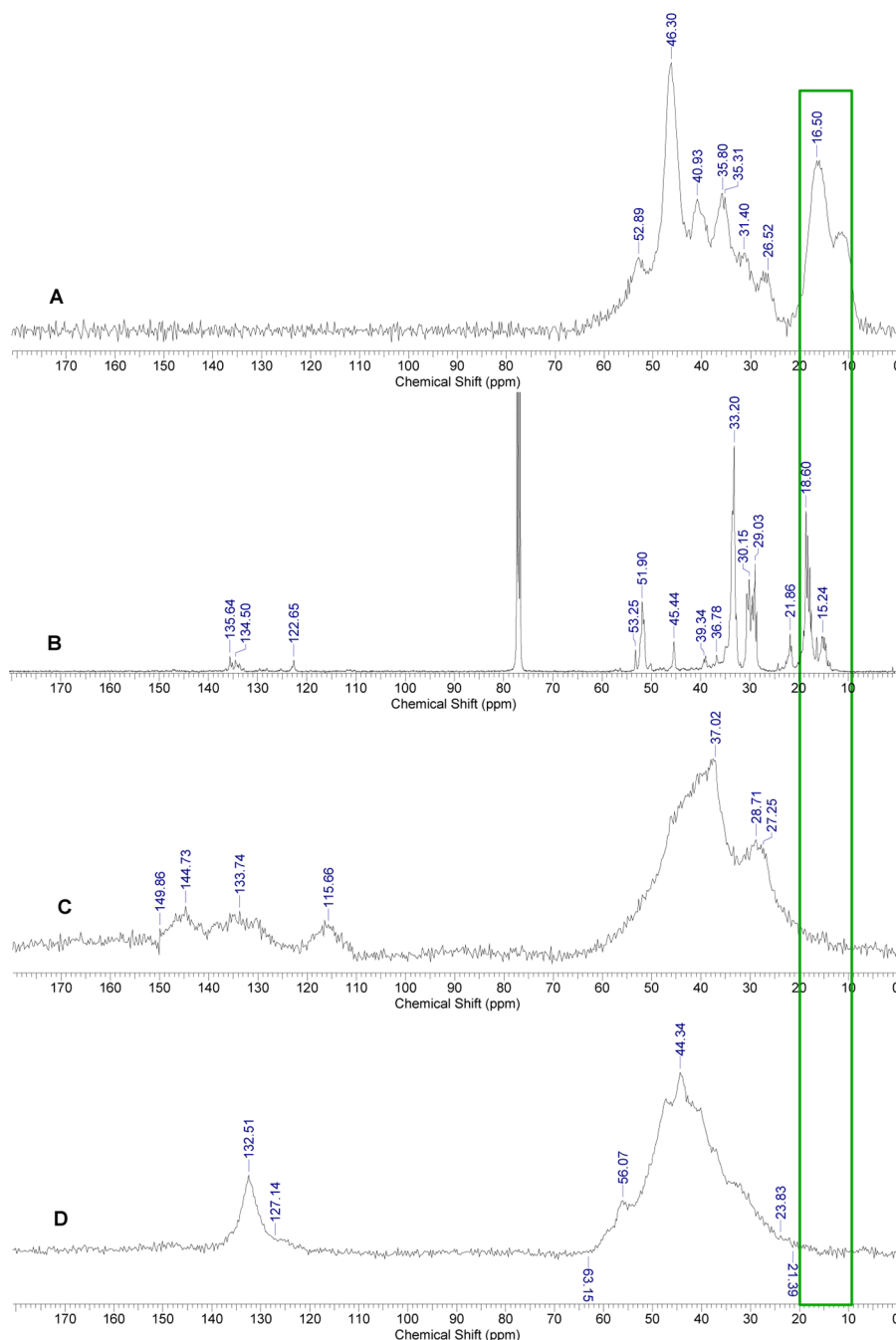


Figure 3. ^{13}C NMR spectra of cationic polymers: (A) PNBD (CP/MAS); (B) PENB (CDCl_3); (C) PVNB (CP/MAS); (D) PDCPD (CP/MAS).

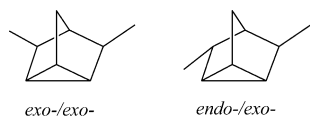
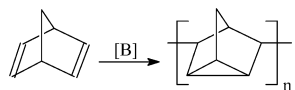


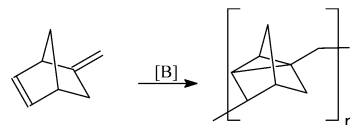
Figure 4. Isomers of monomer units in the cationic PNBD.

Scheme 2. Polymerization of NBD in the Presence of $\text{B}(\text{C}_6\text{F}_5)_3$ -Containing Systems



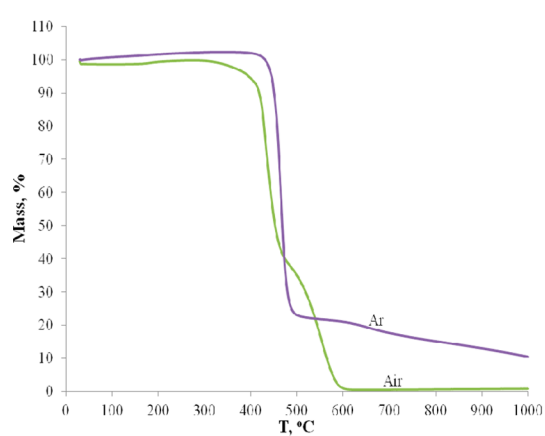
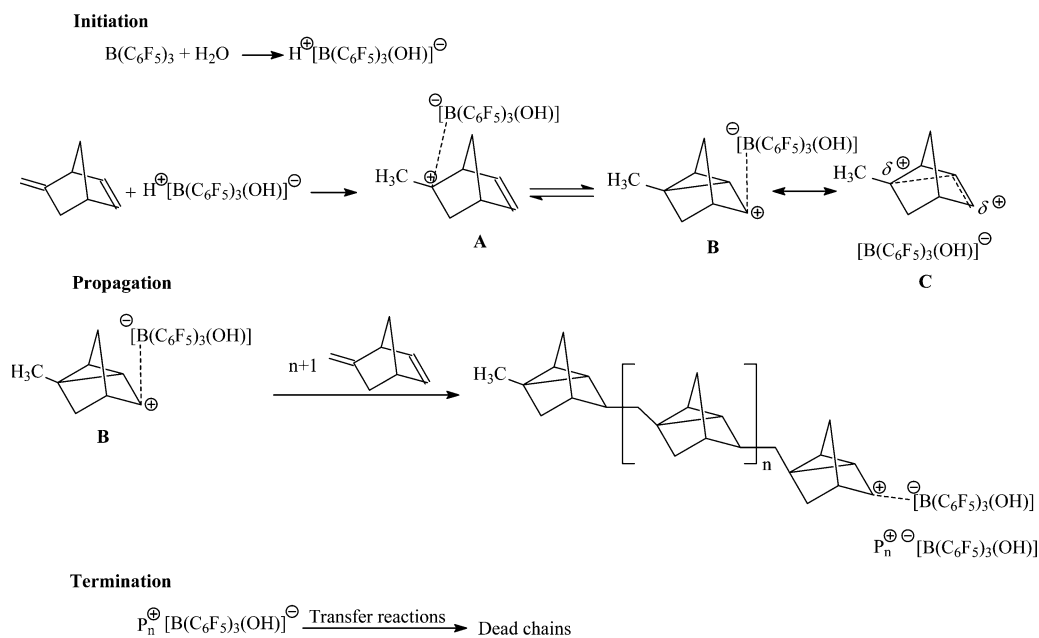
The synthesized cationic PMNB was soluble in warm organic solvents (40–60 °C, toluene, chloroform), had high thermal

Scheme 3. Polymerization of MNB in the Presence of $\text{B}(\text{C}_6\text{F}_5)_3$ -Containing systems

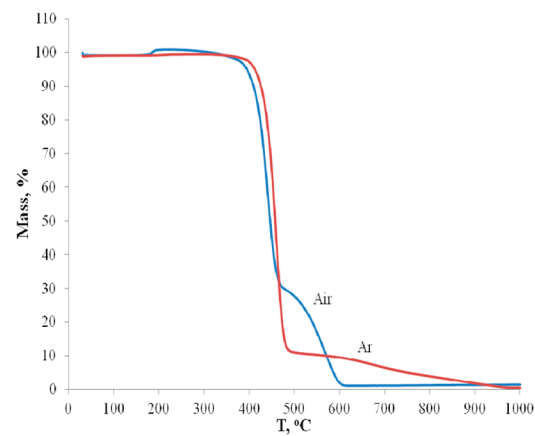


stability (Figure 5a) and demonstrated a lower glass transition temperature (100 °C, Figure 6, Table 1) than the cationic PENB.

It should be noted that in the DSC curve of PMNB, the “cold crystallization” and the melting of the polymer were also observed at 120–125 °C and at about 195–205 °C correspondingly (Figure 6).

Scheme 4. Proposed Mechanism for MNB Polymerization Catalyzed by $\text{H}_2\text{O}/\text{B}(\text{C}_6\text{F}_5)_3$ 

a



b

Figure 5. TGA curves of PMNB (a) and PENB (b).

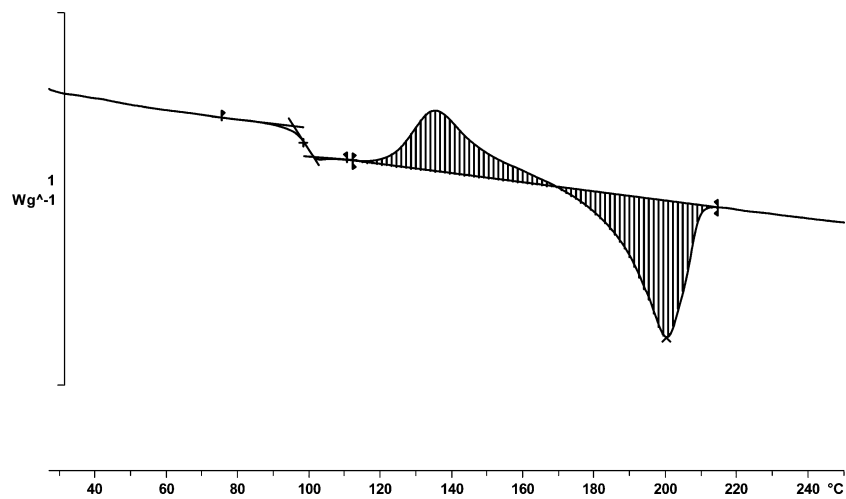


Figure 6. DSC curve of the cationic PMNB.

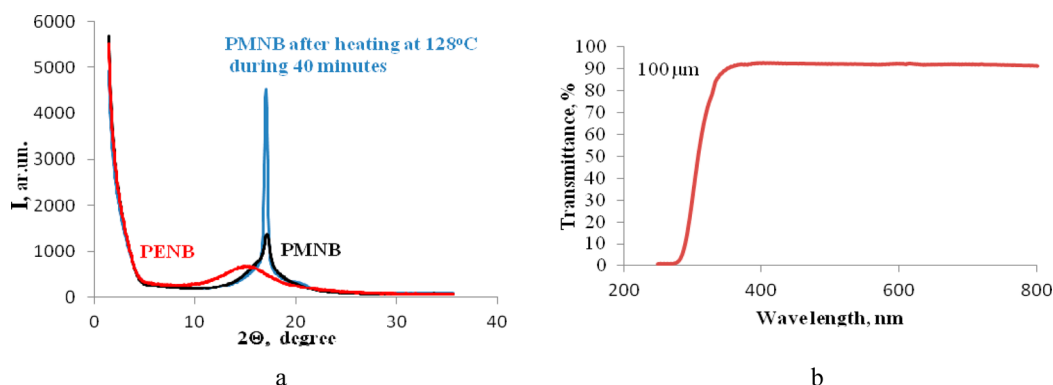


Figure 7. (a) WAXD analysis of PMNB and PENB and (b) transmittance of PENB at different wavelength.

This could be assigned to the presence of some extent crystallinity in the polymer. Actually according to WAXD data (Figure 7a), PMNB was found to be partially crystalline, and the extent of the crystallinity became higher after the heating of a polymer sample higher than its glass transition temperature. The formation of partially crystalline cationic PMNB earlier was also observed when the polymerization was performed using Al and V-containing co-initiators.^{22,48} On the basis of the facts that the obtained PMNB was a partially crystalline polymer and it had a very simple NMR spectra, it could be assumed that the polymer had a high order of main chain structure, namely “head-to-tail” linkages.

Polymerization of 5-Ethylidene-2-norbornene (ENB). Addition^{28,44–46} and metathesis²⁸ polymerization of ENB had been studied earlier. At the present time, ENB is used as a component in the synthesis of ternary copolymers based on ethylene, propene and ENB.⁴³ Although in some cases Lewis acids were applied as activators in addition homo- and copolymerization of ENB,^{44–46} there had not been any evidence concerning cationic polymerization of ENB for a long time. It has only been recently that such a type of polymerization of ENB using organoaluminum compounds has been briefly described in the patent.⁴⁷

In this work, we first investigated in detail the behavior of ENB in the presence of boranes which are usually used as activators in addition polymerization.^{2,13–15} The general scheme of polymerization of ENB using boranes is presented in Scheme 5; the

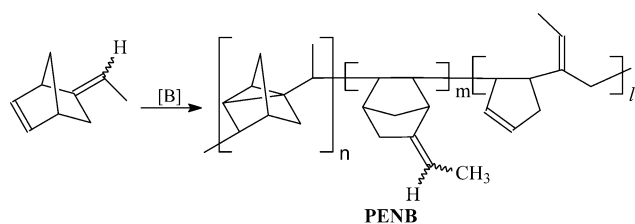
Furthermore, the polymers obtained in the presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ contained high amounts of unsaturated units (up to 30 mol % vs 10–16 mol % for $\text{B}(\text{C}_6\text{F}_5)_3$). The higher activity and selectivity of $\text{B}(\text{C}_6\text{F}_5)_3$ can be explained by the possibility of stabilizing the corresponding carbocation of a propagation chain with help of sterical hindrance due to bulky C_6F_5 -groups, which more likely promoted the isomerization step.

As initiators to $\text{B}(\text{C}_6\text{F}_5)_3$ *n*-octanoic acid, water and 1-phenylethanol were used (Table 3). *n*-Octanoic acid was applied as an easily accessible compound possessing enough high molecular weight to perform more accurate experiments. It was shown previously⁵¹ that the length of $\text{C}_n\text{H}_{2n+1}$ radical in the organic acid does not influence on the activity of $\text{C}_n\text{H}_{2n+1}\text{COOH}/\text{BF}_3 \cdot \text{Et}_2\text{O}$ initiating systems in the cationic polymerization of isobutylene. Earlier 1-arylethanol turned out to be effective initiators for cationic polymerization of styrene derivatives in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$,⁵³ so we decided to test this type of initiators also in the polymerization of ENB.

As it could be seen from Table 3, ENB was readily polymerized in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ initiated by an organic acid, water or an alcohol. The corresponding polymers based on ENB were obtained with high molecular weights and with moderate or good yields. According to NMR and IR spectroscopy, the obtained polymers consist of saturated and unsaturated units (Scheme 5). The ^1H NMR spectrum showed the presence of 2.0–3.2% of olefinic protons (Table 3), depending on the synthesis conditions (the monomer ENB contains 25% olefinic protons, 3 out of 12). The transannular unit (saturated units in Scheme 5) did not contain olefinic protons, whereas addition polymer unit had 8.3% (1 proton out of 12). Thus, based on the NMR data, we could conclude that the obtained polymers predominantly consist of norbornene units (84–90 mol %), and the composition of the polymers weakly depends on polymerization conditions, namely monomer conversion, the nature of an initiator, $\text{B}(\text{C}_6\text{F}_5)_3/\text{ENB}$ ratio.

Data of Table 3 clearly demonstrate that the catalyst system activity is strongly depended on the nature of an initiator and the molar ratio of initiator/ $\text{B}(\text{C}_6\text{F}_5)_3$. It can be seen that an excess of Lewis acid ($\text{B}(\text{C}_6\text{F}_5)_3$) is required in the case of *n*- $\text{C}_7\text{H}_{15}\text{COOH}$ or 1-phenylethanol for efficient initiation of carbocationic polymerization. This is in an agreement with earlier published results for cationic polymerization using Lewis acids.⁶⁹ The most active initiating system for ENB polymerization was found to be *n*- $\text{C}_7\text{H}_{15}\text{COOH}/\text{B}(\text{C}_6\text{F}_5)_3$, while 1-phenylethanol/ $\text{B}(\text{C}_6\text{F}_5)_3$ showed the least activity. The highest activity of *n*- $\text{C}_7\text{H}_{15}\text{COOH}/\text{B}(\text{C}_6\text{F}_5)_3$ system was achieved at the ratio of the acid/ $\text{B}(\text{C}_6\text{F}_5)_3 = 1/2$ (Table 3). It is quite possible that this is because of the

Scheme 5. Cationic Polymerization of ENB



conditions of polymerizations as well as the properties of the obtained cationic polymers are in Tables 1–4.

Among easily accessible boranes, the most active and selective catalyst for the cationic polymerization of ENB turned out a system based on $\text{B}(\text{C}_6\text{F}_5)_3$ (Tables 2 and 3). At the same time, it was expected that $\text{B}(\text{C}_6\text{H}_5)_3$ would be quite inactive in the polymerization. $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ containing systems gave low molecular weight polymers of ENB, with lower yields than catalyst based on $\text{B}(\text{C}_6\text{F}_5)_3$ at the same conditions (Tables 2 and 3).

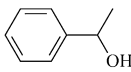
Table 2. Cationic Polymerization of ENB in the Presence of Different Boranes^a

borane (B)	molar ratio		yield, %	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n^c	olefinic protons content, ^d %
	ENB/B	H ₂ O/B					
BF ₃ ·O(C ₂ H ₅) ₂	50/1	<i>b</i>	28	3.41	1.91	1.79	3.9
	50/1	1/1	83	9.41	3.74	2.52	6.1
	50/1	2/1	42	2.84	1.74	1.63	4.2
	50/1	3/1	4	1.97	1.46	1.35	—
	100/1	1/1	34	5.60	2.78	2.01	4.3
B(C ₆ H ₅) ₃	50/1	1/1	0	—	—	—	—

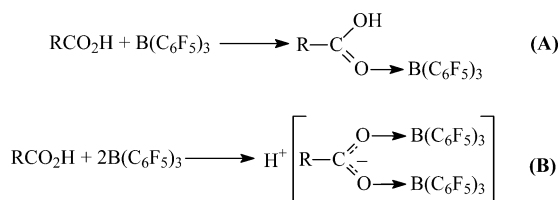
^aThe polymerization conditions were toluene, 20 °C; the reaction time was 15 min; the initial concentration of a borane in toluene was 0.15 M.

^bThe adventitious water content in BF₃·O(C₂H₅)₂ after distillation ca. 0.7% w/w, as was determined by Karl Fischer analysis. ^cMolecular weights and PDI were determined with help of GPC according to polystyrene standards. ^dThe content (%) of olefinic protons in cationic polymers was determined as a ratio of the integral at 6.0–4.9 ppm to the sum of all integrals in ¹H NMR spectra according to the following equation $I_{6.0-4.9\text{ppm}}/(I_{6.0-4.9\text{ppm}} + I_{3.0-0.5\text{ppm}}) \times 100\%$.

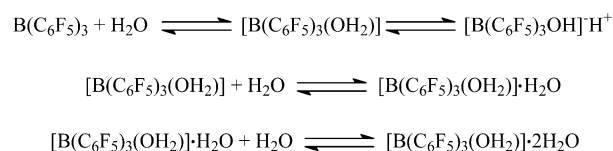
Table 3. Cationic Polymerization of ENB in the Presence of B(C₆F₅)₃ Initiated by Different Compounds^a

Initiator (I)	Molar ratio		Yield, %	$M_w \cdot 10^{-3}$	$M_n \cdot 10^{-3}$	M_w/M_n^d	Olefinic protons content, ^e %
	ENB/B(C ₆ F ₅) ₃	I/B(C ₆ F ₅) ₃					
H ₂ O	50/1	— ^a	29	67.2	17.7	3.8	2.4
	50/1	1/1	95 ^b	not soluble			—
	50/1	1/1	73 ^c	74.1	8.9	8.3	3.2
	50/1	2/1	49	33.0	7.5	4.4	3.2
	50/1	3/1	44	26.4	6.6	4.0	3.0
	50/1	4/1	30	19.7	7.0	2.8	2.6
	100/1	1/1	38	274	20.0	13.7	2.4
	50/1	1/2	57 ^b	not soluble			—
	50/1	1/1	12	11.3	5.9	1.9	2.2
	50/1	2/1	traces	—	—	—	—
<i>n</i> -C ₇ H ₁₅ COOH	50/1	1/2	95 ^b	not soluble			—
	50/1	1/1	37	12.8	6.4	2.0	2.3
	50/1	2/1	20	5.1	3.2	1.6	2.0
	100/1	1/2	85 ^b	not soluble			—
	1000/1	1/2	7	157	56.1	2.8	2.2

^aThe polymerization conditions were toluene, 20 °C; the reaction time was 15 min; the initial concentration of B(C₆F₅)₃ was 0.15 M. Key: (a) The adventitious water content in B(C₆F₅)₃ after the second sublimation ca. 0.2% w/w, as determined by Karl Fischer analysis; (b) the reaction was stopped after 2 min because of the gelation; (c) the initial reaction mixture was diluted by toluene 1.5 times; (d) molecular weights and PDI were determined by GPC according to polystyrene standards; (e) the content (%) of olefinic protons in cationic polymers was determined as a ratio of the integral at 4.9–6.0 ppm to the sum of all integrals in ¹H NMR spectra according to the following equation $I_{6.0-4.9\text{ppm}}/(I_{6.0-4.9\text{ppm}} + I_{3.0-0.5\text{ppm}}) \times 100\%$.

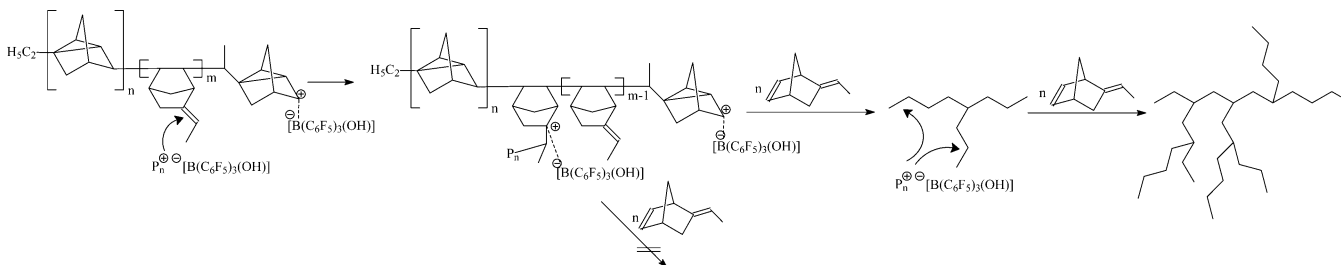
Scheme 6. Possible Complexes of B(C₆F₅)₃ with an Organic Acid⁵¹

formation of the complex (B)⁵¹ possessing stronger acid properties than the adduct (A) (Scheme 6). When the higher ratios of acid/B(C₆F₅)₃ were used the activity of these systems became notably lower.

Scheme 7. Possible Complexes of B(C₆F₅)₃ with Water⁷⁰

In the case of the usage of water as an initiator the formation of several adducts having the water/B(C₆F₅)₃ composition 1/1, 2/1, or 3/1 is proposed (Scheme 7).⁷⁰ The activity of the water/B(C₆F₅)₃ system was the highest at the ratio 1/1 (Table 3). This could be explained by stronger Bronsted acidity of such adduct in comparison with the same systems having compositions at 2/1 and 3/1 ratios.

Scheme 8. Suggested Pathway of a Side-Chain Propagation during the Cationic Polymerization of ENB

Table 4. Cationic Polymerization of ENB in the Presence of *n*-C₇H₁₅COOH/B(C₆F₅)₃ at Different Temperatures^a

temperature, °C	time, minutes	yield, ^b %	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	olefinic protons content, %
20	10	5.2	173	64.0	2.7	2.4
	15	—	196	65.0	3.0	—
	20	8.0	263	71.0	3.7	2.5
	25	—	325	70.9	4.6	—
	30	10.2	413	71.2	5.8	2.4
0	5	—	183	63.1	2.9	—
	10	5.8	216	65.7	3.3	2.4
	15	—	300	80.0	3.8	—
	20	11.0	421	88.5	4.8	—
	25	—	—	—	—	—
−20	5	—	224	69.8	2.3	—
	10	7.5	276	75.3	3.7	2.1
	15	—	352	82.1	4.3	—
	20	12.9	433	82.2	5.3	2.4
	25	—	—	—	—	—

^aThe molar ratio ENB/B(C₆F₅)₃/*n*-C₇H₁₅COOH was 1500/1/0.5. The solvent was toluene, and the initial concentration of B(C₆F₅)₃ in toluene was 0.15 M. ^bThe yield of the isolated polymer of ENB.

The highest activity for the systems based on B(C₆F₅)₃ and 1-phenylethanol was observed at the ratio of the alcohol/B(C₆F₅)₃ equal 1/2. Earlier, for the polymerization of different styrenes in the presence of 1-arylethanol/B(C₆F₅)₃ the close ratio of the alcohol to the borane was applied.⁵³

Molecular weight distributions (Table 3) of PENB at high monomer conversions, as well as the formation of cross-linked polymers (not soluble), are worthy of a special note. Sometimes these values of PDI were too wide even for cationic polymerization. The possible reason for this phenomenon could be a bifunctional nature of ENB containing two double bonds which could take part in the polymerization separately (Scheme 8). Probably, during the cationic polymerization, side chain propagation involving unsaturated units of the formed polymer main chains occurred, i.e., an interaction of the growing chains (P_n⁺[B(C₆F₅)₃(OH)][−]) with a main-chain double bond of another macromolecule (“grafting onto”) proceeded. The similar earlier was described for cationic polymerization of pentadiene-1,3 with ^tBuCl/TiCl₄ initiating system.⁷¹ It seems that the following ENB polymerization (“grafting from”) is an unlike process for the considered example due to the formation of sterically hindered tertiary cations after “grafting onto”. Thus, this may result in the broadening of molecular weight distributions or the obtaining of cross-linked polymers. Indeed at high conversions of ENB, the gelation of the formed polymer was usually observed. The attempts to use more dilute solutions in order to avoid the cross-linking resulted in the obtaining of polymers with low yields and molecular weights (Table 3).

For *n*-C₇H₁₅COOH/B(C₆F₅)₃ as the most active initiating system among the studied systems, we investigated the polymerization of ENB at different temperatures (Table 4). The polymerization was interrupted at low monomer conversion in

order to prevent the cross-linking and, in turn, the formation of polymers with broad molecular weight distribution.

As shown in Table 4, we have succeeded in the synthesis of high molecular weight polymers based on ENB with relatively narrow molecular weight distribution at low monomer conversions. The decrease of the reaction temperature from +20 °C to −20 °C led to an increase of the polymerization rate, and the molecular weights (M_w) were getting slightly higher. It is obvious that molecular weight distributions became sufficiently broaden with an increase of reaction time. If the polymerization was allowed to proceed longer the gelation was observed. The analysis of GPC curves of polymers showed an overlap in the low molar mass region (Figure S6). The peak maximum does not shift with conversion, although a high molecular weight shoulder was observed even at low conversions and it is getting higher with conversion as well as their values. The experimental values of molar masses of polymers are little upper of the theoretical line (Figure S7), which was constructed assuming the formation of one chain per the initiator molecule. All these observations indicate that the polymerization is most likely uncontrolled and the side-chain propagation (cross-linking) proceeded at low monomer conversions. So, the corresponding cationic polymers of ENB were obtained with higher molecular weights at higher molar ratio monomer/catalyst comparing to the results described in the literature earlier.⁴⁷ That allowed for the expectation a lower residue of the catalyst system in the polymer. Thus, we demonstrated that B(C₆F₅)₃-based initiating systems were effective catalysts for the cationic polymerization of ENB. It became possible with these systems to synthesize high-molecular weight cationic polymers based on a norbornene derivative suitable for the investigation of their properties.

The microstructure of the obtained cationic PENB was rather interesting. According to NMR (Figure 3-B, Figure 8) and IR

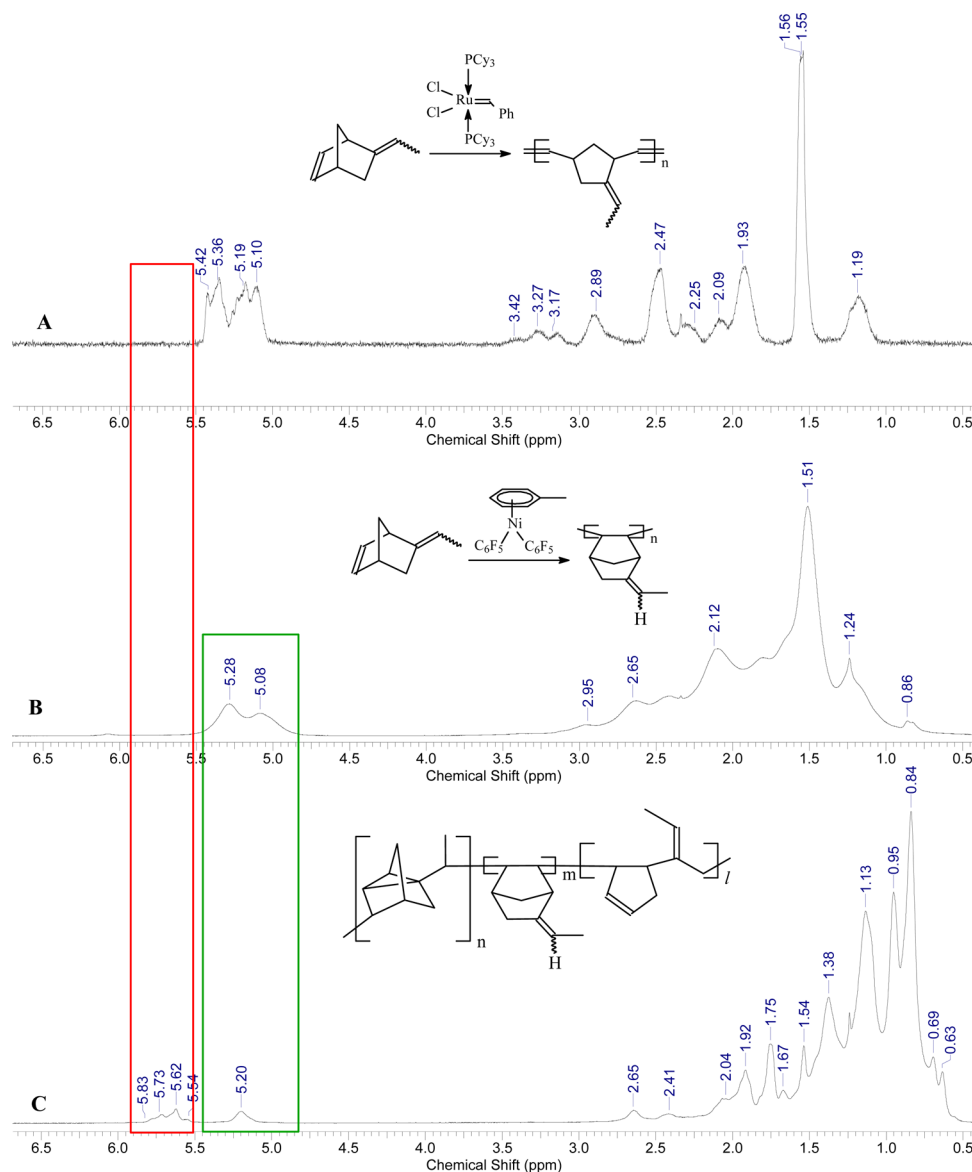


Figure 8. ^1H NMR spectra (CDCl_3) of metathesis (A), addition (B), and cationic (C) PENB.

spectroscopy (Figure S8), the obtained polymer of ENB was a copolymer containing saturated (transannular) and unsaturated units. The formation of a nortricyclene-containing unit in the polymer is illustrated by Scheme 4 and it was confirmed with help of ^{13}C NMR. In ^{13}C NMR spectrum of the cationic PENB there were several strong resonances at 11–19 ppm which were assigned to the cyclopropane-ring of the nortricyclene system (Figure 3B, the field in the frame).^{21,23,40}

In ^1H NMR spectrum of the cationic PENB, two weak resonance signals at 4.80–5.45 and 5.55–5.85 ppm related to unsaturated units were observed (Figure 8). It seemed two types of unsaturated units were formed in the cationic PENB. In order to clarify the structure of these units we synthesized two other possible isomers of PENB – pure metathesis and addition PENB (Figure 8, A and B).

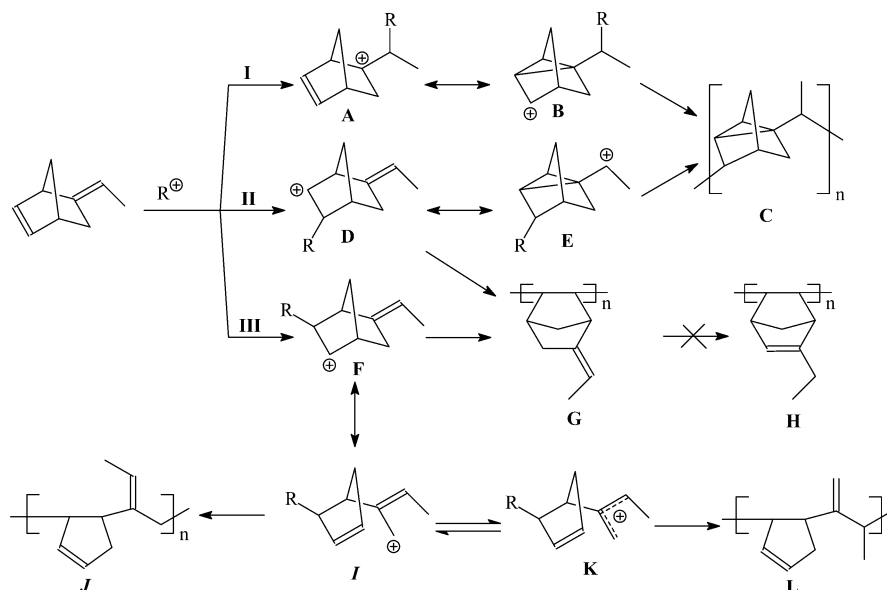
The metathesis PENB ($T_g = 113\text{ }^\circ\text{C}$) was obtained in the presence of the first generation Grubbs catalyst (Figure 8A). Addition polymerization was performed using of $(\eta^6\text{-toluene})\text{-Ni}(\text{C}_6\text{F}_5)_2$, which initiated polymerization of norbornene without activators² and does not contain Lewis acid additives

(Figure 8-B). In case of addition PENB T_g (DSC) was not observed until decomposition started. The chemical shifts' values and the relative intensity of the signals confirmed the formation of two polymers with metathesis or addition nature of monomer units. The comparison of ^1H and ^{13}C NMR spectra of the cationic PENB with the metathesis and addition PENB allowed us to conclude that the resonance signals at 4.80–5.45 ppm in ^1H spectrum of the cationic PENB could be assigned to units of the addition nature.

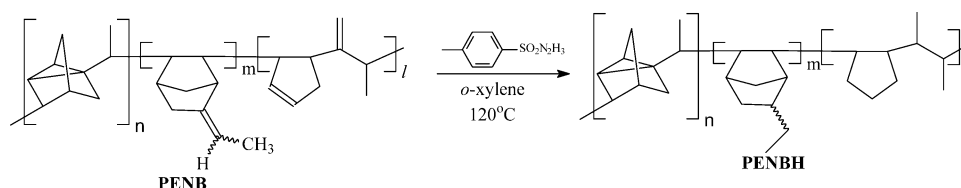
The resonance signals at 5.55–5.85 ppm can correspond to cycloalkenes with a small strain energy like cyclopentene.⁷² The possible appearance of such units in the cationic PENB can be explained by Scheme 9. In this scheme the most probable pathways of the cationic addition to ENB and the possible transformations of the obtained cations were presented.

The addition of the carbocation ion to ENB could proceed via three possible pathways. The first pathway (Scheme 9, I) would give the cation A which rapidly undergoes a transannular rearrangement resulting in the intermediate B. By this pathway nortricyclene cage units (C) would be formed in the backbone of

Scheme 9. Probable Pathways of the Cationic Addition to ENB



Scheme 10. Hydrogenation of PENB



the cationic **PENB**. If the carbocation attacks the norbornene double bond (pathways II and III) then two new carbonium ions could be obtained (**D** and **F**). So the second pathway (II) will result in either the formation of the cation **D**—which could rearrange into **E** with the following formation of units **C**—or would give addition-type units (**G**). Rather interesting results concerning synthesis and thermal stability of cation **E** was published in.⁷³ This cation turned out to be stable for a time at room temperature. It should be mentioned that the isomerization of **G**-type into **H**-type monomer units thermodynamically would not be a favorable process and did not proceed under the studied conditions (the pure addition **PENB** containing only **G**-type monomer units is stable in the presence of systems based on $B(C_6F_5)_3$). The presence of addition type monomer units (**G**) in the cationic **PENB** is in agreement with an earlier work.⁴⁷ The last pathway (III) of carbocation addition to **ENB** would give the cation **F**. This carbocation could form units **G**, but could also result in rearrangement with the destruction of norbornene bicycle. This led to the formation of the cation **I**, which forms the chain units of **J** and **L** types. These units would produce signals similar to those as we observed in NMR spectra of the cationic **PENB**. The same kind of transformation from **F** to **I** earlier was suggested for the decomposition of *p*-toluenesulfonylhydrazide of norbornene, which resulted in products with cyclopentene-containing fragments.⁷⁴ The formation of similar structure was also described in the study of pyrolysis of ethylene-propylene-diene terpolymer with 5-ethylidene-2-norbornene.⁷⁵ On the basis of the results of quantum chemical calculations it can be concluded that structures **A** and **B**, as well as **D** and **E**, **F**, and **I**, are resonance forms of nonclassical carbocations (see the Supporting Information). In the case of

ENB the formation of **D** \leftrightarrow **E** cations is more preferable than **A** \leftrightarrow **B** carbocations, while for **MNB** formation energies of these cations are close according to the performed calculations (Figure S11). It is worth to mention that the formation of **F** \leftrightarrow **I** cations is less favorable process for both monomers. Thus, it appeared that in the cationic **PENB**, there could be three types of monomer units: norbornene (**C**), addition-type (**G**) and cyclopentene-containing fragments (**J** and **L**).

Although the content of olefinic protons in the cationic **PENB** was not high (2–6%, Tables 1–4), the percentage of unsaturated units (Scheme 9, the sum of **G**-, **J**-, and **L**-type monomer units) was in the range 10–30 mol %. The lowest content of unsaturated units was observed for the polymers obtained in the presence of *n*-C₇H₁₅COOH/ $B(C_6F_5)_3$ (10–16 mol %), and the highest content was for polymers synthesized with $BF_3 \cdot O(C_2H_5)_2$ (up to 30 mol %). The molar ratio of (**J** + **L**)/**G** monomer units was approximately the same for all the studied polymers (about 2.9–3.1/1).

The unsaturation in **PENB** could be excluded after its hydrogenation (Scheme 10). It was performed with high yield (95%) with help of *p*-toluenesulfonylhydrazide. The molecular weights of the initial polymer (**PENB**, $M_w = 134\,000$, $M_w/M_n = 2.3$) and the hydrogenated polymer (**PENBH**, $M_w = 131\,000$, $M_w/M_n = 2.1$) were very close. This was allowed assuming that a cleavage of polymer chains did not take place during the hydrogenation.

The Properties of the Cationic PENB. Despite the presence of strain norbornene cages in **PENB**, it demonstrated a very high thermal stability (Figure 5b). TGA-studies showed that decomposition of the polymers started at 380 °C in air and higher than 400 °C under inert atmosphere (Ar). The polymer

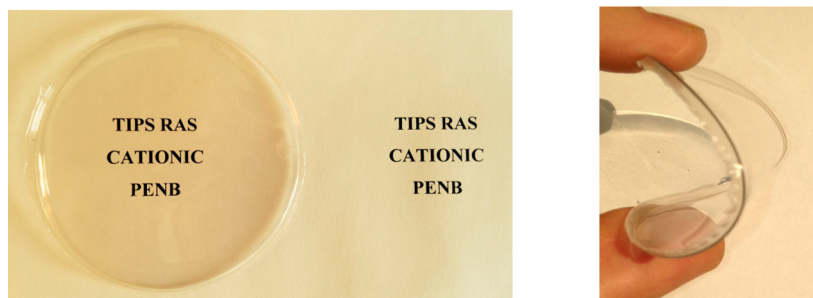


Figure 9. Pictures of PENB.

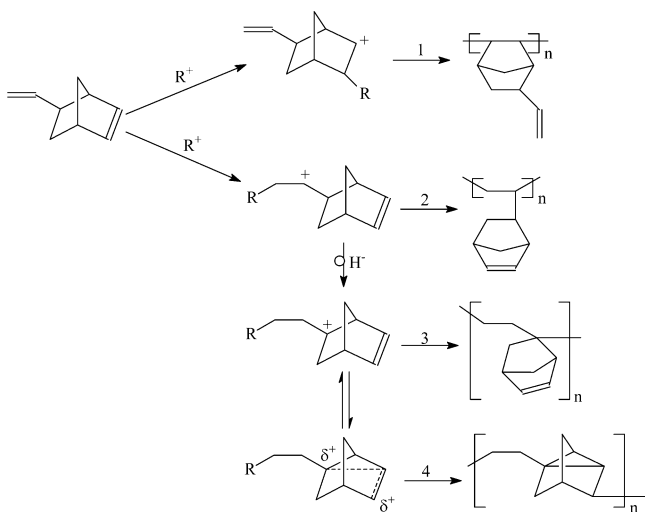
(PENB) had a glass transition temperature at 178–185 °C, which practically did not change after hydrogenation ($T_g(\text{PENBH}) = 186$ °C).

WAXD study revealed the amorphous nature of PENB (Figure 7a). A WAXD pattern gave one peak which was specific for conventional glassy polymers, e.g., polysulfones⁷⁶ or polytricyclonones.⁷⁷

The high molecular weight cationic PENB which was obtained possessed good mechanical properties ($\epsilon = 5\%$, $\sigma = 40$ MPa, $E = 1500$ MPa), and therefore it was suitable for the preparation of thin films (Figure 9). It was found that the transparency of these films was of a very high level (>90%, Figure 7b). Taking into account the accessibility of ENB and the simplicity of the suggested catalytic systems for its cationic polymerization, PENB could be considered as a new attractive polymer for optical materials.

Polymerization of 5-Vinyl-2-norbornene (VNB). The cationic polymerization of VNB could proceed via several pathways (Scheme 11).²² The cationic polymerization of VNB

Scheme 11. Probable Pathways of Cation Addition to VNB

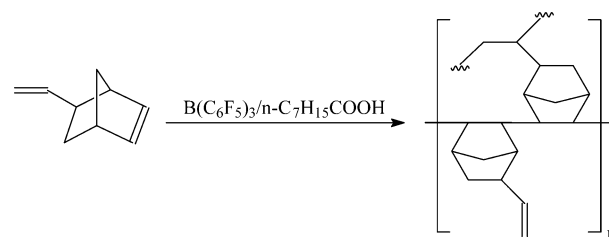


first was studied by Kennedy et al. over $\text{EtCl}/\text{EtAlCl}_2$.²² On the basis of the data of IR spectroscopy, the authors made the conclusion that VNB mainly polymerized according to addition scheme (Scheme 11, pathway 1).

In this work, we first studied the polymerization of VNB in the presence of caprylic acid/ $\text{B}(\text{C}_6\text{F}_5)_3$ initiating system. Although VNB is an isomer of ENB, its polymerization proceeded very slowly. The yields of the corresponding cationic polymer and its molecular weights were low (Table 1). According to the data of ^{13}C NMR and IR spectroscopy, the obtained PVNB does

not contain nortricyclene units: there were no signals of the cyclopropane ring carbons at 10–18 ppm in ^{13}C NMR spectrum (Figure 3C), and no strong absorption at 850 cm^{-1} region in the IR spectrum (Figure S12).²² These factors excluded the possibility of the polymerization of VNB via pathway 4 (Scheme 11). Furthermore, the absence of the signal of the endocyclic double bond protons in ^1H NMR (Figure S13) allowed exclusion of the presence of 2 and 3 type monomer units (Scheme 11). The ^1H NMR spectrum showed the presence of 12% of olefinic protons and this value did not correspond to the polymer formed only via pathway 1 (Scheme 11). The polymer obtained according to pathway 1 should contain 25% olefinic protons (3 out of 12), while the monomer contains 41.7% olefinic protons (5 out of 12). This likely implies that during the cationic polymerization, a part of the vinyl groups formed according to pathway 1 of the cationic PVNB was becoming active in polymerization and became a part of new side polymer chains. Therefore, the total scheme of polymerization could be presented as follows (Scheme 12). It was noted that the same scheme of

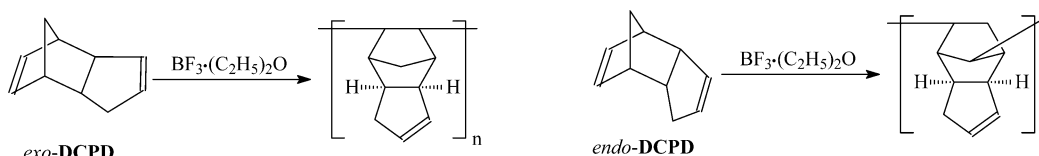
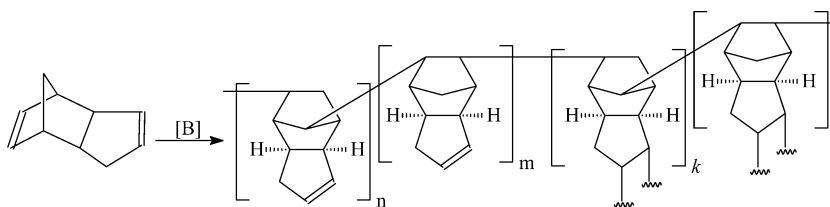
Scheme 12. Polymerization of VNB in the Presence of $\text{B}(\text{C}_6\text{F}_5)_3$ -Containing Systems



polymerization was suggested for addition polymerization of VNB in the presence of Pd-catalysts.⁷⁸

Polymerization of Dicyclopentadiene (DCPD). The cationic polymerization of DCPD was studied in several works^{24,26,27} in the presence of different co-initiators including BF_3 and $\text{BF}_3 \cdot \text{Et}_2\text{O}$. As a result, it was found that in the case of polymerization of *exo*-DCPD, addition type polymer (1,2-) was formed, while *endo*-DCPD gave 1,3-polymer formation after a rearrangement (Scheme 13). The obtained polymers usually were low molecular weight products ($M_n \leq 4.5 \times 10^3$).

Herein we explored the cationic polymerization of DCPD using caprylic acid/ $\text{B}(\text{C}_6\text{F}_5)_3$ initiating systems which was more active than BF_3 -containing systems. DCPD was used as a mixture of isomers with predominate content of *endo*-isomer (>95%). As we established, DCPD was more readily polymerized under the studied conditions (Table 1) than NBD and VNB, giving the cationic polymer with notably higher yields, although molecular weights were also low. According to NMR data, PDCPD did not

Scheme 13. Polymerization of DCPD in the Presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ Scheme 14. Polymerization of DCPD in the Presence of $\text{B}(\text{C}_6\text{F}_5)_3$ -Containing Systems

contain nortricyclicene-units. Analysis of NMR and IR spectra, as well as the value of unsaturation content of PDCPD (Table 1), allowed us to conclude that the polymer included mainly 1,2- and 1,3-polymer units and contained a small part of fully saturated units (the ratio of unsaturated/saturated units is 2.5/1, Scheme 14). The presence of rearranged 1,3-polymer units was confirmed by the strong peak at 2.49 ppm in ^1H NMR spectrum, which corresponded to the shift of the allylic proton of the cyclopentene ring when the fusion of the cyclopentene ring was *exo*.²⁶

CONCLUSIONS

In this work, we demonstrated that cationic polymerization could be an effective approach to synthesis of high molecular weight polynorbornenes. It was shown that accessible boranes in combination with an organic acid, an alcohol or water were active systems for cationic polymerization of norbornenes of different structure (5-alkylidene-2-norbornenes, 5-vinyl-2-norbornene, dicyclopentadiene and norbornadiene-2,5). We systematically investigated the behavior of this family of norbornene derivatives in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ -based initiating systems. The activity of 5-alkylidene-2-norbornenes turned out to be the highest among other monomers used in this work. We have revealed for the first time that $\text{B}(\text{C}_6\text{F}_5)_3$ in combination with caprylic acid, 1-phenylethanol or water allowed the synthesis of high molecular weight polymers that possess good film-forming properties. Catalysts based on $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ were not so active in cationic polymerization of such kind monomers. They produced polymers with a higher content of addition (vinyl) units instead of isomerization units. The polymer structures were studied using NMR and IR-spectroscopy. We have found that the structure of the obtained polymers depended on the nature of a monomer dramatically. In the case of norbornadiene-2,5, 5-methylene-2-norbornene and 5-ethylidene-2-norbornene, the transannular polymerization proceeded, while dicyclopentadiene and 5-vinyl-2-norbornene formed addition type polymers.

ASSOCIATED CONTENT

Supporting Information

Experimental section and figures showing IR, NMR spectra, WAXD analysis, GPC traces, M_n vs conversion plots, and relative energies and structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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