

Addition polymerization of silyl-containing norbornenes in the presence of Ni-based catalysts

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Abstract

Addition polymerization of 5-trimethylsilyl- and *endo*-, *exo*-5,6-bis(trimethylsilyl)-norbornenes was studied in the presence of Ni-based catalytic systems: $[\pi\text{-C}_5\text{H}_9\text{NiCl}]_2\text{-Et}_3\text{Al}_2\text{Cl}_3$, Ni(II) naphthenate-methylaluminoxane (MAO) and $(\pi\text{-C}_5\text{H}_9\text{NiCl})_2\text{-MAO}$. Completely saturated and soluble in aromatic solvents poly(5-trimethylsilyl-2-norbornene) was obtained with the yields up to 80%. In the course of the reaction *exo*-conformer was consumed much faster than *endo*-form independently of the type of catalytic system employed.

Exo-, *endo*-5,6-bis(trimethylsilyl)-2-norbornene was practically inactive in the presence of the studied Ni-catalysts. At the same time its addition copolymerization with norbornene and 5-*n*-hexyl-2-norbornene could be readily realized.

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1. Introduction

Earlier we have shown that norbornenes (and norbornadienes) bearing Me_3Si -groups can be easily polymerized via metathesis route (ROMP) in the presence of simple little-defined catalytic systems on the basis of Ru, W and Re compounds (Scheme 1) [1,2].

Polycarbosilanes obtained had good film-forming and gas transport properties [2–5]. Systematic physico-chemical investigations of a series of metathesis polynorbornenes bearing different side substituents evidenced that exactly Me_3Si groups linked up directly with the main chain were responsible for high membrane parameters [2]. However, the presence of a double bond in each monomer unit imparts to these polymers some disadvantages in particular a rather high chemical activity and poor thermooxidative stability.

The goal of this work was a synthesis of completely saturated polynorbornenes having Me_3Si -substituents as side groups. For this aim we have used the addition polymerization of corresponding Me_3Si -containing norbornenes. In general addition polynorbornenes are of interest as highly transparent materials

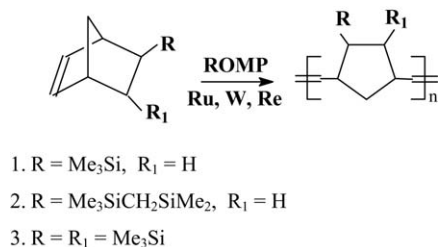
suitable for various optical applications [6,7]. Their gas transport parameters are also actively investigated [8].

2. Experimental

2.1. Materials

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified argon using standard Schlenk and vacuum-line techniques. Toluene was dried over sodium metal and then distilled under argon. Methylaluminoxane was received from Aldrich and used as commercial 1.4 M solution in toluene. Ethylaluminum sesquichloride ($\text{Et}_3\text{Al}_2\text{Cl}_3$) was purchased from Aldrich and used as a toluene solution. Pentenylnickel chloride $[(\pi\text{-C}_5\text{H}_9\text{NiCl})_2]$ was prepared according to literature procedure [9]. Nickel naphthenate $[(\text{Nph})_2\text{Ni}]$ was received from synthetic rubber plant in Yefremov (Russia). Norbornene (99%, Aldrich) was dried over sodium metal and used as a solution in toluene. 5-*n*-Hexyl-2-norbornene (*endo*/*exo* = 78/22) was received as a gift of BF Goodrich Co. and distilled over CaH_2 . 5-Trimethylsilyl-2-norbornene was synthesized by Diels–Alder reaction of dicyclopentadiene and vinyltrimethylsilane according to the

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Scheme 1. ROMP of silyl-containing norbornenes.

literature procedures [10]. *Endo*-,*exo*-5,6-bis(trimethylsilyl)-2-norbornene was prepared according to the previous reported method [2]. The Si-containing monomers were passed through purification column with neutral aluminum oxide for chromatography (Fluka) and distilled over CaH₂ in vacuum before use. All monomers were stored under argon atmosphere.

2.2. Characterization

NMR spectra were recorded on a Bruker MSL-300 spectrometer operating at 300 MHz for ¹H and on a Varian Unity Inova 500 operating at 125 MHz for ¹³C. Each polymer sample was dissolved in CDCl₃ up to a concentration of 10%. Chemical shifts values are reported in ppm using chloroform as an internal reference (¹H: 7.24 ppm for residual protons; ¹³C: 77 ppm for central peak). Model spectra for all of investigated polymers were calculated with Scientific Software ACD/HNMR DB.

IR spectra were obtained with a Specord M-82 spectrometer on KBr plates. Gel-permeation chromatography (GPC) analysis of the polymers was performed on a Waters system with a differential refractometer (Chromatopack Microgel-5, toluene as the eluent, flow rate 1 ml/min). Molecular mass and polydispersity were calculated by standard procedure relative to monodispersed poly(styrene) standards. Differential scanning calorimetry (DSC) was performed on Mettler TA 4000 system at a heating rate 20 °C/min. The *exo*- and *endo*-5-trimethylsilyl-2-norbornene isomers composition in the final polymerization mixture was determined using gas–liquid chromatography (GLC). GLC data were obtained on capillary column SE-30 (50 m) and a FID detector. (The sample was preliminary dissolved in 1 mL of methanol.)

2.3. Polymerization of Si-containing norbornenes and copolymerization with norbornene in the presence of catalytic system (π-C₅H₉NiCl)₂-Et₃Al₂Cl₃

Polymerization was carried out in a 10 mL glass ampoule equipped with a magnetic stirrer. The ampoule was preliminary purged in vacuum and filled with argon, and then the appropriate amounts of (π-C₅H₉NiCl)₂ and Et₃Al₂Cl₃ as solutions in toluene were introduced into ampoule. In standard runs the Al/Ni ratio was 3. The mixture was kept at polymerization temperature for 10 min before the addition of the monomer. After stirring in darkness for a time needed, the polymers were precipitated by acidified ethanol (ethanol–HCl, 10:1). The resulting polymers were separated, washed by several portions of ethanol and dried

Table 1

¹³C NMR assignments for copolymer of 5-trimethylsilyl-2-norbornene (NBSiMe₃) and norbornene (NB)

NBSiMe ₃		NB	
Carbon	δ (ppm)	Carbon	δ (ppm)
1, 4, 2, 3	38–56	2, 3	46–56
7	34–38	1, 4	38–46
5, SiMe	(–2)–3	7	34–38
		5, 6	31–36

in vacuum at 80–90 °C up to a constant weight. Copolymerization runs were carried out in the same way with equimolar mixtures of norbornene and appropriate Si-containing norbornene.

2.4. Polymerization of Si-containing norbornenes and copolymerization with norbornene or 5-*n*-hexyl-2-norbornene in the presence of catalytic systems (π-C₅H₉NiCl)₂-MAO and (Nph)₂Ni (II)-MAO

In a typical procedure, the toluene solution of nickel complex and monomers were introduced into a round-bottom glass ampoule (10 mL). Polymerization was initiated by adding of toluene solution of MAO (Al/Ni was 100). The reaction mixture acquiring red-brown color was continuously stirred in darkness for an appropriate period at ambient temperature. Polymerization processes were stopped with adding of the acidic ethanol. Polymers were separated as showed above. Copolymerization runs were carried out on the same way with equimolar mixtures of norbornene or 5-*n*-hexyl-2-norbornene and Si-containing norbornene.

Poly(5-trimethylsilyl-2-norbornene): ¹H NMR (CDCl₃) (ppm): 2.0–3.2 (C¹H, C⁴H); 0.8–2.5 (C²H, C³H, C⁵H, C⁶H₂, C⁷H₂), 0.05 (*endo*-SiMe₃); –0.03 (*exo*-SiMe₃); ¹³C NMR (CDCl₃) (ppm): 48–60 (C², C³); 40–48 (C¹, C⁴); 28–44 (C⁶, C⁷); 0–4 (C⁵, SiMe₃).

Copolymer of 5-trimethylsilyl-2-norbornene and norbornene: ¹H NMR (CDCl₃) (ppm): 2.0–3.0 (C¹H, C⁴H); 0.5–2.0 (C²H, C³H, C⁵H, C⁶H₂, C⁷H₂), 0.00 (*endo*-SiMe₃); –0.05 (*exo*-SiMe₃). For details of ¹³C NMR (CDCl₃) see Table 1.

Copolymer of *endo*-,*exo*-5,6-bis(trimethylsilyl)-2-norbornene and norbornene: ¹H NMR (CDCl₃) (ppm): 2.0–3.0 (C¹H, C⁴H); 0.5–2.0 (C²H, C³H, C⁵H, C⁶H₂, C⁷H₂), 0.07, 0.00 (SiMe₃); For details of ¹³C NMR (CDCl₃) see Table 2.

Table 2

¹³C NMR assignments for copolymer of *endo*-,*exo*-5,6-bis(trimethylsilyl)-2-norbornene (NB(SiMe₃)₂) and norbornene (NB)

NB(SiMe ₃) ₂		NB	
Carbon	δ (ppm)	Carbon	δ (ppm)
1, 4, 2, 3	36–56	2, 3	44–56
7	32–34	1, 4	38–42
5, 6, SiMe	(–2)–3	7	36
		5, 6	30–33

Table 3

^{13}C NMR assignments for copolymer of *endo-exo*-5,6-bis(trimethylsilyl)-2-norbornene ($\text{NB}(\text{SiMe}_3)_2$) and 5-*n*-hexyl-2-norbornene (NB)

$\text{NB}(\text{SiMe}_3)_2$		$\text{NBC}_6\text{H}_{13}$	
Carbon	δ (ppm)	Carbon	δ (ppm)
1, 4, 2, 3	34–46	1, 4, 2, 3	34–46
7	32–34	5, 6, 7	28–34
5, 6, SiMe	(–2)–3	C_6H_{13}	14, 22, 30–34

Copolymer of *endo-exo*-5,6-bis(trimethylsilyl)-2-norbornene and 5-*n*-hexyl-2-norbornene: ^1H NMR (CDCl_3) (ppm): 1.8–3.0 ($\text{C}^1\text{H}, \text{C}^4\text{H}$); 0.5–2.0 ($\text{C}^2\text{H}, \text{C}^3\text{H}, \text{C}^5\text{H}, \text{C}^6\text{H}_2, \text{C}^7\text{H}_2$), 0.86, 1.25 (C_6H_{13}), 0.05, 0.00 (SiMe_3); For details of ^{13}C NMR (CDCl_3) see Table 3.

3. Results and discussion

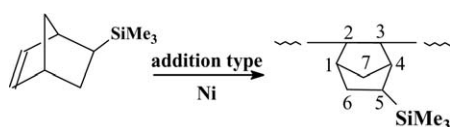
We studied a behavior of silicon-containing norbornenes, such as 5-trimethylsilyl- and *endo-exo*-5,6-bis(trimethylsilyl)-norbornenes under the conditions of addition polymerization initiated by some Ni- and Pd-containing catalytic systems. The catalysts of this type have already demonstrated high activity in addition polymerization of unsubstituted norbornene and its alkyl derivatives [6,7].

The norbornenes bearing one or two Me_3Si -groups were prepared by using Diels–Alder reaction of cyclopentadiene either with trimethylvinylsilane or with *trans*-1,2-bis(trichlorosilyl)ethylene (in this case Diels reaction was followed by methylation of *endo-exo*-5,6-bis(trichlorosilyl)-2-norbornene obtained first). GLC analysis indicated that 5-trimethylsilyl-2-norbornene had 1:1 ratio of *endo*- and *exo*-conformers, whereas 5,6-bis(trimethylsilyl)-2-norbornene was defined as pure *endo-exo*-isomer.

The known Pd-containing catalytic systems: $\{(\eta^3\text{-allyl})\text{Pd}(\text{SbF}_6)\}$ [11] and σ,π -bicyclic complex $[\text{NB}(\text{OMe})\text{PdCl}]_2$ [12] turned out to be practically inactive in polymerization of 5-trimethylsilyl-2-norbornene. On the contrary, Ni-based complexes displayed a real activity in respect to this monomer. As a result saturated cyclolinear polymers were formed according to Scheme 2 of addition polymerization. The absence of any unsaturation in these polymers was confirmed by both IR (no bands in 1620–1680 cm^{-1} region) and ^1H NMR spectroscopy (no signals at 5–6 ppm). Assignment of ^1H and ^{13}C NMR resonances of synthesized polymers was made with the help of assignments reported in [13] and model spectra (see Section 2).

Some details of polymerization process are represented in Table 4.

GLC analysis of the final polymerization mixtures indicated that in the course of the reaction *exo*-conformer was consumed



Scheme 2. Addition polymerization of 5-trimethylsilyl-2-norbornene.

much faster than *endo*-form independently of the type of catalytic system employed.

Addition poly(5-trimethylsilyl-2-norbornenes) were obtained with the yields up to 80%. All of them were completely soluble in aromatic solvents. Among the Ni-based catalytic systems presented in Table 4 Ni(II)naphthenate-MAO and $(\pi\text{-C}_5\text{H}_9\text{NiCl})_2$ -MAO are more active. Polymers prepared in the presence of Ni(II)naphthenate-MAO catalyst had the highest molecular weights and demonstrated good film-forming properties. They did not show any glass transition up to 300 $^\circ\text{C}$ (DSC).

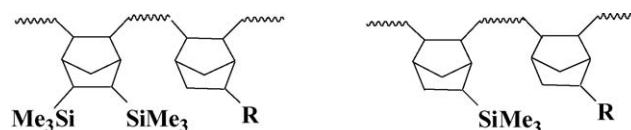
It should be noted that polymerization of 5-trimethylsilyl-2-norbornene proceeded substantially slower than that of unsubstituted norbornene. At the same time *endo-exo*-5,6-bis(trimethylsilyl)-2-norbornene was practically inactive in the presence of Ni catalysts presented in Table 4.

Nevertheless, both mentioned monomers turned out to be capable to take part in copolymerization with norbornene and 5-*n*-hexyl-2-norbornene (Table 5). According to its ^1H NMR spectrum, the copolymer prepared from equimolar mixture of 5-trimethylsilyl-2-norbornene and norbornene contained 42 mol% units of silyl-derivative.

Unlike the total inactivity of *endo-exo*-5,6-bis(trimethylsilyl)-2-norbornene in addition homopolymerization, its copolymerization with norbornene and 5-*n*-hexyl-2-norbornene could be readily realized in the presence of catalytic system Ni naphthenate-MAO (see Table 5). Copolymers with norbornene and 5-*n*-hexyl-2-norbornene contained 32 and 25 mol% bis(trimethylsilyl)-units respectively.

GPC analysis confirmed the formation of copolymers by demonstrating unimodal and rather narrow molecular weight distribution for all the polymers obtained in this study. The data of T_g for the majority of synthesized polymers are not informative ($T_g \geq T_d$). However *endo-exo*-5,6-bis(trimethylsilyl)-2-norbornene, incapable to give addition homopolymers, could copolymerize with 5-*n*-hexyl-2-norbornene giving polymer product with $T_g = 212$ $^\circ\text{C}$.

The structures of copolymers obtained can be depicted as follows:



R = H, n-Hex

Lower activity of 5-trimethylsilyl-2-norbornene as compare with that of unsubstituted norbornene and a total inactivity of *endo-exo*-5,6-bis(trimethylsilyl)-2-norbornene in addition polymerization can be explained by steric hindrances induced by Me_3Si -groups in *endo*-conformation. It is known that norbornene derivatives produced by Diels–Alder reaction are enriched, as a rule, by *endo*-forms. Usually the conformation of substituted norbornene does not have any considerable significance for ROMP process. However, for addition type process, the possibility of polymerization as well as its rate to a great degree depends on the presence of monomer in *exo*-

Table 4
Addition polymerization of 5-trimethylsilyl-2-norbornene by Ni-based catalytic systems at 20 °C

Catalytic system	[M]/[cat] mol/mol	[M], mol/L	Time (h)	Yield (%)	Conversion of isomers % ^a		M_w^b	M_w/M_n
					exo	endo		
$(\pi\text{-C}_5\text{H}_9\text{NiCl})_2\text{-Et}_3\text{Al}_2\text{Cl}_3$, Al/Ni = 3	600	2.25	120	47	77	17	29200	2.0
	600	5.35	48	56	83	28	41000	1.7
	1000	5.43	120	8	15	1	–	–
$(\pi\text{-C}_5\text{H}_9\text{NiCl})_2\text{-MAO}$; Al/Ni = 100	600	2.86	96	80	98	61	104000	1.8
	1000	3.49	19	64	100	28	152000	1.7
$(\text{Nph})_2\text{Ni-MAO}$, Al/Ni = 100	600	2.89	27	63	86	40	270000	2.4
	1000	3.53	24	56	69	27	290000	2.0
	1500	3.98	24	55	–	–	324000	2.9
	3000	4.55	24	32	40	24	270000	2.9

^a Determined by GLC of final polymerization mixture.

^b Determined by GPC relative to polystyrene standards.

Table 5
Addition copolymerization of Me₃Si-containing norbornenes with norbornene hydrocarbons on Ni-based catalytic systems at 20 °C

Catalytic system	Monomers		$[M1]/[M2]/$ [cat]mol/ mol/mol	[M]mol/L	Time, h	Yield %	Copolymer composition ^a , mol %		M_w^b	M_w/M_n
	M1	M2					M1	M2		
	$(\pi\text{-C}_5\text{H}_9\text{NiCl})_2\text{-Et}_3\text{Al}_2\text{Cl}_3$, Al/Ni = 3	NBSiMe ₃	NB	200/200/1	1,54	96	51	42	58	28570
NB(SiMe ₃) ₂		NB	200/200/1	1,38	48	35	20	80	16730	1,55
$(\text{Nph})_2\text{Ni-MAO}$, Al/Ni = 100	NB(SiMe ₃) ₂	NB	200/200/1	1,1	144	56	32	68	64800	1,86
	NB(SiMe ₃) ₂	NBC ₆ H ₁₃	200/200/1	1,1	166	43	25	75	51200	2,49

^a Determined by NMR-spectra.

^b Determined by GPC relative to polystyrene standards.

conformation. The mechanistic reasons of this dependence were discussed by Sen and co-workers [14] on the example of simple 5-alkyl-2-norbornenes polymerization. It is possible that substituted norbornenes with 100% of *endo*-form are incapable at all of polymerizing via addition scheme. But when the mixture of different conformers is present, a part of *endo*-form could participate in copolymerization with *exo*-form. Because it we could obtain sufficiently high yields of poly(5-trimethylsilyl-2-norbornene) from a monomer with nearly equal amounts of *exo*- and *endo*-form. In the case of *endo*-,*exo*-5,6-bis(trimethylsilyl)-2-norbornene one of substituents is always in the disadvantageous *endo*-conformation. This fact excludes the possibility of homopolymerization for this monomer but does not exclude the proceeding of its copolymerization with norbornene itself or with its substituted *exo*-derivative. The data on the transport characteristics of new polymers obtained will be published elsewhere.

4. Conclusion

First addition polymerization of 5-trimethylsilyl- and *endo*-,*exo*-5,6-bis(trimethylsilyl)- norbornenes was studied. The Ni-based catalytic systems: $(\pi\text{-C}_5\text{H}_9\text{NiCl})_2\text{-Et}_3\text{Al}_2\text{Cl}_3$, Ni(II) naphthenate-(MAO) and $(\pi\text{-C}_5\text{H}_9\text{NiCl})_2\text{-MAO}$ were used. Completely saturated and soluble in aromatic solvents poly(5-trimethylsilyl-2-norbornene) was obtained with the yields up to 80%. In the course of the reaction *exo*-conformer was con-

sumed much faster than *endo*-form independently of the type of catalytic system employed. Polymers prepared in the presence of Ni(II)naphthenate-MAO catalyst had the highest molecular weights and demonstrated good film-forming properties.

Exo-,*endo*-5,6-bis(trimethylsilyl)-2-norbornene was practically inactive in the presence of studied Ni-catalysts. At the same time its addition copolymerization with norbornene and 5-*n*-hexyl-2-norbornene could be readily realized.

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