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Synthesis and gas permeation properties of new ROMP polymers from silyl substituted norbornadienes and norbornenes

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Abstract

Using ring opening metathesis polymerization (ROMP) the novel linear polynorbornadiene and polynorbornene (PNB) derivatives bearing silicon-containing moieties were prepared in the presence of $RuCl_3{\cdot}3H_2O$, $RuCl_2(PPh_3)_3$, and WCl_6/tetramethyldisilacyclobutane catalysts with the yields up to 98%. Gas permeation properties (permeability and diffusion coefficients) of the polymers obtained were measured. It was shown that polynorbornadiene containing the $Si(CH_3)_3$ group has the transport parameters similar to those of poly(trimethylsilyl norbornene) studied earlier. On the other hand, PNB bearing two $Si(CH_3)_3$ groups in each repeat unit reveals much greater gas permeability induced mainly by increased solubility coefficients. The latter result is consistent with the much higher glass transition temperature of this polymer.

Keywords: Ring opening metathesis polymerization; Polynorbornenes/norbornadienes; Permeability

1. Introduction

Norbornene, norbornadiene and their derivatives can serve as monomers for the synthesis of highly molecular mass polymers with widely varying structure. This group of cyclic compounds gives an example, how quite different chemical polymer structures and the resulting variation of properties can be achieved not only by a choice of monomer structure but also by a selection of catalyst systems. Depending on the type of catalysts, norbornene and its derivatives can be polymerized in accordance with **A** or **B** directions [1,2] (Scheme 1).

In the presence of ROMP catalysts (e.g. based on W-, Re-, or Ru-compounds) cyclo-linear structures formed by opening of the strained norbornene five-membered-cycle can be synthesized (A) [1–7]. In this way, norbornene polymers with different alkyl-, F, and Si-containing substituents (including alkoxy, carbazolyl, and other groups) have been prepared [8–15]. Some of the polynorbornenes of such type showed rather attractive gas transport parameters, especially those containing the $Si(CH_3)_3$ group [7,11] and perfluorinated side groups [9, 10]. It should be mentioned that PNB with other side groups have also been prepared by the ROMP technique and their transport parameters reported in [15–17].

On the other hand, polymers with entirely different structure can be prepared from the same monomers using Ni- and Pd-containing catalysts (B) [18–20]. In this case the reaction proceeds as a classical addition olefin polymerization retaining strained rings unchanged. Properties of the resulting polymers (e.g. the glass transition temperature) are quite different from those of polynorbornenes obtained by ROMP [19,21].

The present work is focused on an elucidation of the effects exerted by the structure of backbone and side groups on the gas permeation properties of poly(trimethylsilylcyclopentylenevinylene)s and poly(trimethylsilylcyclopentenylenevinylene)s. In pursuing this aim, we have synthesized several 2-silylnorbornadienes and 5,6-bis(trimethylsilyl)-norbornene and carried out their ROMP. Unlike poly(cyclopentylenevinylene)s, polymers prepared by ROMP of 2-silylnorbornadienes, contain double bonds both in the vinylene fragments and in five-membered rings.

The novel polycyclopentylenevinylene prepared and studied in this work bears two side trimethylsilyl groups

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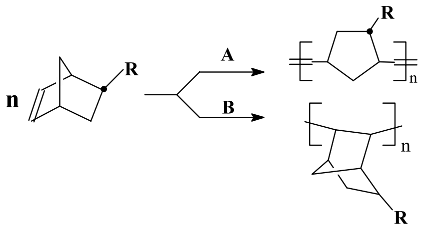


Scheme 1.

in each repeat unit prepared from the new monomer 5,6-bis(trimethylsilyl)norbornene. We undertook this synthesis assuming that introduction of an additional bulky trimethylsilyl group should further increase permeability of the polymer as compared to poly(trimethylsilylcyclopentylenevinylene) studied earlier.

2. Experimental

2.1. Measurements

^{1}H and ^{13}C NMR-spectra were recorded in $CDCl_3$ solutions at 300 and 75, 47 MHz, respectively using a Bruker MSL-300 spectrometer ($CDCl_3$ was used as an internal standard). 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. Chromato-mass-spectrometric analysis was carried out using a Kratos MS-25 RF-instrument.

A mass spectrometric apparatus with MI-1309 instrument was used in permeability measurements. The details of the technique were the same as described in [22]. Gas permeation rate was measured at 22 ± 2 °C with an upstream pressure in the range of 0.1 to 1 atm, and a downstream pressure about 10^{-3} mmHg. In this instrument, time-lag method permitted the simultaneous determination of diffusivity (D) and permeability coefficients (P). The solubility coefficients S were estimated as a ratio $S = P/D$.

Free volume of one of the polymers obtained was studied by means of positron annihilation lifetime spectroscopy using a standard ORTEC instrument. The details of measurements were the same as in previous studies of norbornene polymers (see e.g. [10,14]). The residual metal content in the polymers was determined by the method of Inductively Coupled Plasma Atomic Emission (ICP-AE)

2.2. Materials

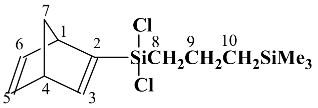
As catalysts, commercial $RuCl_3 \cdot 3H_2O$, $RuCl_2(PPh_3)_3$ were used without preliminary purification. WCl_6 was sublimated and used as 0.01 M solution in absolute toluene. Different compounds used as co-catalysts and intermediates in preparation of monomers such as 1,1,3,3-tetramethyl-1,3-disilacyclobutane [23], 2-trichlorosilylbicyclo[2.2.1]hepta-2,5-diene [24], 2-trimethylsilylbicyclo[2.2.1]hepta-2,5-diene [24], 1,2-bis(trichlorosilyl)ethene [25] were prepared according to published procedures. Solvents were purified and distilled before their use by standard methods.

Monomer preparation: The methods of synthesis of the monomers are disclosed below. All the procedures were carried out under the dry argon.

2.2.1. 2-Trichlorosilylbicyclo[2.2.1]hepta-2,5-diene (**1**) and 2-trimethylsilylbicyclo[2.2.1]hepta-2,5-diene (**2**)

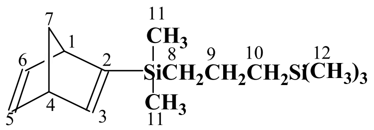
The title compounds were prepared according to published procedures [24]. Their spectral properties are in agreement with the literature data [26–28].

2.2.2. 2-Dichlorolsilyl(trimethylsilylpropyl)bicyclo[2.2.1]hepta-2,5-dien (**3**)



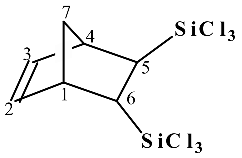
To a stirred diethyl ether solution of $ClMg(CH_2)_3$-$Si(CH_3)_3$ prepared from 0.125 mol Mg and 0.1 mol $Cl(CH_2)_3Si(CH_3)_3$, 20 g (0.0879 mol) **1** in 20 ml dry diethyl ether was slowly added at (−)70 °C. Then temperature was slowly elevated, and the mixture was kept overnight at room temperature. After heating the mixture under reflux for 1.5 h, precipitated $MgCl_2$ was filtered out and washed with diethyl ether. Filtrate was concentrated and fractionated under reduced pressure to yield 17.8 g (0.0584 mol) (68%) of a colorless liquid (bp 97–101 °C, 0.25 mmHg). ^{1}H NMR ($CDCl_3$) δ 7.49 (d, C^3H), 6.79 (s, C^5H), 6.69 (s, C^6H), 3.90 (s, C^4H), 3.78 (s, C^1H), 2.00 (m, C^7H_2), 1.62–1.48 (m, C^9H_2), 1.24 (t, C^8H_2), 0.64 (t, $C^{10}H_2$), 0.011 (s, $Si(CH_3)_3$). IR (KBr): 1296, 1248 (Si–C), 864, 840, 776, 696 (Si–C), 552, 532 cm^{-1} (Si–Cl). MS (70 eV), $C_{13}H_{22}Cl_2Si_2$, Calcd mass = 305: m/z = 304/306/308 (M^+), 289/291/293 ($M^+ - CH_3$), 223/227/225 ($M^+ - CH_3 - C_5H_6$), 196/198 ($M^+ - Me_3Si - Cl$), 73 ($(CH_3)_3Si$), 66 $[C_5H_6]^+$.

2.2.3. 2-Dimethylsilyl(trimethylsilylpropyl)bicyclo[2.2.1]hepta-2,5-diene (**4**)



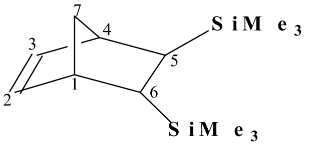
The title compound was prepared by methylation of 14 g (0.046 mol) of **3** with 2.2 mol MeMgI in dry diethyl ether at room temperature for 1 h and under reflux for 1 h. Diethyl ether was distilled off, and the product obtained was diluted with anhydrous hexane, ClMgI was filtered out and a residue was distilled under reduced pressure. The yield of **4** was 71% (bp 95.5–97.5 °C/2 mmHg). ^{1}H NMR ($CDCl_3$) δ 7.04 (d, C^3H), 6.68 (s, C^5H, C^6H), 3.73 (s, C^4H), 3.64–3.60 (m, C^1H), 1.92–1.82 (m, C^7H_2), 1.28–1.41 (m, C^9H_2), 0.52–0.70 (m, C^8H_2, $C^{10}H_2$), 0.11 (s, $C^{11}H_3$), 0.08 (s, $C^{11}H_3$), 0.02 (s, $C^{12}H_9$). IR(KBr): 1296, 1248 (Si–C), 864, 832, 760, 696 cm^{-1} (Si–C). MS (70 eV), $C_{15}H_{28}Si_2$, Calcd mass = 264: $m/z = 264(M^{+\cdot})$, 249($M^+ - CH_3$), 198 ($M^+ - C_5H_6$), 183 ($M^+ - CH_3 - C_5H_6$), 150 ($M^+ - Me_3$-$SiCH_2CH_2CH$), 149 ($M^+ - Me_3SiCH_2CH_2CH_2$), 83 (M^+ - $- Me_3Si(CH_2)_3 - C_5H_6$), 73 $[(CH_3)_3Si]^+$, 66 $[C_5H_6]^{+\cdot}$.

*2.2.4. Endo–exo-5,6-bis(trichlorosilyl)bicyclo[2.2.1]hept-2-ene (**5**)*



6.4 g (97.5 mmol) of cyclopentadiene was added dropwise to 19.2 g (65 mmol) of *trans*-1,2-bis(trichlorosilyl)ethene for 1 h at 50 °C. Then temperature was gradually raised to 90 °C, and the mixture was stirred at this temperature for 3 h. Distillation of resulting mixture under reduced pressure afforded 21.1 g of **5** (yield 90%); bp 69–71 °C/0.05 mmHg. ^{1}H NMR ($CDCl_3$) δ 6.36–6.27 (m, C^2H or C^3H), 6.27–6.18 (m, C^2H or C^3H), 3.50 (s, C^1H or C^4H), 3.39 (s, C^1H or C^4H), 2.27–2.18 (m, C^6H *exo*), 1.65–1.53 (m, C^7H_2), 1.51–1.44 (m, C^5H *endo*). ^{13}C NMR ($CDCl_3$) δ 135.1, 130.5 (C^2, C^3), 45.2(C^7), 43.9, 42.4 (C^1, C^4), 32.9, 32.2 (C^5, C^6).

*2.2.5. Endo–exo-5,6-bis(trimethylsilyl)bicyclo[2.2.1]hept-2-ene (**6**)*



To a stirred solution of CH_3MgI in diethyl ether (prepared from 1.6 mol Mg and 1.6 mol CH_3I) under dry argon 55.3 g (153 mmol) of **5** in 45 ml of dry diethyl ether was slowly added under reflux for 2 h. Then the mixture was stirred under reflux for 1.5 h. Diethyl ether was distilled off, and the product obtained was diluted by 250 ml of anhydrous hexane. Upper layer was removed. Residue product was poured carefully in water and was acidified by a little portion of NH_4Cl water solution. Upper layer was removed again. After removing the solvent the residue was distilled under reduced pressure. The yield of **6** was 28.8 g (80%); bp 81.0–81.5 °C/3 mmHg. ^{1}H NMR ($CDCl_3$) δ 6.1–6.03 (m, 1H, C^2H or C^3H), 5.93–5.85 (m, 1H, C^2H or C^3H), 3.02(s, 1H, C^1H or C^4H), 2.80(s, 1H, C^1H or C^4H), 1.25–1.16 (m, 1H, C^6H *exo*), 1.12–1.02 (m, 2H,C^7H_2), 0.46–0.39(m, 1H, C^5H *endo*), 0.04 (s, 9H, $SiMe_3$ *exo*), -0.06 (s, 9H, $SiMe_3$ *endo*). ^{13}C NMR ($CDCl_3$) δ 137.8 132.8 (C^2, C^3), 49.6, 46.5, 44.9 (C^1, C^4 C^7), 27.8 (C^5, C^6), -0.3 ($SiMe_3$ *exo*) and -0.9 ($SiMe_3$ *endo*).

2.3. Polymerization procedure

The polymerization in the presence of $RuCl_3{\cdot}3H_2O$ and $RuCl_2(PPh_3)_3$ was carried out using the procedure previously described [29].

The polymerization in the presence of WCl_6/1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMSB) was performed under dry argon in a reaction vessel equipped with magnetic stirring bar. TMSB was added to 0.01 M toluene solution of WCl_6 (TMSB/WCl_6 = 3 mol/mol). The color of the solution changed from deep blue to deep purple. After 5–10 min, the monomer was added. The polymers were isolated using standard procedures.

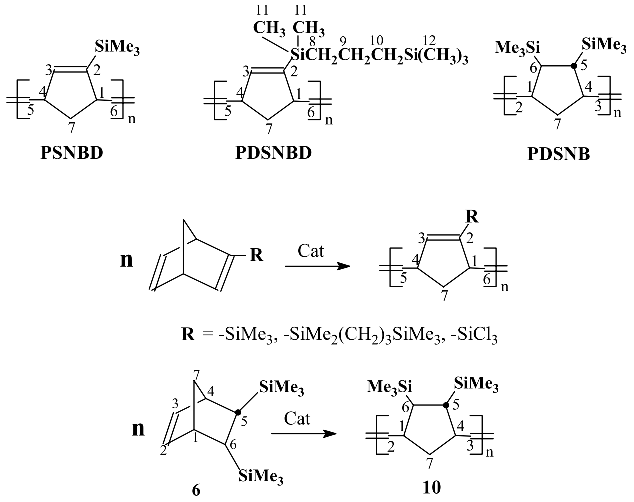
The ^{1}H and ^{13}C NMR spectra were assigned as follows:

Polymer from *2-Dimethylsilyl(trimethylsilylpropyl)bicyclo[2.2.1]hepta-2,5-diene*: ^{1}H NMR ($CDCl_3$) δ 5.82 (broad s, 1H, C^3H), 5.60–4.95 (broad m, 2H, C^5H, C^6H), 3.65 (broad s, 1H, C^4H), 3.27 (broad s, 1H, C^1H), 2.33 (broad s, 1H, C^7H, *syn*), 1.33 (broad s, 3H, C^7H, *anti*, C^9H_2), 0.8–0.47(broad m, 4H, C^8H_2 and $C^{10}H_2$), 0.05 (s, 6H, $Si(CH_3)_2$), -0.01 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$) δ 147.4 (s, C^2), 145.6 (m, C^3), 134.6, 134.3, 133.7, 133.1, 132.2 (C^5, C^6), 54.1, 53.9 (C^4, *trans*), 50.7 (C^1, *trans*), 48.2, 47.9 (C^4, *cis*), 45.8 (C^1, *cis*), 41.2, 40.7, 40.2, 36.1 (C^7), 21.4, 20.2, 18.4 (C^8, C^9, C^{10}), -1.5, -2.4, -2.6 ($Si(CH_3)_2$, $Si(CH_3)_3$).

Polymer from *endo-exo-5,6-bis(trimethylsilyl)bicyclo[2.2.1]hept-2-ene*: ^{1}H NMR ($CDCl_3$) δ 5.6–5.08 (m, 2H, C^2H, C^3H), 3.01, 2.86 (broad s, 2H, C^4H, C^7H, cis), 2.65, 2.50 (broad s, 2H, C^4H, C^7H, trans), 1.74 (broad s, 1H, C^6H, *exo*), 1.42–1.0 (m, 2H, C^7H_2), 0.92 (broad s, 1H, C^5H, *endo*), -0.003 (broad s, 18H, 2 $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ 135.8, 135.2, 134.1, 134.0, 132.2, 132.2, 131.8, 130.7 (C^2, C^3), 48.3, 48.2, 47.3, 47.1, 45.3, 45.2, 44.8, 44.2, 43.9, 43.1, 42.8, 41.8, 41.8, 39.3 (C^1, C^4 C^7).

3. Results and discussion

For elucidation of relationship between the chemical structure of poly(cyclopentylenevinylene)s and poly(cyclopentenylenevinylene)s (the presence, number and location of Me_3Si—side groups) and the gas permeation parameters of the respective polymers the monomers **2**, **4**, **6** (see Section 2) and corresponding polymers were synthesized.



Scheme 2.

Earlier the gas permeation parameters have been reported mainly for polynorbornenes prepared in the presence of ‘classical’ Ru- and W-containing catalysts [8–14]. Because of it the same catalytic systems were used in this work. Hence the synthesis of novel polymers was undertaken and successfully performed in the presence of WCl_6-1,1,3,3-tetramethyl-1,3-disilacyclobutane(TMSB), $RuCl_2(PPh_3)_3$, and $RuCl_3{\cdot}H_2O$ (see Scheme 2). It has been shown that all of them do not interact with Si–C bonds [30].

The results of the ROMP are presented in Table 1.

Only W-containing catalysts turned out to be activity in the ROMP of norbornadienes **1**, **2**, **4**. One can assume that incapability of norbornadiene substrates to ROMP in the presence of Ru-containing catalysts is related to di-*endo* chelation of these molecules to metal carbene centre applying the arguments proposed earlier for unsubstituted norbornadiene [1]. ROMP of highly reactive $SiCl_3$-substituted norbornadiene **1** proceeds with formation of a polymer soluble in the reaction mixture, but crosslinked when it was isolated. Its methoxylation in methanol also led to a cross-linked insoluble polymer.

The characteristics of PSNBD prepared in this work were identical to those described in the literature [27]. In the presence of WCl_6/TMSB the new monomer, di-silyl-substituted norbornadiene **4**, was successfully polymerized giving previously unknown polymer PDSNBD containing two silicon atoms in the side group. NMR and IR spectra confirmed its structure. The *cis*/*trans* ratio of vinylene double bonds determined by ^{1}H NMR according to [27] and by ^{13}C NMR (54.1, 53.9 (C^1, *trans*), 50.7 (C^4, *trans*), 48.2, 47.9 (C^1, *cis*), 45.8 (C^4, *cis*) was 43/57.

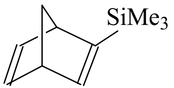
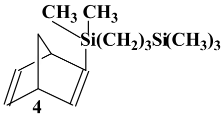
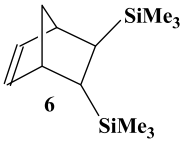
Unlike the studied norbornadienes, the norbornene derivative **6** readily polymerizes in the presence of both Ru- and W-catalysts with the yield up to 98%. A novel polymer PDSNB is easily soluble in aromatic solvents and after 2–3 precipitations in methanol became perfectly white. In agreement with this observation, experimental analysis indicated a low residual content of Ru − 60 ppm. ^{1}H NMR spectra allowed to determine the cis/trans ratio for double bonds in PDSNB on the basis of the signals of allylic protons (Fig. 1). The polymeric products PDSNB prepared in the presence of $RuCl_3{\cdot}3H_2O$, $RuCl_2(PPh_3)_3$, and WCl_6/TMSB contained 6, 9, and 54% of *cis*-double bonds, respectively.

Investigation of the gas permeation parameters of PSNBD and PDSNB provides an opportunity to examine the following effects of the modification of polymer structure:

(i) the appearance of the double bond in the cycle: comparison of PSNBD with poly(trimethylsilyl norbornene) (PSNB) studied earlier [7,14];
(ii) the introduction of the second $Si(CH_3)_3$ group in the repeat unit: comparison of PDSNB with PSNB [7, 14].

However, another factor should be taken into account in

Table 1
ROMP of substituted norbornene and norbornadienes

Monomer (M)	Catalyst	[M]/[cat] (mol/mol)	Solvent	*T* (°C)	*t* (h)	Yield (%)	M_w	PDI	T_g (°C)	*Cis* (%)
 **2**	WCl_6/TMSB	70	$PhCH_3$	16	0.5	97	51,100	2.9	108	42
		250	$PhCH_3$	16	2.5	70	549,000	3.1	–	
 **4**	WCl_6/TMSB	92	$PhCH_3$	25	24	40	318,700	3.0	5	43
 **6**	$RuCl_3{\cdot}3H_2O$	40	PhCl, C_2H_5OH	75	12	98	732,900	1.4	167	6
	$RuCl_2(PPh_3)_3$	42	PhCl	60	6	62	464,400	5.3	–	9
	WCl_6/TMSB	50	$PhCH_3$	20	24	93	291,400	3.1	–	54

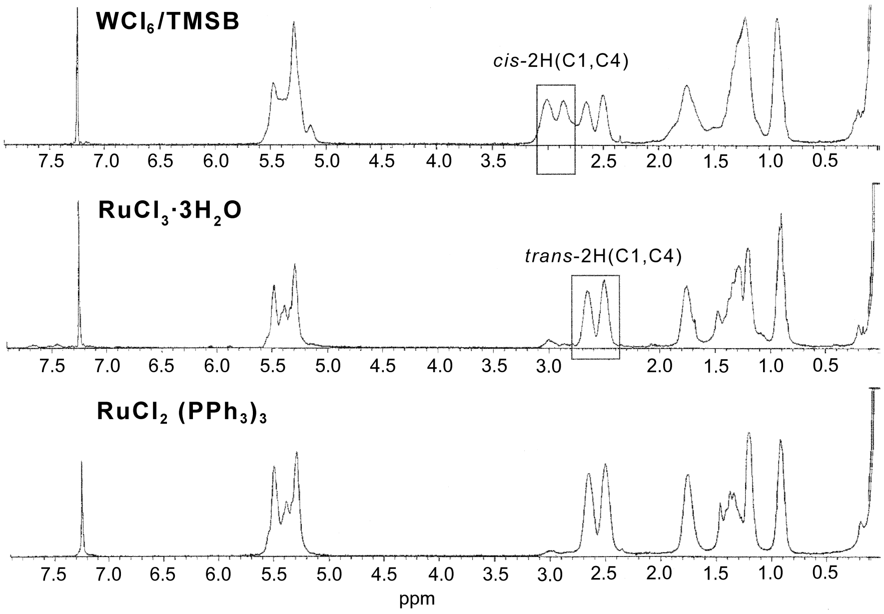


Fig. 1. ^{1}H NMR spectra of poly(bis(trimethylsilyl)cyclopentylenevinylene), synthesized with various catalysts.

such comparison. It has been shown [12,13,31] that cis/trans ratio in the main chain influences the observed transport parameters. These effects are not strong: for example, permeability coefficients of oxygen vary in the range 16.5–20.9 Barrer, when the cis-content is changed from 31 to 75% [14]. Nevertheless, possible influence of this factor was taken into consideration. A comparison of transport properties was realized for the polymers obtained in the presence of the same catalyst.

Permeability coefficients are presented in Table 2. It can be concluded that introduction of a double bond in the cyclopentylene ring in PSNBD does not cause noticeable changes in gas permeability. With one exception (CH_4), these changes can be assumed to be within the statistical error of the determination. In PSNBD double bonds are included in five-membered ring. Because of it the appearance of an additional double bond in the main chain doesn't result in increases in the glass transition temperature as can be seen from the T_g values of PSNB and PSNBD (Table 1).

Entirely different result is observed for PDSNB, the polymer containing two adjacent $Si(CH_3)_3$ groups, prepared on $RuCl_3{\cdot}3H_2O$. As has been mentioned in Introduction, gas permeation properties of numerous polymers of different classes (vinylic, acetylenic, etc) containing silyl groups (SiR_3) have been studied. In all the cases the SiR_3 group appeared only once in the repeat units. If substituents contained more than one Si atom within the same longer side group the observed permeability was rather modest (e.g. 16 Barrer for permeability coefficient of oxygen in silyl-substituted polynorbornene [11]). PDSNB presents a very rare example of design with two $Si(CH_3)_3$ attached to different sites within a repeat unit. The data of Table 2 indicate that its permeability is relatively high: this polymers is characterized by an increase in the permeability coefficients by a factor 6 in average as compared with PSNB containing only one $Si(CH_3)_3$ group and prepared in the presence of the same catalytic system. Introduction of the second $Si(CH_3)_3$ group in the polynorbornene main chain is accompanied by approximately the same increase in permeability as for the first group $Si(CH_3)_3$. Some differences can be noted depending of the gas used for comparison and of the cis/trans configuration of the main chain.

A standard way to compare gas permeation properties of different membrane materials is to use so-called Robeson diagrams [32], that is correlations of permeability coefficients P_i and permselectivity $\alpha = P_i/P_j$, where P_i and P_j are permeability coefficients of two gases. An example of such diagram prepared for different norbornene polymers is shown

Table 2
Permeability coefficients P (Barrer) of silyl-substituted polynorbornenes and polynorbornadiene

Polymer	Catalyst	T_g (°C)	He	H_2	O_2	N_2	CO_2	CH_4	C_2H_6
PSNB [14]	W	101	58	77	21	6.2	79	17	–
	Ru	85	51	67	16	4.8	66	4.8	–
PSNBD	W	108	–	81	20	4.9	64	8.5	4.5
PDSNB	Ru	167	240	375	95	25	445	45	30

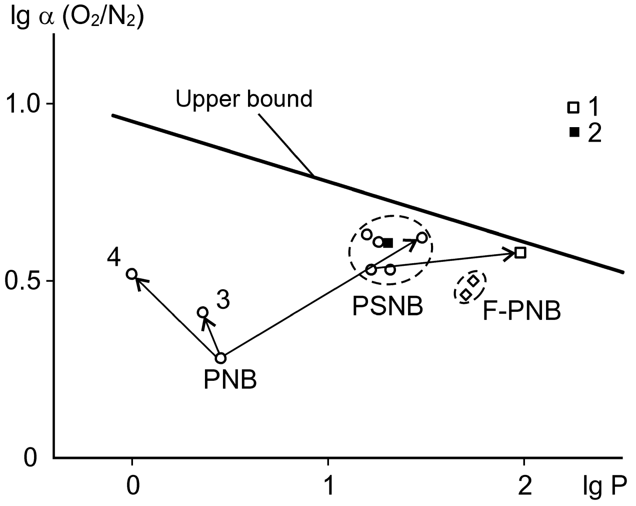


Fig. 2. Correlation of permeability coefficients $P(O_2)$, Barrer and separation factors $\alpha(O_2/N_2)$ for norbornene and norbornadiene polymers. The line shows upper bound according to Robeson [32]. 1—PDSNB, 2—PSNBD, 3—poly(chloronorbornene), 4—polymer of spiro{bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane} [8]; 5—poly(*exo*-norbornene-5,6-dicarboximide) according to Ref. [17]; the group of the data points for PSNB and fluorinated polynorbornene according to Refs. 10,11,14.

in Fig. 2 for gas pair O_2/N_2. The line (so-called 'upper bound' suggested by Robeson [32]) shows upper limit of the achieved P and α parameters for all the polymers studied. Usually, a trade-off between permeability and permselectivity is observed, that is materials with larger permeability are distinguished by smaller permselectivity and vice versa. Such behavior is illustrated in Fig. 2 by the data points for polynorbornene and two its derivatives containing chlorine as the side group and having spiro-heptane structure. Opposite trend is observed due to introduction of the second $Si(CH_3)_3$ group in the structure of PSNB: a significant increase in permeability with no reduction of permselectivity is observed; in fact, the latter quantity even slightly increases. It can be noted that the data point of PDSNB approaches upper bound line, what was not observed for other norbornene polymers. The same behavior can be noted for other gas pairs, for example, for H_2/N_2. It is interesting that the same trend is characteristic for the pair PNB and PSNB as is shown by an arrow. On the other hand, another polynorbornene derivative containing two silicon atoms in the same side group ($Si(CH_3)_2$-$CH_2Si(CH_3)_3$) did not reveal such an effect [11]. It is likely related with self-plasticization effect caused by long side group: T_g of this polymer decreased down to 24 °C, whereas the glass transition temperature of PSNB is in the range 101–113 °C [11,14]. The same conclusion is apparently true for polymerization product of monomer 4 of the present study containing even longer substituent: owing to this, the polymer is rubbery at room temperature (Table 1).

Table 3
Diffusion coefficients $D \times 10^7$ (cm^2/s) in silyl-substituted polynorbornenes and polynorbornadiene

Polymer	Catalyst	O_2	N_2	CO_2	CH_4	C_2H_6
PSNB [14]	W	6.0	2.6	3.2	1.5	–
	Ru	4.2	1.7	2.2	0.90	–
PSNBD	W	2.0	1.7	1.8	0.90	0.12
PDSNB	Ru	4.6	2.8	4.0	1.3	0.16

Table 4
Solubility coefficients S (cm^3(STP)/cm^3 atm) in silyl-substituted polynorbornenes and polynorbornadiene

Polymer	Catalyst	O_2	N_2	CO_2	CH_4	C_2H_6
PSNB [14]	W	0.27	0.18	1.9	0.86	10.8
	Ru	0.30	0.21	2.3	0.40	6.7
PSNBD	W	0.76	0.22	2.7	0.72	2.85
PDSNB	Ru	1.6	0.68	8.5	2.6	14.2

An introduction of bulky side groups is often considered as a way to increase gas permeability, free volume and improve membrane properties of a material. Recently, preparation and gas permeation parameters of poly(*exo*-norbornene-5,6-dicarboximide)s with adamantly, cyclohexyl, and phenyl side groups were reported [17]The results of this work show that this approach does not necessarily lead to enhanced gas permeability: all the polymers mentioned and also the copolymers with norbornene show rather low permeability ($P(O_2)$ in the range 1.2–2.1 Barrer) combined with small separation factors for O_2/N_2 pair. Corresponding data points are shown in the Robeson diagram. One can assume that low gas permeability is induced by strong inter-chain interactions due to the presence of polar C=O and C–N bonds in these polymers.

It is typical for glassy polymers that a variation of the permeability coefficients with the molecular sizes of different gases reveals so-called diffusivity controlled selectivity that is permeability coefficients P for a series of penetrants follow the same trend as the diffusion coefficients D. This is also true for PDSNB: penetrants with small molecules like He and H_2 are characterized by relatively high permeability, permeability of methane is larger than that of ethane.

As gas permeation proceeds according to solution-diffusion mechanism, that is $P = DS$, the changes of permeability can be explained by variation of diffusion (D) or solubility (S) coefficients. These values are given in Tables 3 and 4. It is seen that PDSNB is not distinguished by enlarged diffusion coefficients as compared to other polymers presented in Table 3. On the other hand, solubility coefficients of various gases in PDSNB are significantly higher than those of other norbornene/norbornadiene polymers shown in Table 4. Therefore, it is an increased solubility that is a reason for enhanced gas permeability of this polymer.

Solubility of gases in glassy polymers are well described by semi-empirical the dual mode sorption model [33,34]. The concentration of the sorbed gas C can be expressed as a function of gas pressure p as:

$$C = k_D p + C'_H \frac{bp}{1 + bp} \tag{1}$$

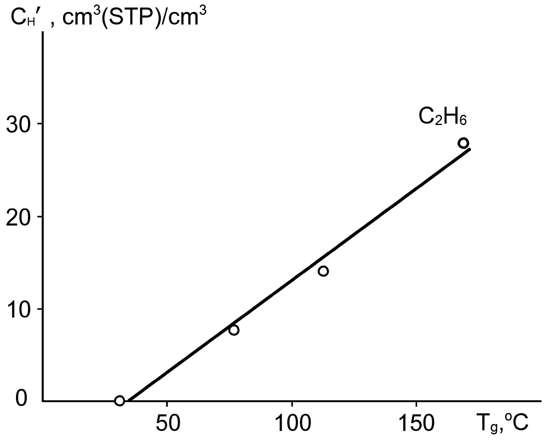


Fig. 3. Effects of the glass transition temperature T_g on the Langmuir sorption capacity C'_H (cm^3(STP)/cm^3) of sorption of ethane in norbornene polymers [10,11].

where k_D is the Henry's law parameter characterizing sorption into the densified equilibrium matrix of the glassy polymer, C'_H is the Langmuir sorption capacity, which characterizes sorption into the non-equilibrium excess volume associated with the glassy state, and b is the Langmuir affinity parameter. At low pressure limit solubility coefficient S can be expressed by

$$S = k_D + C'_H b \tag{2}$$

It has been shown [35] that in glassy polymers the contribution of the second term amounts 90% of the solubility coefficient. On the other hand, the C'_H parameter was shown to increase with the glass transition temperature of polymer [36]. Fig. 3 shows the same dependence for sorption of ethane in different norbornene polymers [10,14]. As two other parameters of the dual mode sorption model, k_D and b, do not depend on T_g, it means that a growth of C'_H should lead to increases in solubility coefficients with T_g. Fig. 4 indicates that this is really the case. Two points that deviate downward from the dependence for Si-containing polynorbornenes were neglected. They correspond to fluorine-containing polynorborenes [10]. This is, probably, another manifestation of negative interactions between hydrocarbon solutes and fluoropolymers (or fluorocarbon solutes and hydrocarbon based polymers) studied by Freeman et al [37–39]. Note that the S values of two novel polymers (PSNBD and PDSNB) obtained via permeability and diffusivity, that is as a ratio $S = P/D$, are in line with the measured by direct sorption method solubility coefficients of other silicon containing norbornene polymers. Therefore, large solubility coefficients of PDSNB are caused by its high glass transition temperature. It means that more rigid chains of this polymer cannot be packed efficiently and larger unrelaxed free volume should be observed for this polymer.

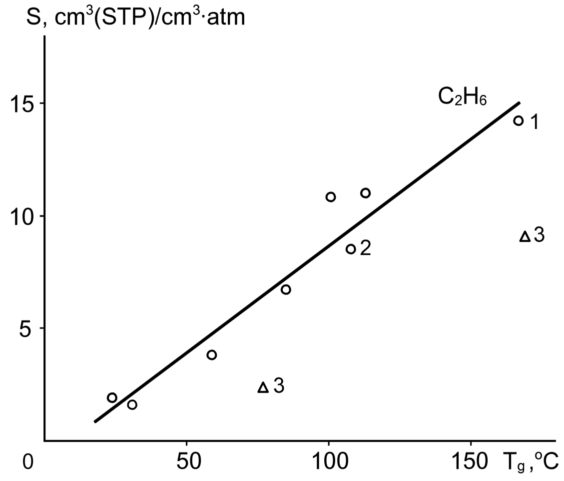


Fig. 4. Effects of the glass transition temperature T_g on solubility coefficients of ethane (cm^3(STP)/cm^3 atm) in norbornene and norbornadiene polymers: 1—PDSNB, 2—PSNBD, 3—fluorine-containing polynorbornenes [10], other data points are based on Refs. 11,14.

Table 5
Positron annihilation lifetime spectra (τ_i, ns, I_i, %) of PSNB [14] and PDSNB (this work) obtained in the presence of Ru catalyst

τ_1	I_1	τ_2	I_2	τ_3	I_3
PSNB					
0.255	53.7	0.798	23.1	2.74	23.2
PDSNB					
0.252	49.6	0.660	17.2	3.18	33.2

This conclusion was confirmed, at least qualitatively, by the study using positron annihilation lifetime spectroscopy. In Table 5, lifetime spectra of PSNB and PDSNB are compared. It is seen that introduction of an additional Si(CH$_3$)$_3$ group leads to an increase in long lived lifetime τ_3, which can be related to the radius of free volume element (FVE) [40,41], and corresponding intensity I_3, which correlates with the concentration of FVE. The increase in τ_3 corresponds to a change of the radius of FVE from 3.4 to 3.8 Å. All this is consistent with an increase in gas permeability of PDSNB.

Permselectivity or separation factors

$$\alpha_{ij} = P_i/P_j \tag{3}$$

are an extremely important parameter of membrane materials. As Table 6 indicates an appearance of an additional double bond or Si(CH$_3$)$_3$ side group in the repeat units does not induce significant changes in permselectivity. Hence, a noticeable increase in permeability of PDSNB is not accompanied by decrease in selectivity.

The separation factors α_{ij} can be presented as a product of components responsible for selectivity diffusion and sorption, that is

$$\alpha_{ij} = \alpha_{ij}^D + \alpha_{ij}^S \tag{4}$$

Possible effects of the structure of repeat units on α_{ij}^D and α_{ij}^S can be analyzed using Tables 7 and 8. It can be concluded that these values do not change significantly due to variation of the structure of repeat unit of the polymers considered.

Table 6
Selectivity of gas permeation $\alpha = P_i/P_j$ of silyl-substituted polynorbornenes and polynorbornadiene

Polymer	Catalyst	H_2/N_2	H_2/CH_4	O_2/N_2	CO_2/N_2	CO_2/CH_4
PSNB [14]	W	12.4	4.5	3.4	12.7	4.6
	Ru	14.0	14.0	3.3	13.7	13.7
PSNBD	W	16.5	9.5	4.1	13.1	7.5
PDSNB	Ru	15	8.3	3.8	17.8	9.9

Table 7
Diffusivity selectivity $\alpha^D = D_i/D_j$ of silyl-substituted polynorbornenes and polynorbornadiene

Polymer	Catalyst	O_2/N_2	CO_2/N_2	CO_2/CH_4
PSNB [14]	W	2.3	1.2	2.1
	Ru	2.5	1.3	2.4
PSNBD	W	1.2	1.1	2.0
PDSNB	Ru	1.6	1.4	3.1

Table 8
Solubility selectivity $\alpha^S = S_i/S_j$ of silyl-substituted polynorbornenes and polynorbornadiene

Polymer	Catalyst	O_2/N_2	CO_2/N_2	CO_2/CH_4
PSNB [14]	W	1.5	16.3/10.6	3.4/2.2
	Ru	1.4	13.7/11.0	3.0/5.7
PSNBD	W	3.5	12.3	3.8
PDSNB	Ru	2.4	12.5	3.3

4. Conclusions

Novel 2-dimethylsilyl(trimethylsilylpropyl)bicyclo[2.2.1]hepta-2,5-diene and *endo–exo*-5,6-bis(trimethylsilyl)bicyclo[2.2.1]hept-2-ene have been polymerized by ROMP scheme in the presence of $RuCl_3{\cdot}H_2O$, $RuCl_2(PPh_3)_3$, and WCl_6/tetramethyldisilacyclobutane catalysts. High molecular mass silyl-substituted and poly(cyclopentylenevinylene)s poly(cyclopentenylenevinylene)s have been prepared. Transport properties of novel aliphatic cyclo-linear glassy polymers are studied. Permeability, diffusion and solubility coefficients of poly(trimethylsilyl norbornadiene) virtually coincide with those of poly(trimethylsilyl norbornene). Thus, appearance of double bond in five-membered ring does not influence the transport properties of the polymer. On the other hand, an introduction of the second $Si(CH_3)_3$ group in the cyclopentyl ring results in strong increase in gas permeability. Comparison of the diffusion and solubility coefficients, as well as the glass transition temperatures of structurally relative polynorbornene derivatives containing one and two $Si(CH_3)_3$ groups indicates that the increase in permeability is caused by larger rigidity of the chains leading to larger solubility coefficients and non-equilibrium free volume. The latter conclusion is confirmed by positron annihilation lifetime spectra.

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