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Addition-Type Polynorbornenes with $Si(CH_3)_3$ Side Groups: Synthesis, Gas Permeability, and Free Volume

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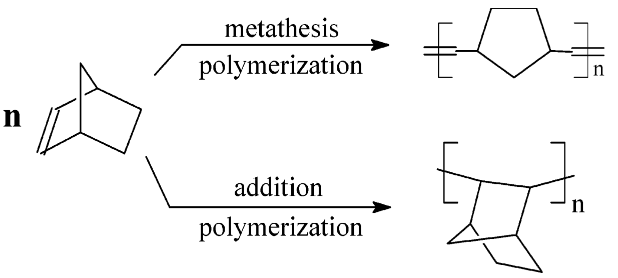
ABSTRACT: Polymerization of norbornene bearing $Si(CH_3)_3$ groups in the 5-position with the opening of double bonds and its copolymerization with 5-(*n*-hexyl)norbornene were realized in the presence of nickel(II) naphthenate/methylaluminoxane catalyst system. The completely saturated homopolymer containing $Si(CH_3)_3$ group (APNSi) and a copolymer containing both $Si(CH_3)_3$ and *n*-hexyl side groups (ACPNHSi) were prepared. The polymers have molecular mass of about 300 000 and a high glass transition temperature (T_g > 340 °C). Gas permeation properties of the polymers obtained were studied. APNSi reveals unusually high gas permeation parameters, e.g., $P(O_2)$ of about 800 Barrer for different samples. This polymer also exhibits solubility controlled gas permeation: the permeability coefficients increase in the series of *n*-alkanes C_1-C_4 when the size of the penetrant increases. Free volume in addition type substituted polynorbornenes was studied using positron annihilation lifetime spectroscopy (PALS). This method indicated that very large sizes of free volume elements are characteristic for APNSi what explains its great gas permeability. Another interesting feature of this polymer is an independence of the annihilation parameters (lifetimes τ_i and intensities I_i) of temperature in a wide range of its variation. Thus, APNSi is a novel representative of high free volume, high permeability glassy polymers, and it is a potential material for gas separation membranes.

Introduction

Polymerization of norbornene and its derivatives opens possibilities for preparing of a big wealth of materials with variations of both chemical and spatial structures. In the presence of catalysts on the basis of WCl_6, $RuCl_3$, and Re_2O_7/Al_2O_3, as well as Grubbs Ru complexes ring-opening metathesis polymerization (ROMP) takes place with formation of cyclolinear structures shown in Scheme 1. Polymers of norbornene itself and its various derivatives with side groups such as CN, $Si(CH_3)_3$, $Ge(CH_3)_3$, CF_3, Cl, etc. have been prepared and investigated as potential membrane materilas.[1−6] Because of the presence of double bonds in the main chain, different cis−trans configurations of the polymer units can be obtained depending on the choice of the catalysts.[7,8] It was shown that the properties of the polymers prepared (such as gas permeability, free volume, solubility coefficients) strongly depend on the nature of the side groups and the cis-content in the main chains. All ROMP-type polynorbornenes have relatively flexible chains: the glass transition temperatures in the most cases are in the range 24−140 °C.

However, since norbornenes are cycloolefins, they can be also polymerized via the opening of double bonds in the presence of Ni and Pd catalysts.[9−11] This reaction, addition-type polymerization, leads to bulky bicyclic repeat units that do not contain unsaturated bonds (Scheme 1). Properties of addition−polymerized polynorbornenes (APNs) are entirely different from those of the ROMP polymers: APNs, nonsubstituted or with small alkyl side groups, have extremely high glass transition temperatures. Though these polymers were considered as candidates for use as optical materials, electrical insulators, and barrier materials, too high a T_g made practically impossible their processing by usual methods. However, the copolymers of norbornene and ethylene[12] preserving the best properties of APNs have T_g's in a reasonable temperature interval. Such copolymers now are being produced in industrial scale by Ticona Co (Germany) under the trade-name TOPAS.

Scheme 1



APNs produced with different catalysts may have different microstructure.[13,14] Depending on the direction of the bridgehead carbon atom of five-membered cycle in APN, the main chain may have a diisotactic, a disyndiotactic, or an atactic structure. This can partly explain rather big variation of gas permeation properties of APNs prepared in the presence of different catalysts.[15,16]

Both ROMP polynorbornenes and APNs can attract interest as potential materials for gas and vapor separation membranes. However, ROMP polymers include double bonds, and this makes them relatively unstable materials: thus, unsubstituted polynorbornene shows obvious signs of deterioration (appearance of color and brittleness) after several weeks of storage in

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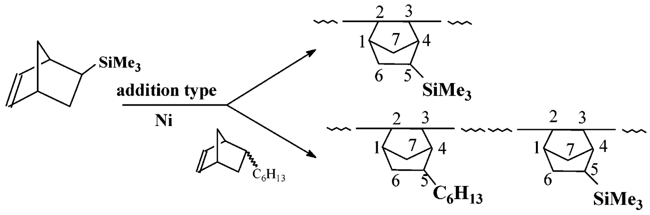
Scheme 2



the ambient atmosphere. On the contrary, APNs are saturated polymers, so their chemical stability must be much better.

According to contemporary wisdom on highly permeable polymers, among the prerequisites for high gas permeability and large free volume materials there are: presence of bulky nonpolar substituents, rigid main chains (great rotation barriers in them), and appearance of periodic kinks (frequent chain disruption).[17−19] All of these features can be anticipated in APNs (see, e.g., ref 20), so an appropriately selected catalytic system for the synthesis, chemical structure of a monomer, and molecular mass that would provide sufficiently good film forming properties can lead to APNs with attractive gas permeation properties.

Studies of the transport properties of unsubstituted addition type polynorbornene and polyalkylnorbornenes have been just started.[15,21] Some results have been reported for norbornene-ethylene copolymers of different composition.[22]

In the present work, we report a successful synthesis of a novel APN, polymer bearing $Si(CH_3)_3$ group in the 5-position (Scheme 2). Appearance of this substituent, by analogy with other polymer classes,[17] would strongly enhance gas permeability and free volume. With this in mind, we have studied gas permeation parameters for a number of gases and investigated free volume using positron annihilation lifetime spectroscopy (PALS). For comparison, we also prepared and studied two other APNs: nonsubstituted polynorbornene and random copolymer of 5-trimethylsilyl-2- norbornene and 5-*n*-hexyl-2-norbornene.

Experimental Section

Materials. Methylaluminoxane or MAO (cocatalyst) was received from Aldrich and used as commercial 1.4 M solution in toluene. Nickel naphtenate $[(Nph)_2Ni]$ (catalyst) was received from Yefremov Synthetic Rubber Plant (Russia). Norbornene (99%, Aldrich) was dissolved in toluene and dried over sodium metal. 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 procedures described in the literature.[10] It was purified by passing through a column with neutral aluminum oxide for chromatography (Fluka) and distilled over CaH_2 in a vacuum. 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.

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 500 operating at 125 MHz for ^{13}C. Each polymer sample was dissolved in $CDCl_3$ up to a concentration of 10%. 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. Thermal gravimetric measurements were carried out using a Perkin-Elmer TGA-7 instrument. The content of the *exo*- and *endo*-5-trimethylsilyl-2-norbornene isomers in the final polymerization mixture was determined using gas−liquid chromatography (GLC). GLC data were obtained on a capillary column SE−30 (50m) and a FID detector. (The sample was preliminary dissolved in 1 mL of methanol). Wide-angle X-ray scattering (WAXS) study was carried out on an instrument with two-coordinate AXS detector (Bruker) with the Cu Kα line (wavelength of 0.154 nm).

Polymerization Procedure. In the typical procedure, the toluene solution of nickel naphtenate $[(Nph)_2Ni]$ and monomer were introduced into preliminary purged in a vacuum and filled with argon round-bottom glass ampule (10 mL). Polymerization was initiated by adding toluene solution of MAO (Al/Ni was 100). The reaction mixture acquiring slightly red-brown color was continuously stirred in darkness for an appropriate period at ambient temperature. The polymers were precipitated by acidified ethanol (ethanol:HCl = 10:1), separated, washed by several portions of ethanol and dried in a vacuum at 80−90 °C up to a constant weight. The ^1H NMR spectrum of APNSi ($CDCl_3$) (ppm): 2.0−3.2 (C^1H,C^4H); 0.8−2.5 (C^2H,C^3H, C^5H,C^6H_2,C^7H_2), 0.05 (*endo*-$SiMe_3$); −0.03 (*exo*-$SiMe_3$); ^{13}C NMR ($CDCl_3$) (ppm): 48−60 (C^2,C^3); 40−48 (C^1,C^4); 28−44 (C,$^6C^7$); 0−4 (C,^{5} $SiMe_3$).

Copolymerization runs were carried out in the same way with equimolar mixtures of 5-*n*-hexyl-2-norbornene and 5-trimethylsilyl-2-norbornene. ^1H NMR of copolymer ($CDCl_3$) (ppm): 1.5−3.2 (C^1H,C^4H); 0.5−2.0 (C^2H,C^3H,C^5H,C^6H_2,C^7H_2); 0.86; 1.25(C_6H_{13}); −0.05; −0.01 ($SiMe_3$).

Film Casting. The films of the polymers studied were cast from the 2−3 mass % solution in toluene (or cyclohexane in the case of nonsubstituted APN). The solvent was allowed to evaporate from caps with the bottom formed by stretched cellophane film. After formation of the films, cellophane was wetted, what permitted to detach the film from it. Before testing, the films were kept in a vacuum until the constant weight is attained (for about 1 week). The thickness of the films was in the range 100−200 μm.

Gas Permeation Measurement. Permeability coefficients of novel APNs were determined using the gas chromatographic method.

The steady stream of penetrant gases under atmospheric pressure flew around the upstream part of the film, while the downstream part of it was moved around by the gas carrier—helium or nitrogen (the latter was used in the measurement of permeation rate of H_2 and He). The permeability coefficients were determined by measuring the penetrant concentration in the gas-carrier and the total flow of this mixture. The temperature in the cell was 20−22 °C.

Positron Annihilation Lifetime Spectroscopy. PALS experiments were performed in a vacuum at continuous pumping using a conventional fast−fast coincidence system EGG@ORTEC having a high counting rate (more than 1 million integral number of events in 1 h) and time resolution of about 300 ps full width at half-maximum (fwhm) of the coincidence curve.[23,24] For the temperature controlled PALS experiments, a sample with a 1 MBq ^{22}Na positron source was placed in a refrigerator, i.e., into the cooling system CW303 made by Iwatani Co. Ltd. The temperature was changed automatically by 5 deg steps every hour in the range from 35 to 200 °C. Every PALS spectrum was automatically saved also every hour, resulting in 1−2 million events in the each spectrum. The spectra were analyzed in terms of three or four lifetime components using the PATFIT program: it was shown that a much better fit was achieved and for the four components description. Only the longest lifetime components (lifetime τ_3 and τ_4 and intensity I_3 and I_4) were related to orthopositronium.

Results and Discussion

Synthesis and Properties of APNs. Nonsubstituted polynorbornene (APN), APNSi, and ACPNHSi were obtained by addition polymerization and copolymerization of appropriated monomers on the nickel(II) naphthenate/MAO catalyst system. As a result, saturated polymers were formed according to Scheme 2. The absence of any unsaturation in these polymers

Table 1. Addition Polymerization of 5-(Trimethylsilyl)-2-norbornene and Its Copolymerization with 5-*n*-Hexyl-2-norbornene on the $(Nph)_2Ni{-}MAO$ Catalytic System (MAO/Ni = 100)

comonomers					polymer composition[a]			
M1	M2	[M1]/[M2]/[Cat]	time, h	yield, %	M_1	M_2	M_w[b]	M_w/M_n
$NBSiMe_3$		600	27	63	100		270 000	2.4
$NBSiMe_3$		1000	24	56	100		290 000	2.0
$NBSiMe_3$		1500	24	55	100		324 000	2.9
$NBSiMe_3$		3000	24	32	100		270 000	2.9
$NBSiMe_3$	NBC_6H_{13}	300:300:1	45	68	58	42	229 000	2.1
$NBSiMe_3$	NBC_6H_{13}	750:750:1	120	63	64	36	442 000	1.9

[a] Determined by NMR spectra. [b] Determined by GPC relative to polystyrene standards.

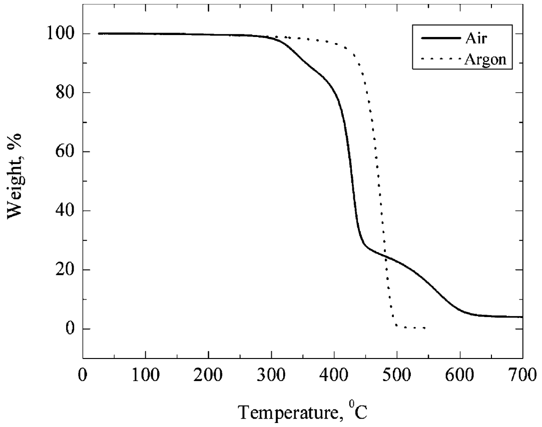


Figure 1. TGA scan of APNSi.

was confirmed by both ^1H NMR (no signals at 5−6 ppm) and IR spectroscopy (no bands in the 1620−1680 cm^{-1} region).

It should be noted that polymerization of 5-trimethylsilyl-2-norbornene proceeded substantially slower than that of unsubstituted norbornene. When norbornene was polymerized with the catalyst $(Nph)_2Ni{-}MAO$ ([norbornene]:[Ni]:[MAO] = 1000:1:50), the reaction mixture became immobile already after 1 min. After 3−4 h the yield of polynorbornene amounted to 90% while the yield of APNSi was 50−60% even after 24 h. The APN obtained was insoluble in toluene and chlorobenzene but was soluble in cyclohexane. Some details of the 5-trimethylsilyl-2-norbornene polymerization process are presented in Table 1. The initial monomer consisted of equimolar mixture of its endo/exo isomers. After addition polymerization, the endo isomer comprised the main part of unreacted monomer (according to GLC analysis). When monomer/catalyst mole ratio increased the molecular mass of polymer became somewhat higher and its film-forming properties improved. ACPNHSi synthesized under the same conditions (Table 1) contained about 40% of the units with *n*-hexyl substituent. GPC analysis confirmed the formation of copolymers by demonstrating unimodal and rather narrow molecular mass distribution for all the polymers obtained in this study. APNSi and ACPNHSi were soluble in aromatic solvents and chloroform. According to DSC data, the synthesized polymers did not show any glass transition up to 300 °C. The TGA scans indicated that APNSi has 5% decomposition in air of 340 °C and in argon of 450 °C (Figure 1). It means that the glass transition of this polymer is significantly higher than 340 °C.

The density of APNSi was found to be equal to 0.883 ± 0.001 g/cm^3. This value (so-called geometric density) was obtained as the ratio of the mass of a film with uniform thickness and its volume averaged for five specimens. This corresponds to the fractional free volume FFV = 0.275 as estimated using the Bondi method.[25] This value can be considered as a relatively large. The density of unsubstituted APN is much higher (1.025 ± 0.01 g/cm^3) and, hence, the FFV of this polymer is significantly smaller. The values of FFV obtained in the present work and taken from the literature for addition type polynorbornenes are compared in Table 2. It is seen that the $Si(CH_3)_3$ side group indeed exerts a strong influence on free volume in APNs.

Table 2. Fractional Free Volume (FFV) of Addition Type Polynorbornenes with Different Side Groups R

R	FFV	refs
$Si(CH_3)_3$	0.275	this work
H	0.15	this work
H	0.115	21
CH_3	0.181−0.188	16
CH_3	0.1704	15

The results of the X-ray investigation of APNSi indicated that this polymer is completely amorphous. Its WAXS pattern included two broad peaks with the maxima at 6.5 and 15.5° of 2θ (Figure 2). This corresponds to a periodicity (*d* spacing) of 13.6 and 5.7 Å, respectively, found via Bragg's law $d_B = \lambda/(2 \sin\theta)$. The first value that is attributed to intersegmental *d* spacing[16] can be considered as an indication of loose chain packing similar to those observed for poly(trimethylsilylpropyne) (PTMSP).[26,27] It is worthwhile to note that the conventional glassy polymers like polycarbonates and polysulfones are characterized by much smaller values of *d* spacing (4−6 Å); that is, they have more densely packed chains.[28]

It is interesting to compare the results of X-ray scattering patterns for three addition type polynorbornenes studied so far—polymers having the following side groups in 5-position: H, CH_3, and $Si(CH_3)_3$ (refs 21 and 16 and this work, respectively). This is done in Table 3. All three polymers can be characterized by two amorphous halos, but the relative intensity of the peak at smaller angles is significantly larger for APNSi than that for

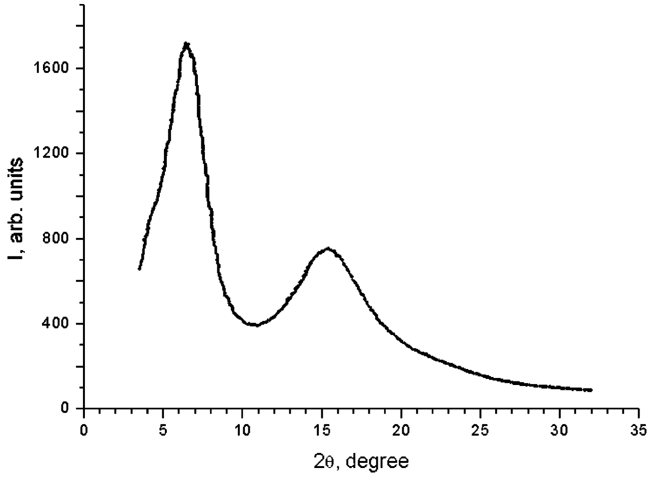


Figure 2. Wide-angle X-ray diffractogram for APNSi.

Table 3. X-ray Scattering Data of Addition Type Polynorbornenes with Different Side Groups

R	$(2\theta)_1$, deg	$(2\theta)_2$, deg	d spacing, Å[a] $(d_B/d_{ic})_1$	d spacing, Å[a] $(d_B/d_{ic})_2$	ref
H	10	18.5	8.8/10.8	4.7/5.8	21
CH_3	9.3	18.2	9.3/11.6	4.9/5.9	16
$Si(CH_3)_3$	6.5	15.5	13.6/16.6	5.7/7.0	this work

[a] The first value is the Bragg's distance $d_B = \lambda/(2 \sin \theta)$, the second one is the interchain distance $d_{ic} = 1.22d_B$.

APN. Different scales for interchain spacing are used in the literature. It is common to find *d* spacing from the maximum angle of the peak diffraction intensity via Bragg's law. On the other hand, it has been proposed that the interchain distance is larger than Bragg's distance by a factor 1.22.[29] To avoid arbitrariness in assessment we used both scales in comparison of norbornene polymers in Table 3. It is seen that when the bulkiness of the side group increases the *d* spacing values estimated via either method also increase. In conclusion, it should be noted that the WAXS pattern obtained for APNSi is consistent with the low density and large FFV of this polymer. It is also in a qualitative agreement with the estimation of free volume using the PALS method (see later in this article).

Depending on the catalyst used in the preparation of APNs, the polymer can have different stereoarchitectures: they differ by mutual directions of bridgehead carbons in the neighboring units. Thus, ^{13}C NMR study indicated atactic structure of APN prepared in the presence of $Ni(acac)_2/MAO$ catalyst,[21] while the molecular simulation results were consistent with 2,3-erythro-diisotactic or 2,3-erythro-disyndiotactic structures of the methyl-substituted polynorbornenes synthesized in the presence of Pd- and Ni-containing catalyst systems.[16] Additional complications can results due to different spatial orientation of the bulky $Si(CH_3)_3$ group in every repeat unit of APNSi (it can be a mixture of endo, exo, head-to-head, head-to-tail, and tail-to-tail arrangements of the repeated unit). Indeed, its NMR spectrum shows a broad unresolved pattern. So no specific assignment of the stereoarchitecture of this polymer can be made at present. An elucidation of this problem may emerge from computer modeling of its structure that is in progress.

Permeability Coefficients. Table 4 presents permeability coefficients of APNs synthesized in this work and those described earlier. It is seen that APNSi is characterized by much higher gas permeability coefficients than other APNs studied so far. Thus, an increase in the *P* values due to replacement of CH_3 to $Si(CH_3)_3$ substituent can be as large as 2 orders of magnitude (depending of the gas and microstructure of methyl-substituted APNs taken for comparison). By the level of gas permeability coefficients, APNSi can be considered among the group of highly permeable polymers including amorphous Teflon AF2400, poly(methyl pentyne) (PMP), some other polyacetylenes, or "polymers with intrinsic microporosity" or PIM.[30−32,19] It can be also concluded that APNSi is much more permeable than its isomers, the ROMP polymer containing the $Si(CH_3)_3$ group.[1,7] It can be noted that that these differences are much less marked for nonsubstituted polynorbornenes of addition and ROMP types. On the other hand, permeability coefficients of the most permeable polymer, poly(1-trimethylsilyl-1-propyne) (PTMSP), are higher by about 1 order of magnitude.[33]

ACPNHSi has gas permeability much lower than that of APNSi (Table 4). This is consistent with the data reported by M. Rezac et al.[15] for alkyl-substituted APNs with long alkyl chains.

Figure 3 shows the Robeson diagram[34] for the pair O_2/N_2 and addition type polynorbornenes studied in the present work and reported in the literature. For comparison, some data for ROMP polynorbornenes are also included. The structure−transport properties relationships are different for polynorbornenes of the two classes. Addition type polynorbornenes show more drastic changes of the permeability caused by the structure variation. Thus, introduction of the $Si(CH_3)_3$ group into the main chain of the addition type polynorbornenes leads to an increase in permeability by more than 2 orders of magnitude, while the corresponding variation of the structure of ROMP polynorbornenes induces only 10-fold increases in permeability. Hence, the range of variation of permeability in addition type polynorbornenes spans a much wider range of the *P* values. Permeability and permselectivity values of APNs follow, as can be seen from Figure 3, the traditional "tradeoff" trend for these parameters: the higher permeability, the lower is the permslectivity. On the other hand, structural modification of ROMP polynorbornenes results (sometimes but not always) in joint increases in the *P* and α values.

Permselectivity or separation factors $\alpha(M_1/M_2) = P(M_1)/P(M_2)$ are compared in Table 5 for APNSi and some high permeability polymers. It is seen that this polymer is more permselective than PTMSP and AF2400 in the most cases.

An interesting peculiarity that can be potentially important from the practical viewpoint is solubility controlled selectivity of some high permeability, high free volume polymers revealed in separation of hydrocarbons according to their molecular mass. As permeability coefficients can be presented as the product $P = DS$, where *D* is the diffusion coefficient and *S* is the solubility coefficient, the variations of the *P* values for the series penetrants can be ascribed to corresponding trends of the *D* and *S* values.[38] In conventional glassy polymers, size sieving or mobility selectivity, which is determined by the variations of the diffusion coefficients, prevails, so the separation factors, reveal higher permeation rates of lighter components; e.g., $\alpha(C_4H_{10}/CH_4) < 1$. On the other hand, in rubbers the diffusion coefficients only weakly depend on the penetrant size, so the opposite inequality, $\alpha(C_4H_{10}/CH_4) > 1$, is valid, because the solubility coefficient becomes a parameter more sensitive to penetrant size and properties. It is important that in some high free volume glassy polymers (first and foremost, PTMSP) also solubility controlled permeation behavior is observed. [33]

In this regard, it was interesting to compare permeability coefficients of APNSi for *n*-alkanes $C_1−C_4$ (Table 6). It can be concluded that this polymer reveals the solubility controlled selectivity of separation: permeability coefficient of *n*-butane is much greater than that of methane.[39] This is a common type of behavior of several high free volume polymers as the data for some polyacetylenes also show (Table 6). It can be ascribed to open porosity kind of free volume typical for these polymers. For PTMSP, it was confirmed by a computer simulation study using molecular dynamics.[40,41] So it can be assumed that the nanostructure of APNSi includes large and partly opened pores. This subject will be considered in more detail in the next section.

As has been described in the Experimental Section, measurements of the permeability coefficients were performed at upstream of 1 atm. Depending on the nature of penetrants some plasticization effect can be exerted by gases with great solubility in membrane material. It means that large permeability coefficients *P* of such gases as butane and carbon dioxide can be partly induced by the pressure dependence of *P*. This subject is under scrutiny now and will be considered elsewhere.

Table 4. Permeability Coefficients *P* (Barrer) of APNBs

R	catalyst	*T*, °C	*P*						ref
			He	H_2	O_2	N_2	CO_2	CH_4	
H	$Ni(acac)_2$	25−28			10.8	2.7	49.1		21
	Ni[a]	22	29.4	41.5	6.9	1.5	33.6	2.6	this work
CH_3	*b*	35	309.4	502.1	89.2	24.1	396.3	30.3	15
	Pd[c]	35	174.4			12.6	202.1	16.9	16
	Ni[c]	35	88.8			4.3	81.1	5.6	16
$Si(CH_3)_3$	Ni[a]	22	790	1680	780	297	4350	790	this work
			840	1800	980	390	4480	993	
ACPNHSi: $C_6H_{11}/Si(CH_3)_3$	Ni[a]	22		164	60	19	330	48	this work
n-C_4H_9	*b*	35	66.7	110.7	33.3	11.2	141.9	28.4	15
n-$C_{10}H_{21}$	*b*	35	38.9	62.4	25.3	8.7	111.1	28.1	15
ROMP: $Si(CH_3)_3$	WCl_6^- PhC_2H	22	58.4	76.8	20.9	6.2	79.3	17.0	7

[a] $[(Nph)_2Ni]$−methylaluminoxane. [b] No information on the nature of the catalyst used. [c] No additional information on catalyst nature disclosed.

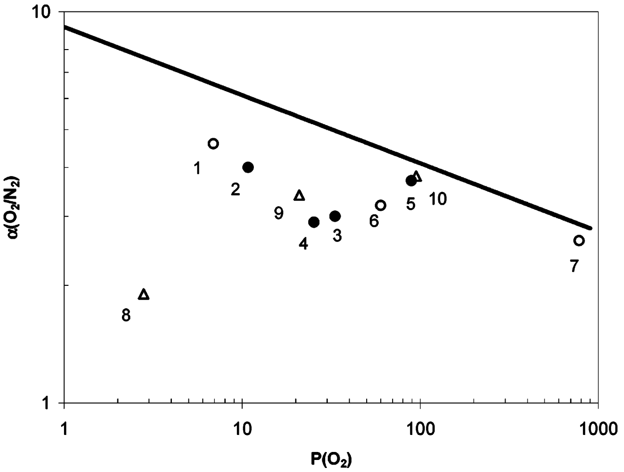


Figure 3. Robeson diagram for O_2/N_2 pair in various norbornene polymers. Circles: addition type polynorbornenes (opened circles, this work; filled circles, literature data); triangles: ROMP polynorbornenes, where the line is the upper bound of Robeson. Key: (1, 2) APN (this work and ref 21, respectively); (3) poly(5-*n*-butyl-2-norbornene) (ref 15); (4) poly(5-*n*-decyl-2-norbornene) (ref 15); (5) poly(5-methyl-2-norbornene) (ref 15); (6) ACPNHSi (this work); (7) APNSi (this work); (8) ROMP polynorbornene (ref 1); (9) ROMP poly(5-trimethylsilyl-2-norbornene) (ref 7); (10) poly(bis-5,6-trimethylsilyl-2-norbornene) (ref 35).

Table 5. Separation Factors $\alpha(M_1/M_2) = P_1/P_2$ for Some Gas Pairs

M_1/M_2	APNSi	PTMSP[36]	AF2400[30]
O_2/N_2	2.6	1.7	2.0
H_2/N_2	5.7	2.9	4.3
CO_2/N_2	14.6	10.5	4.7
CO_2/CH_4	5.5	4.4	6.0
C_4H_{10}/CH_4	22	5.1[37]	0.32

It is well-known that the introduction of bulky $Si(CH_3)_3$ group in various main chains results in a noticeable increase in gas permeability.[17] However, the quantitative effects can be different for various polymer classes. These structure−properties effects are compared in Table 7 for the novel APNSi and the polymers of other classes using oxygen as the penetrant. In the case of relatively flexible main chain (vinylic type polymers like PE and PS) the increases in the *P* values amount usually one order. The same is true for ROMP polynorbornenes. For APNs the effect is much stronger—*P* increases by about 2 orders of magnitude. The same trend can be observed for other gases. It can be related to much more rigid main chains in APNs. Because of the crystalline nature of polyacetylene, such a comparison could be impossible for another high permeability polymer—PTMSP.

Table 6. Permeability of High Free Volume Polymers with Respect to Hydrocarbons

polymer	*P*, Barrer				ref
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	
APNSi	790	1 430	1 740	17 500	this work
PTMSP	15 000	31 000	38 000		33
PMP	2 900	3 700	7 300	26 000	31
AF2400	435	252	97		30

Table 7. Effects of Introduction of $Si(CH_3)_3$ Groups in Various Main Chains

polymer type[a]	$P(O_2)$, Barrer	$\alpha(O_2/N_2)$	ref
PE	2.9	2.9	42
PVTMS	44	4.0	43
PS	2.9	5.5	44
PTMSS	56.0	3.5	45
ROMP:			
PNB	2.6	3.5	46
PTMSNB	20.9	3.4	7
APN	6.9	4.6	this work
APNSi	780	2.6	

[a] Key: PE, polyethylene; PVTMS, poly(vinyltrimethylsilane); PS, polystyrene; PTMSS, poly(*p*-trimethylsilylstyrene); PNB, polynorbornene; PTMSNB poly(trimethylsilylnorbornene).

Table 8. Effect of Accelerated Aging on Permeability of APNB−$SiMe_3$

sample	*P*, Barrer	
	O_2	N_2
original film	980	390
film after heating in air at 80 °C for 16 h	900	350

Aging. Continuous reduction of permeability in time is a well-known peculiarity of PTMSP (see review[32] and references therein) and some other polyacetylenes.[47] The mechanism of this aging can include volume relaxation (densification), absorption of impurities from environmental atmosphere during storage, and chemical destruction involving oxidation of double bonds of polyacetylene.[48] Such aging can be considered as a shortcoming of potential membrane materials, so it is quite desirable to test time stability of the permeation parameters for any high free volume, high permeability polymers. Bearing this in mind, we undertook a preliminary study of the effects of aging on permeability coefficients of APNSi. Though a reduction of permeability of PTMSP is observed at room temperature, it is strongly accelerated at elevated temperatures.[32] So heat treatment of APNSi was also used in this work. The results are given in Table 8. It can be concluded that some aging takes place in the case of APNSi as well, however, it is relatively

Table 9. PALS data of APNs

R	catalyst	τ_3, ns	I_3, %	τ_4, ns	I_4, %	R_3/R_4, Å	ref
H	Ni(acac)$_2$	2.87	36.4			3.58 (R_3)	21
	a	2.0	25.0	3.6	8.9	2.9/4.1	this work
CH$_3$	Pd	3.49	32.2			3.95 (R_3)	16
	Ni	3.15	33.3			3.74 (R_3)	16
Si(CH$_3$)$_3$	*a*	3	10	7	30	3.7/5.7	this work
ACPNHSi	*a*	1.52	4.4	3.19	28	2.4/3.8	this work

[a] [(Nph)$_2$Ni]−methylaluminoxane.

slow. Indeed, permeability coefficients $P(O_2)$ of PTMS decrease by one order after heating for 8 h at 100 °C.[49] or by about 2 orders of magnitude for 8 h at 120 °C.[50]

Results of PALS Measurements. This method is based on the measurement of lifetime spectra of positrons in polymers—lifetimes τ_i (ns) and corresponding intensities I_i (%).[51] Longer lifetimes τ_3 (or τ_3 and τ_4) (so-called o-orthopositronium lifetimes) can be related to the mean size of free volume elements (FVE) in polymers:[52−54]

$$\tau_i = {}^1/_2\,[1 - (R_i/R_o) + ({}^1/_2\pi)\sin(2\pi R_i/R_o)]^{-1} \tag{1}$$

where $\tau_i = \tau_3$ or τ_4 are o-Ps lifetimes and $R_i = R_3$ or R_4 are the radii of FVE elements, expressed in nanoseconds and angstroms, respectively; $R_o = R_i + \Delta R$, where $\Delta R = 1.66$ Å is the fitted empirical parameter. In this work, all the three addition type polynorbornenes were studied using the PALS technique, but more systematic investigation was carried out for APNSi. Earlier studies[21,16] with other APNs with H and CH$_3$ substituents revealed relatively short lifetimes τ_3 and small sizes of FVE in these polymers. Table 9 presents the PALS data obtained for the APNs investigated. First, the treatment of the primary experimental results shows that much better statistical fit can be obtained for bimodal lifetime and FVE size distribution for APNSi. According to Tao-Eldrup eq 1, very large FVE are present in this polymer. Second, it should be reminded that bimodal lifetime distribution observed for APNSi is a common feature of all polymers with great gas permeability.[55,56]

The two other addition type polynorbornenes studied show much shorter lifetimes τ_3 and τ_4. It means that these polymers include significantly smaller FVE (holes), and this is consistent with their lower gas permeability. The sizes of microcavities R_3 and R_4 in these two polymers turned out to be similar. However, ACPNHSi is characterized by much higher value of the intensity I_4 as compared to APN (28 vs 8.9%), which can indicate a much higher hole number density N_4 of this polymer. This is in agreement with its higher gas permeability.

The PALS method enables an accurate estimation of the hole number density N_i (cm^{-3}), where $i = 3$ and/or 4 and, hence, an evaluation of the fractional free volume FFV $= N_i v_{fi}$, where the volume of a spherical hole is $v_{fi} = (4/3)\pi R_i^3$. It can be noted that the standard method for the determination of N_3 is based on comparison of the slopes of $\tau_3(T)$ and $\alpha(T)$ above and below the glass transition temperature T_g, where α is the volume expansion coefficient at $T > T_g$ (α_r) and $T < T_g$ (α_g).[57,23] However, APNSi does not show any glass transition, so another approach was used for the determination of N_3 and N_4 in this polymer.

The method employed for the estimation of the number densities N_i is based on the assumption that the intensities of the long-lived o-Ps components are determined by both N_i values and the number density of electrons in the positron spur.[58,23] In other words, orthopositronium is formed before localization in the holes and has some chance to annihilate before trapping; i.e., the trapping rate is comparable with the annihilation rate of nonlocalized positronium ($\nu_i^{tr} \le \lambda_f$). The kinetic equation describing such a case gives the following relationship between intensities of the long-lived o-Ps components I_i, mentioned above rates and the rate of o-positronium annihilation in the free volume of "*i*"-type γ_i

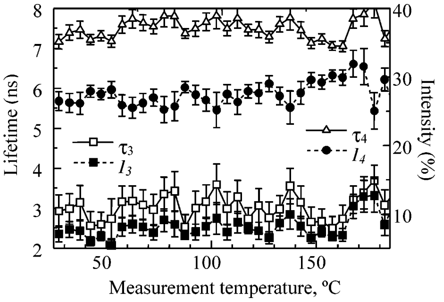


Figure 4. Temperature dependence of the PALS parameters of APNSi.

$$I_i = (3Q/4)[\nu_i^{tr}/(\lambda_f - \gamma_i + \sum_i \nu_i^{tr})] \tag{2}$$

where $\tau_i = 1/\gamma_i$ and $\nu_i^{t} = 4\pi D_{Ps}^{f} R_i N_i$. Parameter Q is the fraction of the positrons forming Ps in the system and D_{Ps}^{f} means effective diffusion coefficient of nonlocalized o-Ps. The following equations hold for the trapping rate in the two types of holes in the polymer:

$$\nu_3^{tr} = (I_3/A)[(\lambda_f - \gamma_3)(3Q/4 - I_4) + (\lambda_f - \gamma_4)I_4]$$

$$\nu_4^{tr} = (I_4/A)[(\lambda_f - \gamma_4)(3Q/4 - I_3) + (\lambda_f - \gamma_3)I_3]$$

$$A = (3Q/4 - I_3)(3Q/4 - I_4) - I_3 I_4 \tag{3}$$

provided $Q = 1 - I_2$.[58] With $\tau_4 = 7$ ns ($I_4 = 30\%$) and $\tau_3 = 3$ ns ($I_3 = 10\%$), which correspond to $R_3 = 3.7$ Å and $R_4 = 5.7$ Å, eq 3 gives $N_3 = 5.0 \times 10^{19}$ cm^{-3} and $N_4 = 9.8 \times 10^{19}$ cm^{-3}, i.e., N_4 is only twice as larger as N_3, though I_4 is three times larger than I_3.

For comparison, assuming the same value of D_{Ps}^{f} for PTMSP[59] the PALS parameters of this polymer gave: $R_3 = 3.4$ Å and $R_4 = 7$ Å, $N_3 = 5.6 \times 10^{19}$, and $N_4 = 26 \times 10^{19}$ cm^{-3}; i.e., this polymer should be characterized by a larger free volume, which is in agreement with its greater permeability.

Now, using the found values of R_i and N_i one can calculate the fractional free volume of APNSi. For the fractional free volume of this polymer the following value FFV $= (v_{f3}N_3 + v_{f4}N_4)100 = 8.6\%$ can be found. The corresponding value of FFV that can be calculated for PTMSP using the R_i and N_i values given above is about three times larger.

The temperature dependence of PAL spectra (τ_i and I_i) was measured in the range 25−185 °C. The results are shown in Figure 4. It is obvious that neither lifetimes nor intensities depend on temperature in this rather wide range. This result seems to be fairly unexpected, since for vast majority of polymers lifetimes linearly increase with temperature.

Table 10 presents a survey of the numerous results reported for the temperature dependence of the positronium lifetime τ_3 for conventional glassy polymers. The polymers included into consideration have permeability coefficient of oxygen in the range 0.05−170 Barrer. The slope of these dependences below T_g in the vast majority of polymers is close to 10^{-3} K^{-1}. The only exception is the result of Liu et al. [63] that showed much weaker dependence for polystyrene. Note that other PALS

Table 10. Slopes of the Dependence $\tau_3(T)$ for Polymers Below Their T_g[a]

polymer[b]	α_h, K^{-1}	$P(O_2)$, Barrer (at 25−35 °C)	refs
PE	1×10^{-3}		60, 61
PS	1×10^{-3}	1.2−2.9	60, 61
	0.8×10^{-3}		62
	1×10^{-4}		63
	1×10^{-3}		64
PVA	0.7×10^{-3}	0.18	65
AF1600	1.6×10^{-3}	170	66
PC	1.1×10^{-3}	1.2−1.6	62, 67
PET	2×10^{-3}	0.05−0.07	68

[a] The permeability coefficients are taken from Database No. 3585 "Gas permeation parameters of glassy polymers"; TIPS, Informregistr RF: Moscow, 1998. [b] Key: PE, polyethylene; PS, polystyrene; PVA, poly(vinyl acetate); AF1600, amorphous Teflon AF1600 (DuPont); PC, polycarbonate; PET, poly(ethylene terephthalate).

studies of the same polymer gave 1 order of magnitude higher slopes, which is consistent with the data for other polymers from Table 10.

A notable exception from this behavior observed so far is PTMSP,[56] whose lifetimes (τ_3 and τ_4) are constant in the range 24−103 °C. It can be added that a very weak temperature dependence of free volume in PTMSP was registered independently by the method of electrochromism.[69] Such a trend observed for both high free volume polymers can be explained as follows. In conventional glassy polymers, increases in the hole size with temperature are caused mainly by small scale movements of groups that form "walls" of FVE in polymers. In extra high permeability polymers like APNSi and PTMSP, the sizes of holes (and corresponding lifetimes) are determined mainly by loose packing of rigid chains, so this small scale mobility is masked by structure porosity frozen in polymer matrix. An investigation of the temperature dependence $\tau_i(T)$ for other high free volume polymers is now in progress.

Conclusions

In this work, we report successful synthesis and first detailed characterization of the addition type polynorbornenes with $Si(CH_3)_3$ substituents. The most interesting results were obtained for the homopolymer, APNSi. This amorphous glassy polymer showed several unusual properties.

First, it reveals very high gas permeability coefficients similar to those of some polyacetylenes and amorphous Teflon AFs. The solubility controlled permeation is characteristic for this polymer; that is, the permeability coefficients increase with the size of the penetrant, e.g. *n*-alkane C_1-C_4. A very high permeability coefficient of *n*-butane was measured equal to 17500 Barrer. Such gas permeation behavior can be interpreted assuming high free volume and open porosity of this polymer, similar to those reported for other high free volume polyacetylenes (e.g., PTMSP).

Indeed, physical investigations of APNSi confirmed these assumptions. The WAXS method revealed fairly large *d* spacing, that is, large interchain distances in this polymer. The PALS study showed that very large free volume elements ($R = 5.7$ Å) with the concentration about 10^{20} cm^{-3} are present in it. In contrast to conventional glassy polymer, free volume size and concentration in APNSi do not depend on temperature in the range 25−180 °C. It means that small-scale mobility of the polymer groups does not virtually affect the size of free volume elements, which are imbedded into the matrix of the rigid-rod-type chains of this polymer that retains bicyclic structure of the monomer.

By and large, this polymer can be considered as an interesting candidate for novel membrane materials for gas separation. An additional advantage of it is that it exhibited a relatively low rate of aging (reduction of gas permeation parameters in time), an Achilles' heel of many high permeability polymers.

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