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New High Permeable Addition Poly(tricyclononenes) with $Si(CH_3)_3$ Side Groups. Synthesis, Gas Permeation Parameters, and Free Volume

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ABSTRACT: Addition polymerization of two tricyclononene monomers bearing one and two $Si(CH_3)_3$ groups was performed in the presence of Pd-containing catalysts. The polymers were obtained with high yields and were completely saturated. Good mechanical and film forming properties are observed for the polymers prepared in the presence of $Pd(OAc)_2/B(C_6F_5)_3$ catalyst. Their glass transition temperature was not observed until the onset of thermal decomposition (> 370 °C) and the molecular weights are high (M_w up to 7×10^5). Study of gas permeation parameters of the obtained poly[3-(trimethylsilyl)tricyclononene-7] and poly[3,4- bis(trimethylsilyl)tricyclononene-7] showed that both glassy polymers revealed substantially high gas permeability. Other transport characteristics (increase in permeability in the series C_1-C_4 alkanes and negative activation energies of permeation) indicate that these polymers reveal so-called solubility controlled permeation, which is typical for some extra-high permeability polymers. Positron annihilation lifetime spectroscopy indicated that both polymers are characterized by very large sizes of free volume elements.

Introduction

Addition polymerization (AP) of norbornene and its derivatives has been first accomplished nearly 20 years ago.[1] However, relatively little has been reported on the membrane parameters of these polymers,[2−4] though their rigid chains as manifested in high glass transition temperatures can imply interesting properties.

Some time ago we have reported the results of successful preparation and investigation of gas permeation parameters, thermodynamic properties and free volume of the addition polynorbornene containing one $Si(CH_3)_3$ side group per monomer unit.[5,6] The transport parameters of addition poly(trimethylsilylnorbornene) (PTMSN) indicate that it can be included in the group of highly permeable polymers like poly(trimethylsilylpropyne) (PTMSP) and amorphous Teflon AF2400.[7] The results obtained also showed that well-known effects of introduction of bulky $Si(CH_3)_3$ group as a substituent are stronger for addition polymers with rigid chains compared to metathesis polynorbornenes having more flexible main chains.[5] All this justifies further efforts on preparation of other glassy polymers of this class with Si-containing side groups.

Introduction of proper pendant groups in monomer unit of addition polynorbornene is the way to get polynorbornenes with desired properties. However, the appearance of substituents in norbornene molecules resulted in a decrease of the catalytic activity as monomers.[8,9] In the case of ring-opening metathesis polymerization (ROMP) this effect is softened to some extent by substantial thermodynamic driving force in the process appeared as a result of opening highly strained bicyclic norbornene skeleton. AP is not so thermodynamically favorable process. It is well-known that in the case of AP the introduction of substituents, especially bulky or functional groups, leads to a dramatic decrease in activity of norbornene derivatives in the presence of all tested catalysts.[10−13] Probably, this is one of the reasons for limited number of publications devoted to AP of silyl-substituted norbornenes.

It should be noted that AP of 5-trimethylsilylnorbornene-2 ($NBSiMe_3$) proceeded substantially slower than that of unsubstituted norbornene.[14] Unlike ROMP, activity in AP to a great extent depends on the presence of *endo*-conformation in the monomer. Probably the presence of a bulky group in *endo* position prevents the coordination of monomer double bond with catalyst. As a result, activity of *endo* norbornene derivatives was substantially lower in comparison with that of *exo*-isomers,[5,11,14] whereas in some cases *endo*-isomers were completely inactive.[13] According to the publication[10] some steric hindrances arise even in more suitable *exo*-isomers. Norbornenes and norbornadienes with two $Si(CH_3)_3$-substituents turned out to be practically inactive in the presence of Ni- and Pd-catalysts.[14,15] On the other hand, their copolymerization with norbornene, 5-*n*-hexylnorbornene and $NBSiMe_3$ could be readily realized with catalyst system nickel(II) naphtenate—MAO.

In the case of the studied bis-$Si(CH_3)_3$-norbornenes (Scheme 1), one of the substituents is always in the disadvantageous *endo*-conformation. Probably, this is a reason for their inactivity in AP. But when the mixture of different conformers is used, a part of *endo*-form could participate in copolymerization with *exo*-form. This fact does not allow to realize homopolymerization of these monomers but at the same time does not exclude the proceeding of their copolymerization with norbornene itself or with its substituted *exo*-derivatives. A similar inactivity of norbornene monomers having geminal electron-withdrawing ester and trifluoromethyl substituents in AP in the presence of common Ni- and Pd-catalyst systems were found by Grubbs et al.[16]

In contrast to bis-$Si(CH_3)_3$-norbornene, the derivatives of disubstituted tricyclo[4.2.1.0^{2,5}]non-7-enes (tricyclononenes) turned out to be active monomers in AP.[15,17] In tricyclononene molecules one or two $Si(CH_3)_3$-groups are moved by an additional C−C-bond away from the double bond and therefore from reaction catalytic center. Synthesis of bis-$Si(CH_3)_3$-substituted tricyclononene was carried out from quadricyclane and trans-1,2-bis(trichlorosilyl)-ethylene. This route of synthesis provided formation of norbornene-type monomers with 100% *exo*-configuration of cyclobutane

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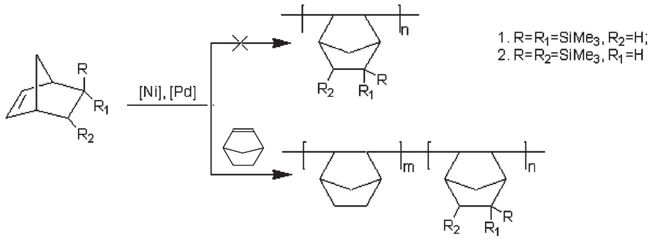
Scheme 1. Behavior of Disubstituted Silicon Containing Norbornenes in Conditions of AP



fragment that reduced steric hindrances in AP. That is why this monomer was active in AP catalyzed with common Ni-catalyst systems.[15]

Unfortunately, homopolymers of *exo,endo*-3,4-bis(trimethylsilyl)-tricyclononene (3,4-TCNSi2) prepared in the presence of naphtenate Ni(II)/ methylaluminoxane (MAO) catalyst had relatively low molecular masses (M_w up to 4×10^4).

In this work, we report AP of mono- and bis-$Si(CH_3)_3$ substituted tricyclononenes in the presence of Pd-containing catalysts, gas permeation and other physicochemical properties of two obtained novel highly molecular mass rigid chain polymers, having the structures of the type noted in Scheme 2. In contrast to rather low molecular mass polymers formed on Ni-catalyst,[15,17] they showed good film forming properties, giving a chance to study their gas permeation parameters.

Experimental Section

Materials. All manipulations involving air- and moisture-sensitive compounds were carried out under dried and purified argon using standard Schlenk and vacuum-line techniques. All monomers were stored under argon. As catalysts, commercial $Pd(OAc)_2$, $Pd(AcAc)_2$ and cocatalysts MAO (1.4 M solution in toluene), $B(C_6F_5)_3$ were received from Aldrich and used without preliminary purification as toluene solutions. Quadricyclane (Aldrich) was distilled over sodium metal under argon. Vinyltrichlorosilane (Merck) was distilled under argon. 1,2-trans-bis-(trichlorosilyl)ethylene and 3,4-bis(trimethylsilyl)tricyclononene-7 (TCNSi2) were obtained according to the published procedures (refs 18 and 17, respectively). Methyl iodide was distilled over CaH_2. Solvents were purified and distilled before their use by standard methods.

Monomer Preparation. The method of monomer synthesis is disclosed below. All the procedures were carried out under dry argon.

Synthesis of 3-(Trichlorosilyl)tricyclononene-7. An oven-dried 100 mL ampule equipped with a magnetic stirring bar was charged with quadricyclane (10.7 g, 116 mmol) and vinyltrichlorosilane (47.0 g, 291 mmol). The mixture was degassed. The sealed ampule was heated for 150 h at 95°. The reaction mixture was concentrated under reduced pressure (0.5 mmHg, 25−40 °C) to afford the 3-(trichlorosilyl)tricyclononene-7 as a colorless oil. Yield: 19.5 g, 66% (based on quadricyclane used).

^1H NMR ($CDCl_3$, ppm): 5.62 m (2H, C(7)H, C(8)H), 2.74 s (0.36H, C(1)H, C(6)H), 2.41−2.25 m (2H), 1.95 m (1.66H), 1.80 m (1.66H), 1.52 m (0.68H), 1.32 m (1.66H), 1.08 m (1H) (C(1)H, C(6)H, C(2)H, C(3)H, $C(4)H_2$, C(5)H, $C(9)H_2$).

^{13}C NMR ($CDCl_3$, ppm): 135.43, 134.99, 134.70, 134.19 (C(7), C(8)), 44.76, 44.44, 44.37, 43.15 (C(1), C(6)), 40.93, 39.78 (C(9)), 39.30, 37.09, 36.25, 34.93 (C(2), C(5)), 27.53, 26.78 (C(3)), 22.82, 21.42 (C(4)).

Synthesis of 3-(Trimethylsilyl)tricyclononene-7 (TCNSi). To a MeMgI solution prepared from Mg (12.35 g, 0.51 mol) and methyl iodide (71.1 g, 0.50 mol) in diethyl ether (200 mL) 3-(trichlorosilyl)tricyclononene-7 (20.5 g, 80.9 mmol) in diethyl ether (20 mL) was added dropwise so as the mixture gentle refluxed. Then the reaction mixture was refluxed additionally for 8 h, cooled to room temperature, and allowed to stay overnight. The solvent was removed under atmospheric pressure and the residue was extracted with absolute hexane (5 × 80 mL). Combined extracts were concentrated, product distilled under reduced pressure (bp 75°/4 mmHg). Yield: 12 g (77%).

^1H NMR ($CDCl_3$, ppm): 5.90 m (2H, C(7)H, C(8)H), 2.71 s (0.3H, C(1)H, C(6)H), 2.58 m (1H, C(1)H, C(6)H), 2.54 s (0.7H, C(1)H, C(6)H), 2.19 m (0.35H), 2.01 m (0.72H), 1.90−1.78 m (3H), 1.72 m (0.7H), 1.40 m (0.7H), 1.5−1.12 m (1.5H), 0.84 m (0.7H) (C(2)H, C(3)H, $C(4)H_2$, C(5)H, $C(9)H_2$), −0.02 m (9H, Me_3Si).

^{13}C NMR ($CDCl_3$, ppm): 135.93, 134.92, 134.62, 134.54 (C(7), C(8)), 45.65, 44.79, 44.55, 44.14 (C(1), C(6)), 40.85, 39.95 (C(9)), 39.07, 37.72, 36.81, 35.36 (C(2), C(5)), 22.38, 21.64 (C(4)), 20.53, 20.20 (C(3)), 0.86, −3.73 (Me_3Si).

MS: 100% (73, Me_3Si), 5% (192, M^+).

Polymerization Procedure. In the typical procedure (the example is given for ratio 3,4-TCNSi2/$Pd(OAc)_2$/$B(C_6F_5)_3$ = 3000/1/150), the 0.06 M toluene solution of $Pd(OAc)_2$ (0.1 mL, 0.000556 mmol) and monomer (0.48 mL, 1.67 mmol) were introduced into round-bottom glass ampule (5−10 mL) equipped with a magnetic stirrer preliminary purged in vacuum and filled with argon. Polymerization was initiated by adding of 0.09 M toluene solution of $B(C_6F_5)_3$ (0.94 mL, 0.084 mmol). The reaction mixture was continuously stirred for 24 h at ambient temperature. The polymers were precipitated by acidified ethanol (ethanol:HCl = 10:1), separated, washed by several portions of ethanol and dried in vacuum. It was twice reprecipitated by ethanol from toluene solution and dried in vacuum at 80−90 °C up to a constant weight.

Addition Poly(3-trimethylsilyltricyclononene-7). ^1H NMR ($CDCl_3$, ppm): 3.00−0.50 broad m (11H, C(1)H, C(2)H, C(3)H, $C(4)H_2$, C(5)H, C(7)H, C(8)H, $C(9)H_2$, C(6)H), −0.04 b m (9H, $Si(CH_3)_3$).

^{13}C NMR ($CDCl_3$, ppm): 52.34−39.66 bm, 29.35 m (C(1), C(6), C(7), C(8), C(9), C(2), C(5)), 22.69 m (C(3), C(4)), −0.86, −3.63 m ($Si(CH_3)_3$).

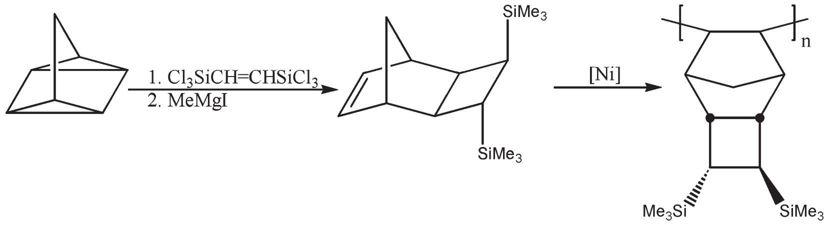
IR (KBr): 650−870 (Si−C), 1250 ($Si\text{-}CH_3$), 2900−3000 (CH) cm^{-1}.

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. Chromato-mass-spectrometric analysis was carried out using a Kratos MS-25 RF-instrument. Thermal gravimetric measurements were carried out using a Perkin-Elmer TGA-7 instrument. 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).

Film Casting. The films of the polymers studied were cast from the 1.5−2 mass % solution in toluene. The solvent was allowed to evaporate from caps with the bottom formed by stretched cellophane film. After formation of the films, cellophane was wetted, thus the films were detached from it. Before testing, the films were kept in 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 gas chromatographic method. The steady stream of penetrant gases under atmospheric pressure flew around upstream part of the film, while downstream part of it was flown around by gas-carrier—helium or nitrogen (the latter in measurement of permeation rate of H_2 and He). The permeability coefficients were determined by measuring the

Scheme 2. Synthesis and AP of *exo,endo*-3,4-Bis(trimethylsilyl)tricyclononene



penetrant concentration in the gas-carrier and the total flow of this mixture. Partial pressure of the penetrants was 1 atm in upstream part of the cell and close to zero in the downstream part. Temperature in the cell was 20−22 °C.

Positron Annihilation Lifetime Spectroscopy. The positron annihilation lifetime decay curves were measured at room temperature using an EG@G Ortec "fast−fast" lifetime spectrometer. A nickel-foil-supported [^{22}Na] sodium chloride radioactive positron source was used. Two stacks of film samples, each with a total thickness of about 1 mm, were placed on either side of the source. Measurements were performed in inert (nitrogen) atmosphere. The time resolution was 230 ps (full width at the half-maximum (fwhm) of the prompt coincidence curve). The contribution from annihilation in the source material, a background, and instrumental resolution were taken into account in the PATFIT program for treating the experimental lifetime data. The detailed procedures have been described elsewhere.[19,20] The resulting data were determined as an average value from the several spectra collected for the same sample, having an integral number of counts of at least 10^6 in each spectrum.

Results and Discussion

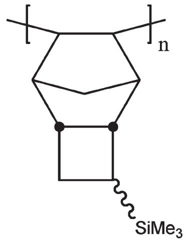
Polymerization. In our short communication,[15] we have described synthesis of an addition polymer of polynorbornene type bearing two $Si(CH_3)_3$ substituents in the repeat unit, namely the polymer of 3,4-bis(trimethylsilyl)tricyclo-[4.2.1.^{2,5}]non-7-ene (3,4-TCNSi2) prepared in the presence of $(Nph)_2Ni/MAO$ catalyst (Scheme 2). Attempts undertaken in the present work to prepare the polytricyclononenes of high M_w by the use of different catalysts ($Ni(OAc)_2/MAO$, $Ni(OAc)_2/B(C_6F_5)_3$, $Ni(COD)_2/B(C_6F_5)_3$), and different reaction conditions (mole ratio M/Ni/B/MAO = 600−3000/1/5−10/100−500, 70−700 h) did not give polymers capable to form durable films suitable for membrane measurements.

A substantial increase in catalytic activity was demonstrated when the Pd-containing system $Pd(OAc)_2/B(C_6F_5)_3$ was used (Table 1). By variation of the monomer/Pd/B ratio, it was possible to select the conditions for preparation of the addition polymer of 3,4-TCNSi2 having $M_w = (5-7) \times 10^5$ with the yields of 60−100% (Table 1). In these conditions the AP polymerization of 3-TCNSi was accomplished and high molecular mass polymer was obtained.

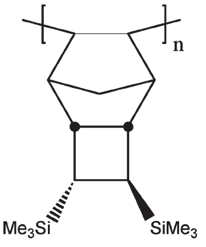
The effects of various cocatalysts on the activity of Pd-containing systems were also studied, and the results are also presented in Table 1. It was shown that $B(C_6F_5)_3$ is the most active cocatalyst. Replacement of $B(C_6F_5)_3$ by other activators did not lead to increases in catalytic activity. For example, when $BF_3 \cdot Et_2O$ was used, the polymeric product was obtained in trace quantity. Replacement of $B(C_6F_5)_3$ for MAO resulted in obtaining the polymer with good yield though smaller than in the presence of $B(C_6F_5)_3$. Unfortunately, it was insoluble in toluene and chloroform. Combined use of $B(C_6F_5)_3$ and MAO did not give any advantages.

The polymer structure was confirmed with NMR and IR spectroscopy methods. They showed that polymers had not double bonds, at the same time $Si(CH_3)_3$ groups were completely retained in the polymers.

In general, the determination of microstructure of substituted polynorbornenes is very intricate problem since they have unresolved NMR-spectra. Now it is known that AP of norbornene can be performed in the presence of different catalysts, and the polymers obtained are characterized by different microstructure. On the basis of molecular simulation[4,21] it was concluded that the polynorbornenes produced using Pd-catalysts have a highly stereoregular 2,3-erythro diisotactic structure. On the other hand, polymers prepared in the presence of Ni catalysts are atactic and include a combination of 2,3-erythro diisotactic and 2,3-erythro disyndiotactic structures. Excellent agreement between experimental data (wide-angle X-ray scattering, fractional free volume (FFV) determination), the results of computer modeling (*ab initio* quantum chemical calculations, molecular dynamics and Monte Carlo simulations)[4,21,22] and NMR confirmation of stereochemical assignment[23] seem to be an argument that norbornene polymers obtained in the presence of Ni and Pd catalysts have units of 2,3-configurtaion in the main chain. In the case of AP of 3-TCNSi and 3,4-TCNSi2 in the presence of Pd-catalyst systems the polymer structures look like as following:



poly(3-TCNSi)



poly(3,4-TCNSi2)

All polytricyclononenes obtained with the $Pd(OAc)_2/B(C_6F_5)_3$ catalytic system were soluble in toluene and chloroform. Their glass transition temperature was not fixed until the onset of thermal decomposition (> 370 °C).

Mechanical properties of poly(3,4-TCNSi2) and poly-(3-TCNSi) were measured using an Instron 2111 instrument. Both polymers prepared in this work have relatively high strain strength and elongation at break. Elongation at break was 6.7% for poly(3-TCNSi) and 14% for poly(3,4-TCNSi2). Strain strength accomplished was 32 MPa for (3-TCNSi) and 26 MPa for poly(3,4-TCNSi2). These parameters are certainly higher than those characteristic for addition poly-(trimethylsilyl norbornene) (PTMSN), some samples of which were brittle. This result explains good film forming properties of poly(3,4-TCNSi2) and poly(3-TCNSi).

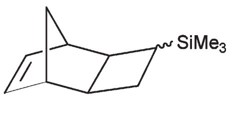
Gas Permeability. As is seen in Table 2, both new polymers, poly(3,4-TCNSi2) and poly(3-TCNSi), are highly permeable materials. Permeability coefficients of poly(3-TCNSi) having one $Si(CH_3)_3$ substituent are very similar to those early reported for PTMSN.[5] It means that appearance of cyclobutane ring in the structure of poly(3-TCNSi) does not exert strong effects on

Table 1. AP of Silicon-Substituted Tricyclononenes in the Presence of $Pd(OAc)_2$[a] Catalyst with Different Co-Catalysts

monomer (M)	catalyst	mol ratio, M/Pd/B	time, h	polymer yield, %	M_w	M_w/M_n
M1[b]	$Pd(OAc)_2/B(C_6F_5)_3$	4000/1/200	24	72	574 000	2.5
		6000/1/200	24	35	700 000	1.7
M2[b]	$Pd(OAc)_2$	500/1/0	168	0		
	$Pd(OAc)_2$/MAO	500/1/100	58	insoluble		
	$Pd(OAc)_2/ BF_3\cdot Et_2O$	500/1/25	traces			
	$Pd(OAc)_2/B(C_6F_5)_3$	500/1/25	24	100	120 000	1.1
		1500/1/75	24	100	420 000	2.8
		3000/1/150	24	73	550 000	1.7
		3200/1/150	24	60	673 000	1.7
		6000/1/200	24	37	730 000	1.5
		6000/1/500	24	36	650 000	1.9

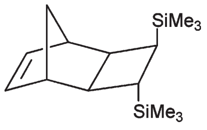
[a] [Pd] = 0.005 ÷ 0.0002 M, 20 °C, toluene. [b] Left (b): **M1** = 3-TCNSi. Right (c): **M2** = 3,4-TCNSi2.

[b]M1-



(3-TCNSi)

[c]M2-



(3,4-TCNSi2)

Table 2. Permeability coefficients *P*, barrer, of Poly(3,4-TCNSi2) and Poly(3-TCNSi)

polymer	He	H_2	O_2	N_2	CO_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	ref.
poly(3-TCNSi)	930	2060	990	390	5300	1010	1360	1470	13 030	this work
poly(3,4-TCNSi2)	1890	4090	2380	1240	11 280	3320	6040	7530	26 910	this work
PTMSN[a]	790	1680	780	300	4350	790	1430	1740	17 500	5
PMP[b]	2630	5800	2700	1330	10 700	2900	3700	3100−6900[d]	11700−23700[d]	28
PVTMS[c]	160	220	44	11	190	13	7.4	3.5	1.2	31, 32

[a] Poly(trimethylsilyl norbornene). [b] Poly(4-methyl-2-pentyne). [c] Poly(vinyltrimethyl silane). [d] This range of *P* reflects the effects of feed pressure.

permeability which is more sensitive to the presence of bulky $Si(CH_3)_3$ group, because both polymers are much more permeable than addition polynorbornene.[5]These effects are well documented in the literature, but the influence of the bulky substituent is much stronger for polymers with rigid backbones, i.e., in the case of addition norbornene polymers. Thus, an introduction of $Si(CH_3)_3$ group into polystyrene[24,25] or ROMP polynorbornene[26,27] increases the *P* values by one order, while for addition polymers of norbornene class the change of *P* values corresponds to two orders.

Poly(3,4-TCNSi2) is characterized by even larger *P* values. This polymer is similar to poly(4-methyl-2-pentyne).[28] Hence, the results obtained for these new polymers as well as those reported earlier for addition PTMSN[5,6] indicate that rigid chain Si-containing polynorbornenes form a new class of highly permeable membrane materials in addition to polyacetylenes and amorphous Teflons AF.

Another interesting feature of poly(3,4-TCNSi2) and poly(3-TCNSi) is the trend observed for permeation of hydrocarbons. In common glassy polymers increases in the size of penetrants result in decreases in permeability as is illustrated in Table 2 for glassy poly(vinyltrimethyl silane). Such behavior is explained by stronger effects of diffusivity and not solubility on the permeability coefficients. For all addition Si-containing polynorbornenes (PTMSN and its structure analogues) solubility controlled permeation is characteristic, that is, the changes of *P* and the solubility coefficients S are similar for penetrants series: P values increase when the critical temperature of the penetrants increases. Such behavior has been reported for several but not all polyacetylenes[29] (and not for amorphous Teflons AF[7]). It can be caused by weak size sieving ability of polyacetylenes having unusually large free volume and its specific spatial distribution (open porosity) as was confirmed by computer simulation.[30] As will be shown in subsequent sections of this paper, novel Si-containing polymers described in this work also have large free volume.

Table 3. Separation Factors α_{ij} for Different Gas Pairs at Room Temperature

polymer	O_2/N_2	H_2/N_2	CO_2/CH_4	C_4H_{10}/CH_4
poly(3-TCNSi)	2.5	5.3	5.2	12.9
poly(3,4-TCNSi2)	1.9	3.3	3.4	8.1
PTMSN	2.6	5.6	5.5	22.2
PMP	2.0	4.4	3.7	4.0−8.2
PVTMS	4.0	20	14.6	0.09

As can be expected, high permeability of the described polymers is coupled with low permselectivity, as compared to conventional glassy polymers, for the pairs of permanent gases (Table 3). Some trade-off can be noted within the group of studied Si-containing addition norbornene polymers: less permeable polymers have somewhat higher permselectivity. Note that separation factors $\alpha(C_4H_{10}/CH_4)$ reflect pressure dependence of permeability in respect of butane: because of this two values are given in Table 3 for PMP.

Aging. For some polyacetylenes, a rapid reduction in time of the permeability was observed.[33] The rate of this aging is especially high for the most permeable polymer, poly(trimethylsilyl propyne): the permeability coefficients of isobutene decreased by nearly 2 orders of magnitude during storage for 100 days in vacuum.[34] Different mechanisms of this process have been proven[35] (volume relaxation, absorption of impurities from ambient atmosphere and chemical reactions involving double bonds). Since Si-containing polymers described in this work are completely saturated, the latter mechanism can be excluded. On the other hand, high permeability, especially in the case of poly(3,4-TCNSi2), makes it relevant to test possible changes of the permeability coefficients in time. The results of such experiments are presented in Figure1.

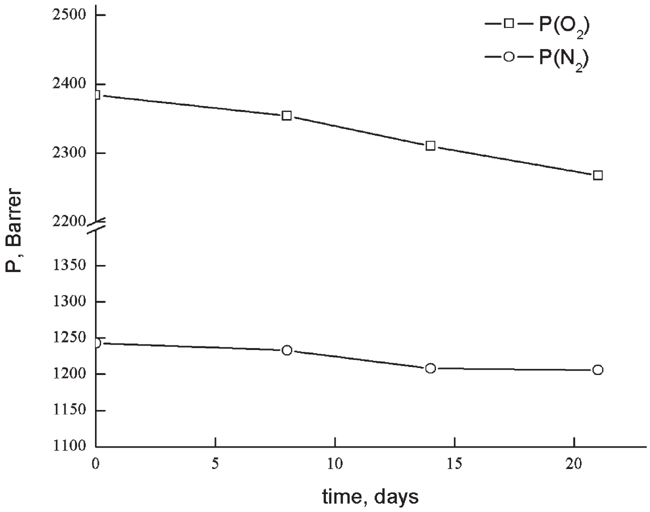


Figure 1. Changes of permeability coefficients in poly(3,4-TCNSi2) at room temperature.

The film of poly(3,4-TCNSi2) was kept in gas permeation cell while temperature dependence of permeability was measured for different gases. Periodic tests of $P(O_2)$ and $P(N_2)$ at room temperature were made during time of 3 weeks. It is seen that only 3−5% reduction of permeability occurred during this period. This rate of aging is much smaller than the one observed for PTMSP. This result is important for possible future application of this polymer as membrane material.

A natural question can be posed regarding the reasons of slower rate of aging of the polymers studied as compared to other high permeability glassy polymers. It should be noted that this phenomenon drew a great attention because the stability of the transport parameters in time is important for practical application of membrane materials. Therefore, let us consider briefly some results of other studies of aging in other membrane materials. It is worth to emphasize that we consider here gradual reduction of transport parameters of films and membranes stored at ambient temperature. Hence, we shall not consider well-known phenomena of aging (structural relaxation) of glassy polymers subjected to annealing at temperatures close the glass transition temperatures (see, e.g., the monograph in ref 36). The most detailed results were obtained for membrane materials with large free volume, first and foremost for PTMSP,[37−41] copolymers of trimethylsilylpropyne (TMSP) with other comonomers,[42] functional derivatives of PTMSP,[43] other polyacetylenes.[41,43] These works indicated that the rate of aging strongly depend on the thickness of tested film or membrane:[38] in thin layers of membranes (1−3 μm) the aging proceeds much slower than in thick (85 μm) dense films. The rate of aging is also sensitive to the conditions during the aging process (vacuum, the presence of impurities, e.g. vapors of vacuum oil, permeation of penetrants) and also to the nature of penetrants, whose rate of penetration is used as a measure of aging. All this complicates formulation of quantitative criteria for prediction of the aging rate. Nonetheless, the qualitative picture seems to be quite clear. The higher is the permeability of the original film or membrane, the larger are the observed rates of aging. As an example that confirms such tendency, it is possible to consider the data of Nagai et al.[42] for PTMSP samples prepared in the presence of different catalysts, the blends of PTMSP as well as copolymers of TMSP (Table 4).

Poly(3,4TCNSi2) studied in the present work has gas permeability much smaller that PTMSP: $P(O_2) = 2380$ barrer. Accordingly, the observed smaller rate of aging observed for it is in agreement with this trend characteristic for polymers with larger free volume. For comparison it can be noted that PTMSN having permeability coefficient $P(O_2) = 780$ barrer also showed relatively small rate of aging.[5,6]

Table 4. Different Rates of Aging of PTMSP, Its Blend with Poly(phenylpropyne) (PPP) and Copolymers of TMSP and Phenylpropyne (PP) (the Data Taken from Figure 7 of Ref 42)

material	P(O$_2$), barrer, at t = 0	P(O$_2$), barrer, at t = 14 days
PTMSP (catalyst $TaCl_5 \cdot Ph_3Bi$)	14 000	3500
copoly(TMSP-PP) (95:5)	12 000	6000
PTMSP (catalyst $TaCl_5$)	8000	4000
blend PTMSP - PPP	6000	5500
copoly(TMSP-PP) (90:10)	4200	3800

The same is true for PIM-1 (polymer of intrinsic microporosity) having $P(O_2) = 590$ barrer.[44] It can be assumed that the greatest rate of relaxation of the unrelaxed volume should be characteristic for polymers with more opened structure. This is especially typical for PTMSP still having unchallenged highest permeability coefficients among all polymeric materials. Additional arguments for this viewpoint are provided by the parameters of the temperature dependence of permeability of poly(3,4TCNSi2) (see next section).

Temperature Dependence of Permeability. It is known that high permeability polymers that exhibit solubility controlled permeation are characterized by unusual temperature dependence of permeability. Hence, it was necessary to investigate Arrhenius dependence of the polymers studied in the present work. It was made for more permeable poly(3,4-TCNSi2). Since heating in the process of measurements can induce some changes in permeability, the film cast from toluene solution after removal of residual solvent was subjected to heating at 60 °C for 24 h. before the measurement of the temperature dependence of permeability. The measurements were performed in the range 25−60 °C. The Arrhenius dependence is shown in Figure2.

It can be seen that permeability coefficients of all gases except helium and hydrogen decrease when temperature increases; i.e., negative activation energies of permeation are observed. This is unusual behavior though characteristic for highly permeable polymers with solubility controlled permeation.[28,45] On the other hand highly permeable amorphous Teflon AF2400 having permeation trend normal for glassy, size sieving polymers exhibits positive, though small activation energies of permeation.[46] Computer simulation of the structure of this polymer indicated that it includes closed porosity, whereas PTMSP is characterized by open porosity.[30] It can be assumed that the same type of porosity is characteristic for poly(3,4-TCNSi2).

Activation energies of permeation in poly(3,4-TCNSi2) are compared in Table 5 with those observed in PMP and PTMSP. The negative activation energies E_P measured in this work are smaller by absolute value than those reported for the two polyacetylenes, though there is no direct correlation with the permeability coefficients. Note that another but less permeable Si-containing norbornene polymer, PTMSN, shows negative activation energies of permeation only for two penerants, carbon dioxide and ethane, that have larger solubility coefficients than other tested penetrants.[6] It can be added that for conventional glassy polymers the E_P values are positive and much larger by absolute value: thus $E_P(H_2)$ and $E_P(CH_4)$ are in the range 4−35 kJ/mol for polyimides.[47]

Since activation energy of permeation is the sum $E_P = E_D + \Delta H_s$, where E_D is the activation energy of diffusion and ΔH_s is the enthalpy of sorption, low values of E_P mirror small energy barriers of diffusion, what is typical for many high

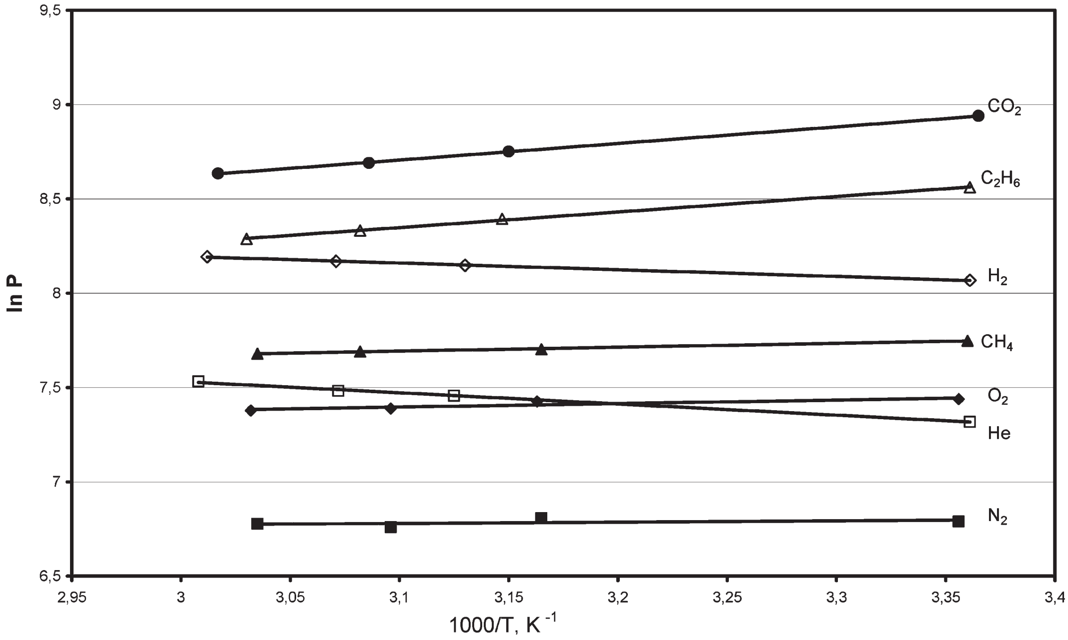


Figure 2. Arrhenius dependence of permeability coefficients, barrer, in poly(3,4-TCNSi2).

Table 5. Activation Energies of Permeation E_P, kJ/mol

polymer	He	H_2	O_2	N_2	CH_4	CO_2	C_2H_6	ref
poly-(3,4-TCNSi2)	5.0	2.9	−1.6	−0.52	−1.7	−7.3	−6.8	this work
PMP	−0.8	−4.0	−7.8	-	−8.3	−13.6	−11.9	28
PTMSP	−0.4	−2.7	−6.7	−5.1	−6.3	−9.7	-	36

permeability polymers. Therefore, stronger effects of ΔH_s on activation energy of permeation are observed. It is known that ΔH_s correlate with the critical temperature of penetrants.[46] A similar correlation holds for E_P measured for poly(3,4-TCNSi2) (Figure 3). PTMSP behaves in a similar way. So prevailing role of the thermodynamic component of permeability is displayed not only in the changes of the *P* values for hydrocarbon series, but also in the parameters of the temperature dependence of permeability of all gases.

Less negative activation energies of permeation of poly(3,4-TCNSi2) in comparison with those of PTMSP can be considered as an evidence that its "pore structure" is not that opened as that of PTMSP. Therefore, PTMSP should be more prone to structural relaxation than poly(3,4-TCNSi2).

Negative and small by absolute value activation energies of permeation E_P determine unusual temperature dependence of the separation factors $\alpha_{ij} = P_i/P_j$. Usually in polymers, a trade-off is observed between permeability and permselectivity: increases in P values are accompanied by decreases in separation factors. This is not true for the studied poly(3,4-TCNSi2) as can be seen from Table 6: separation factors are weak and decreasing functions of temperature for all considered gas pairs except H_2/CH_4.

Positron Annihilation Lifetime Spectroscopy. Method of positron annihilation lifetime spectroscopy (PALS) is considered as the most accepted and reliable technique for investigation of free volume in polymers.[19,20] It is based on measurements of lifetimes of positrons emitted by ^{22}Na isotope and trapped in the material. In condense media positrons form a bound state, hydrogen-like positronium (Ps) atom (e^+-e^-). When Ps gets into free volume elements (FVE) within a polymer, o-Ps having parallel spins of e^+ and e^- survive until annihilation for longer times the larger is the size of FVE. This is seen in the PAL spectra, that is, lifetimes τ_i, ns and their statistical weights or corresponding intensities I_i,%. Thus, o-Ps components of PAL spectra that correspond to longer lifetimes bring forth the information on nanostructure of free volume in polymers. In conventional glassy polymers these lifetimes are in the range of 1.5−3.0 ns. In highly permeable polymers much longer lifetimes are observed.[48] The relation between lifetimes and the size of FVE is given by the semiempirical Tao−Eldrup equation,[49,50] for a spherical potential well:

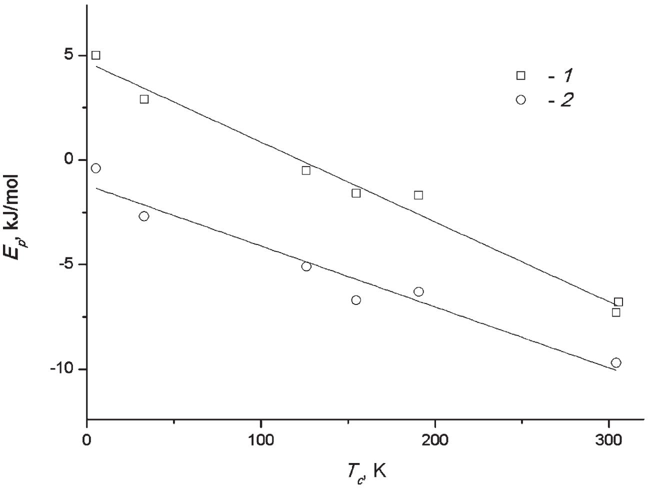


Figure 3. Correlation of activation energy of permeation and the critical temperature of penetrants T_c: (1) poly(3,4-TCNSi2); (2) PTMSP.

Table 6. Separation Factors $\alpha_{ij} = P_i/P_j$ in Poly(3,4-TCNSi2)

T, °C	H_2/CH_4	O_2/N_2	CO_2/N_2	CO_2/CH_4	C_2/C_1
25	1.4	1.9	8.6	3.3	2.3
43	1.6	1.9	7.0	2.8	2.0
57	1.7	1.8	6.4	2.6	1.8

$$\tau_i = \left\{\lambda_0^T + 2\left[1 - \frac{R_i}{R_i + \Delta R} + \frac{1}{2\pi}\sin\frac{2\pi R_i}{R_i + \Delta R}\right]\right\}^{-1}$$

Table 7. PAL Spectra of Poly(3,4-TCNSi2) and Poly(3-TCNSi) Measured in Atmosphere of N_2

parameter	poly(3-TCNSi) (this work)	poly(3,4-TCNSi2) (this work)	PTMSN[5]
τ_3, ns	1.74 ± 0.09	2.65 ± 0.15	3.0
I_3, %	10.08 ± 0.38	10.69 ± 0.33	10
τ_4, ns	6.1 ± 0.05	10.13 ± 0.17	7
I_4, %	22.46 ± 0.31	27.96 ± 0.48	30
R_3/R_4, Å	2.6/5.35	3.45/6.8	3.7/5.7

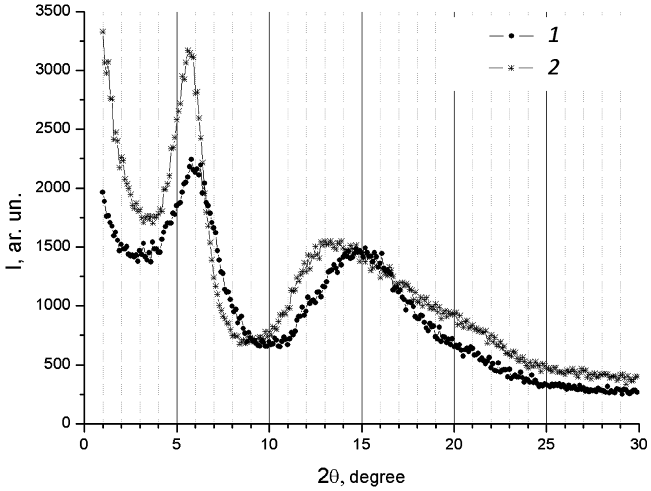


Figure 4. Wide angle X-ray diffractogram for poly(3-TCNSi) (1) and poly(3,4-TCNSi2) (2).

where τ_i (ns) is o-Ps lifetime, R_i is the corresponding radius of a spherical FVE, and $R_o = R_i + \Delta R$ (where the adjustable parameter ΔR is usually fixed at 1.66 Å[51]). In conventional glassy polymers o-Ps component is presented in the spectra by one lifetime τ_3 or a single Gauss peak in the case of continuous treatment of the experimental lifetimes, however, in highly permeable polymers much better statistical fit has been obatined by two or even three long-lived components of PAL spectra.[48]

In this work, PALS method was used for the investigation of free volume in poly(3,4-TCNSi2) and poly(3-TCNSi). The results are given in Table 7. As in the cases of other high free volume polymers better statistical fit was obtained for bicomponent o-Po lifetimes, so two lifetimes and intensities are shown in the table. The values of lifetimes τ_4 and the radii R_4 found using Tao-Eldrup equation indicate that rather large FVEs exist in both polymers. The τ_4, and R_4 values are similar to those obtained for other highly permeable polymers.[48] For illustration, the data for another addition norbornene polymer, PTMSN, having similar permeability as poly(3-TCNSi) are also given in the table. This comparison once more indicates the existence of strong correlation between PALS parameters and the permeability of polymers.

An additional experiment was performed with poly(3,4-TCNSi2): PALS measurement was carried out in air. The observed lifetimes decreased ($\tau_3 = 2.0$, $\tau_4 = 6.7$ ns) in comparison with the results obtained in the inert (N_2) atmosphere. This effect is explained by the quenching of o-Ps by oxygen molecules and is typical for high free volume polymers.[52]

Wide Angle X-ray Scattering. Wide angle X-ray diffraction (WAXD) indicated that both polymers studied, poly(3,4-TCNSi2) and poly(3-TCNSi), are completely amorphous (Figure 4). WAXD pattern is presented by two peaks that are not as broad that is characteristic for conventional glassy polymers, e.g. polysulfones.[53] The maxima of the peaks are located at smaller angles indicating in general larger intersegmental *d*-spacing.

Table 8. X-ray Scattering Data of Addition Type Polynorbornenes of Different Structure

polymer	$(2\theta)_1$, deg	*d*-spacing, Å	$(2\theta)_2$, degree	*d*-spacing, Å	ref
poly(3-TCNSi)	6.0	14.8	15	5.9	this work
poly(3,4-TCNSi2)	5.6	15.8	13	6.8	this work
PTMSN	6.5	13.6	15.5	5.7	5
PNB	10	8.8	18.5	4.7	3

It is of interest to compare these scattering angles and the values of *d*-spacing (d_B) found in assumption that Bragg's formula $d_B = \lambda/(2 \sin \theta)$ is valid for various addition-type norbornene polymers. It is made in Table 8.

Larger values of *d*-spacing of the polymers studied in the present work can be considered as an evidence of loose chain packing similar but more pronounced to what has been observed for PTMSN. In nonsubstituted addition polynorbornene investigated by Zhao et al.[3] the chains are packed more densely. This is consistent with higher gas permeability of Si-containing addition polymers and is in agreement with the results of PALS method.

Conclusions. In this work, a successful synthesis of two novel rigid chain addition type Si-containing polytricyclononenes was accomplished. The polymers prepared in this work, poly(3,4-TCNSi2) and poly(3-TCNSi), together with PTMSN studied earlier form a new group of highly permeable materials (silylated addition polynorbornenes) beside polyacetylenes and perfluorinated polymers extensively investigated so far. The properties observed for addition Si-containing polynorbornenes indicate that quite different chemical structure of repeat units can result in similar behavior, namely, high gas permeability and large free volume. On the other hand, common feature of all the polymers with high permeability is very rigid main chains. It is the stiffness of the main chains that makes stronger effects of bulky groups attached to them.

The increases in permeability in the series of C_1-C_4 alkanes and negative activation energies of permeation are the manifestation of solubility controlled permeation, that is, stronger effects exerted by solubility and not diffusivity on the permeability coefficients. The large size of free volume elements in more permeable polymer studied, poly(3,4-TCNSi2), found via the PALS method is also typical for highly permeable glassy polymers, and it was corroborated by wide-angle X-ray diffraction study.

All these results obtained for addition Si-containing polynorbornenes allow us to assume that they should be characterized by opened porosity, so further studies namely, mixed gas permeation investigation and molecular dynamics modeling, are desirable.

The observed properties of the two studied polymers allow one to assume that they can be used as membrane materials for separation of light hydrocarbons, in particular for removal of the components C_{3+} from natural and associated petroleum gas.

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References and Notes

(1) Mehler, C.; Risse, W. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 255–259.

(2) Dorkenoo, K. D.; Pfromm, P. H.; Rezac, M. E. *J. Polym. Sci., Part B:. Polym. Phys.* **1998**, *36*, 797–803.

(3) Zhao, C.; do Rosario Ribeira, M.; dePinho, M. N.; Subrahamnyam, V. S.; Gil, C. L.; de Lima, A. P. *Polymer* **2001**, *42*, 2455–2462.

(4) Wilks, B. R.; Chung, W. J.; Ludovice, P. J.; Rezac, M. E.; Meakin, P.; Hill, A. J. *J. Polym. Sci., Part B:. Polym. Phys.* **2003**, *41*, 2185–2199.

(5) Finkelshtein, E.; Makovetskii, K.; Gringolts, M.; Rogan, Yu.; Golenko, T.; Starannikova, L.; Yampolskii, Yu.; Shantarovich, V.; Suzuki, T. *Macromolecules* **2006**, *39*, 7022–7029.

(6) Starannikova, L.; Pilipenko, M.; Belov, N.; Yampolskii, Yu.; Gringolts, M.; Finkelshtein, E. *J. Membr. Sci.* **2008**, *323*, 134–143.

(7) Yampolskii, Yu.; Pinnau, I.; Freeman, B. D., Eds., *Materials Science of Membranes for Gas and Vapor Separation*: Wiley: Chichester, U.K., 2006.

(8) Blank, F.; Janiak, Ch. *Coord. Chem. Rev.* **2009**, *253*, 827–861.

(9) Hennis, A. D.; Polley, J. D.; Long, G. S.; Sen, A.; Yandulov, D.; Lipian, J.; Benedikt, G. M.; Rhodes, L. F.; Huffman, J. *Organometallics* **2001**, *20*, 2802–2812.

(10) Funk, J. K.; Andes, C. E.; Sen, A. *Organometallics* **2004**, *23*, 1680–1683.

(11) Myagmarsuren, G.; Lee, K.-S.; Jeong, O-Y.; Ihm., S.-K. *Polymer* **2005**, *46*, 3685–3692.

(12) Kaita, Sh.; Matsushita, K.; Tobita, M.; Maruyama, Y.; Wakatsuki, Y. *Macromol. Rapid Commun.* **2006**, *27*, 1752–1756.

(13) Jung, I. G.; Seo, J.; Chung, Y. K.; Shin, D. M.; Chun, S. H.; Son, S. U. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3042–3052.

(14) Finkelshtein, E. Sh.; Makovetskii, K. L.; Gringolts, M. L.; Rogan, Y. V.; Golenko, T. G.; Lakhtin, V. G.; Filatova, M. P. *J. Mol. Catal. A: Chem.* **2006**, *257*, 9–13.

(15) Gringolts, M. L.; Bermeshev, M. V.; Makovetsky, K. L.; Finkelshtein, E. Sh. *Eur. Polym. J.* **2009**, *45*, 2142–2149.

(16) Sanders, D. P.; Connor, E. F.; Grubbs, R. H.; Hung, R. J.; Osborn, B. P.; Chiba, T.; MacDonald, S. A.; Willson, C. G.; Conley, W. *Macromolecules* **2003**, *36*, 1534–1542.

(17) Gringolts, M. L.; Bermeshev, M. V.; Kaz'min, A. G.; Finkelshtein, E. Sh. *Dokl., Chem.* **2009**, *424*, 49–51.

(18) Feiring, A. E.; Schadt, F. L.; Petrov, V. A.; Smart, B. E.; Farnham, W. B. WO/2004/014964 E. I. Du Pont Co.

(19) Jean, Y. C., Mallon, P. E., Schrader, D. M., Eds. *Principles and applications of positron and positronium chemistry*; World Scientific: New Jersey, London, Singapore, and Hong Kong, 2003.

(20) Shantarovich, V. *J. Polym. Sci., Part B: Polym. Phys.* **2008**, *46*, 2485–2503.

(21) Wilks, B. R.; Chung, W. J.; Ludovice, P. J.; Rezac, M. E.; Meakin, P.; Hill, A. J. *J. Polym. Sci.: Part B:. Polym. Phys.* **2006**, *44*, 215–233.

(22) Ahmed, S. *Stereochemical structure-property relationships in polynorbornene from simulation.* Ph.D. Dissertation, Georgia Institute of technology: Atlanta, GA, 1998.

(23) Barnes, D. A.; Benedikt, G. M.; Goodall, B. L.; Huang, S. S.; Kalamarides, H. A.; Lenhard, S.; McIntosh, L. H.; Selvy, K. T.; Shick, R. A.; Rhodes, L. F. *Macromolecules* **2003**, *36*, 2623–2632.

(24) Puleo, A. C.; Miruganandam, N.; Paul, D. R. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 2385–2406.

(25) Khotimskii, V. S.; Filippova, V. G.; Bryantseva, I. S.; Bondar, V. I.; Shantarovich, V. P.; Yampolskii, Yu. P. *J. Appl. Polym. Sci.* **2000**, *78*, 1612–1620.

(26) Yampolskii, Yu. P.; Finkelshtein, E. Sh.; Makovetskii, K. L.; Ostrovskaya, I. Ya.; Portnykh, E. B.; Gringolts, M. L.; Ishunina, Yu. G.; Kevdina, I. B.; Shantarovich, V. P. *Polymer Sci., A* **1996**, *38*, 959–963.

(27) Yampolskii, Yu. P.; Finkelshtein, E. Sh.; Makovetskii, K. L.; Bondar, V. I.; Shantarovich, V. P. *J. Appl. Polym. Sci.* **1996**, *62*, 349–357.

(28) Morisato, A.; Pinnau, I. *J. Membr. Sci.* **1996**, *121*, 243–250.

(29) Masuda, T.; Nagai, K. In *Materials science of membrane for gas and vapor separation*; Yampolskii, Yu., Pinnau, I., Freeman, B. D., Eds.; Wiley: Chichester, U.K., 2006; p231.

(30) Hofmann, D.; Entrialgo-Castano, M.; Lerbret, A.; Heuchel, M.; Yampolskii, Yu. *Macromolecules* **2003**, *36*, 8528–8538.

(31) Yampolskii, Yu. P.; Durgaryan, S. G.; Nametkin, N. S. *Vysokomol. Soed., B* **1979**, *21*, 616–621.

(32) Paul, D. R., Yampolskii, Yu. P., Eds., *Polymeric gas separation membranes*: CRC Press: Boca Raton, FL, 1994, p 177.

(33) Nagai, K.; Masuda, T.; Nakagawa, T.; Freeman, B. D.; Pinnau, I. *Prog. Polym. Sci.* **2001**, *26*, 721–798.

(34) Shimomura, H.; Nakanishi, K.; Odani, H.; Kurata, M. *Rep. Progr. Polym. Phys. Jpn.* **1987**, *30*, 233–236.

(35) Starannikova, L.; Khodzhaeva, V.; Yampolskii, Yu. *J. Membr. Sci.* **2004**, *244*, 183–191.

(36) Struik., L. C. E. *Physical aging in amorphous polymers and other materials*; Elsevier: New York, 1978.

(37) Nagai, K.; Higuchi, A.; Nakagawa, T. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 289–298.

(38) Dorkenoo, K. D.; Pfromm, P. H. *Macromolecules* **2000**, *33*, 3747–3751.

(39) Shimomura, H.; Nakanishi, K.; Odani, H.; Kurata, M. *Rep. Progr. Polym. Phys. Jpn.* **1987**, *30*, 233–236.

(40) Nagai, K.; Higuchi, A.; Nakagawa, T. *J. Appl. Polym. Sci.* **1994**, *54*, 1207–1217.

(41) Tsuchihara, K.; Masuda, T.; Higashimura, T. *Macromolecules* **1992**, *25*, 5816–5820.

(42) Nagai, K.; Mori, M.; Watanabe, T.; Nakagawa, T. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 119–131.

(43) Nagai, K.; Sugawara, A.; Kazama, S.; Freeman, B. D. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 2407–2418.

(44) Budd, P. M.; McKeown, N. B.; Ghanem, B. S.; Msayib, K. J.; Fritsch, D.; Strannikovas, L.; Belov, N.; Sanfirova, O.; Yampolskii, Yu.; Shantarovich, V. *J. Membr. Sci.* **2008**, *325*, 851–860.

(45) Masuda, T.; Iguchi, Y.; Tang, B.-Z.; Higashimura, T. *Polymer* **1988**, *29*, 2041–2049.

(46) Merkel, T. C.; Bondar, V. I.; Nagai, K.; Freeman, B. D.; Yampolskii, Yu. P. *Macromolecules* **1999**, *25*, 8427–8440.

(47) Yampolskii, Yu.; Shishatskii, S.; Alentiev, A.; Loza, K. *J. Membr. Sci.* **1998**, *148*, 59–69.

(48) Yampolskii, Y.; Shantarovich, V. Positron annihilation lifetime spectroscopy and other methods for free volume evaluation in polymers. In *Materials Science of Membranes for Gas and Vapor Separation*; Yampolskii, Yu., Pinnau, I., Freeman, B. D., Eds.; John Wiley & Sons: Chichester, England, 2006; Chapter 6, pp 191−210.

(49) Tao, J. *J. Chem. Phys.* **1972**, *56*, 5499–5510.

(50) Eldrup, M.; Lightbody, D.; Sherwood, J. N. *Chem. Phys.* **1981**, *63*, 51–58.

(51) Jean, Y. C. *Microchem. J.* **1990**, *42*, 72–102.

(52) Goldanskii, V. I.; Mokrushin, A. D.; Tatur, A. O.; Shantarovich, V. P. *Appl. Phys.* **1975**, *5*, 379.

(53) Pixton, M. R.; Paul, D. R. In *Polymeric gas separation membranes*; Paul, D. R., Yampolskii, Yu. P.; Eds ; CRC Press: Boca Raton, FL, 1994; p 83.