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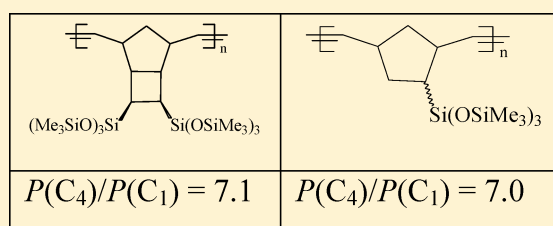
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S Supporting Information

ABSTRACT: Polymers of a new class of glassy materials that demonstrate unusual solubility controlled permeability—metathesis Si–O–Si containing polynorbornenes—are synthesized. The introduction of bulky Si(OSiMe₃)₃ substituents into the polynorbornene backbone is shown to provide the polymers with increased gas permeability, higher than all other known metathesis polynorbornenes. The prepared glassy polymers reveal behavior similar to that known for rubbers and, in particular, siloxanes: permeability coefficients increase for the penetrants of larger size. That is, these polymers are capable to remove higher hydrocarbons from natural and associated petroleum gases.



INTRODUCTION

In spite of great success made by membrane gas separation in the last few decades,^{1,2} there are several and still hardly solved, in industrial scale, but important problems: separation of hydrocarbon vapors or volatile organic compounds from their mixtures with permanent gases, separation of hydrocarbons in natural and associated petroleum gases, capture of gasoline vapors from air. Feasibility of realization of various tasks of gas separation depends mainly on the set of properties of the materials used in membranes.

Membrane materials can be characterized by solubility or diffusivity controlled permeation. Since the permeability coefficient P of a polymer can be described as the product $D \times S$, where D is the diffusion coefficient and S is the solubility coefficient, all the polymers can be partitioned into two groups: those with (1) diffusivity controlled gas permeation and (2) solubility controlled gas permeation. In the first group of the polymers the variation of the P values in the series of penetrants follows the changes of the diffusion coefficients. This group, the most numerous, is represented by glassy materials which can be used for separation of permanent gases (O₂, N₂, H₂, He, CO₂).^{1–4} The second group in which the variation of the P values follows the changes of the solubility coefficients originally was represented by rubbers (e.g., siloxanes)^{5,6} and semicrystalline polyolefins and is characterized by higher permeability of heavier components of the mixture. In other words, it is selectivity that is dominated by diffusion coefficients in common glassy polymers or by solubility coefficients in rubbers. Because of this rubbery membranes can be used for hydrocarbon separation: the permeates are enriched with heavier hydrocarbons.

The reason for such behavior is that for a series of penetrants (e.g., alkanes C₁–C₄) the variation of the diffusion coefficient is weaker than that of the solubility coefficient, so the latter exerts stronger effects on P than D values. It means that higher driving force of the separation process makes the permeability coefficients of, e.g., *n*-butane, $P(C_4H_{10})$, higher than $P(CH_4)$.

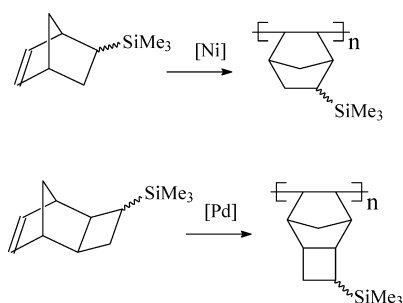
An important discovery of the last few decades of the 20th century was the synthesis of glassy poly(trimethylsilyl propyne) (PTMSP)⁷ and other highly permeable polyacetylenes which quite unexpectedly showed the solubility controlled gas permeation of hydrocarbons.^{8–10} For a long time they formed the only group of glassy polymers, for which the solubility controlled permeation was observed. By several reasons, none of polyacetylene materials have found practical application for separation of hydrocarbons with different size or molecular weight. Hence, the search for other polymers with solubility controlled permeation properties is still relevant and attracts attention of researchers. In the framework of this problem we have realized synthesis and polymerization of silicon-substituted norbornenes and tricyclononenes according to addition mechanism (Scheme 1).

This led to discovery of new highly permeable glassy polymers—addition silicon-substituted norbornene-type polymers (polynorbornenes and polytricyclononenes) with very rigid main chains and high glass transition temperatures.^{11–14} It was found that along with the high permeability they demonstrated the solubility controlled gas permeation like

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Scheme 1. Addition Polymerization of Silicon-Substituted Norbornenes and Tricyclononenes

polyacetylenes. This means that they are capable to enrich higher hydrocarbon gases (e.g., butane) in mixture with methane. This was proven not only by the experiments with individual gases but also in separation of binary and multicomponent hydrocarbon mixtures.^{15,16}

Polymerization of norbornene derivatives can also proceed along the ring-opening scheme. Metathesis polynorbornenes have been studied more extensively. It was shown that the polymers of this class have a modest permeability and reveal diffusivity controlled permeation.¹⁴ In the present work we demonstrate that glassy metathesis polynorbornenes that contain side groups with several flexible Si—O—Si-containing structure elements show solubility controlled permeation of hydrocarbons C₁–C₄. Preliminary results on a single polymer of such structure have been reported earlier.¹⁷

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.

Chemicals. Quadricyclane¹⁸ was obtained according to published procedure described in literature and was distilled over sodium metal before use. 1,2-Bis(trichlorosilyl)ethylene was synthesized according to the literature procedure.¹⁹ 3,4-Bis(trichlorosilyl)tricyclononene-7¹² and Me₃SiONa²⁰ were obtained following the procedures described in literature. Diethyl ether and toluene were distilled over sodium. All other chemicals were purchased from Aldrich and used as received. The first generation Grubbs catalyst was purchased in Aldrich. *p*-Toluenesulfonylhydrazide was obtained as described.²¹ *o*-Xylene was purchased in Aldrich and dried over sodium.

Methods. NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 400.1 MHz (¹H NMR), 133.3 MHz (¹³C NMR), 79.49 MHz (²⁹Si NMR) in CDCl₃ solution. Chemical shifts δ are reported in parts per million relative to an internal reference (residual CHCl₃ signal). Mass spectra were recorded on a Thermo Focus DSQ II (ionization energy 70 eV, source temperature 230 °C). CCDC 940417 contains supplementary crystallographic data for TCNSi6. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

Gel-permeation chromatography (GPC) analysis of the polymers was performed on a Waters system with a differential refractometer (Chromatopack Microgel-S, 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 K/min. Thermal gravimetric measurements were carried out using a Perkin-Elmer TGA-7 instrument. All DMA measurements were performed in the temperature range of 20 to 300 °C and at 1 Hz frequency under Ar at a heating rate 3 K/min. The samples for DMA were 0.1 mm in thickness and 6.35 mm in the

diameter and the corresponding measurements were carried out using a Mettler Toledo DMA/SDTA861^e instrument.

Synthesis of 3,4-Bis{tris(trimethylsiloxy)silyl}tricyclononene-7 (TCNSi6). To Me₃SiONa (89 g, 0.8 mol) in diethyl ether (400 mL) 3,4-bis(trichlorosilyl)tricyclononene-7 (23.0 g, 0.06 mol) in diethyl ether (20 mL) was added dropwise so as the mixture gently refluxed. Then the reaction mixture was refluxed additionally for 100 h, cooled to room temperature, and poured into water (400 mL). The diethyl ether layer was separated and the water layer was extracted with diethyl ether (3 × 100 mL). Organic fractions were combined, washed with water (3 × 100 mL) and dried over MgSO₄. The solvent was removed under reduced pressure and the residue colorless oil was passed through neutral aluminum oxide column (eluent: hexane). The eluent was evaporated and the crystalline product was washed with ethanol and dried under reduced pressure (mp 89–92 °C). Yield: 10.6 g (25%).

¹H NMR (CDCl₃, ppm): 5.89–5.84 (2H, m, H-7, H-8), 2.92 (1H, s, H-1, H-6), 2.58 (1H, s, H-1, H-6), 2.10 (1H, d, *J* = 9.1 Hz, H-9), 1.98–1.92 (1H, m), 1.92–1.85 (1H, m), 1.83–1.78 (1H, m), 1.15 (1H, d, *J* = 9.1 Hz, H-9), 0.94–0.90 (1H, m, H-9), 0.11, 0.10 (54H, s, Si(CH₃)₃).

¹³C NMR (CDCl₃, ppm): 135.29, 134.44 (C-7, 8), 45.47, 44.35, 40.81, 37.47, 37.00, 20.28, 18.47 (C(1), C(2), C(3), C(4), C(5), C(6), C(9)), 2.11, 2.05 (Si(CH₃)₃).

²⁹Si NMR (CDCl₃, ppm): 6.83, 6.66, –67.46, –69.03.

MS (EI): 708 (2%, M⁺), 295 (17%, ((CH₃)₃SiO)₃Si⁺), 207 (100%, ((CH₃)₃SiO)₂SiH⁺), 73 (52%, (CH₃)₃Si⁺).

Metathesis Polymerization Procedure. In the typical procedure (the example is given for ratio 3,4-bis{tris(trimethylsiloxy)silyl}tricyclononene-7/(PCy₃)₂Cl₂Ru=C(H)Ph = 1500/1), the solution of TCNSi6 in toluene (1:1 w/w, 4.0 g, 2.8 mmol) was placed into a round-bottom glass ampule (*V* = 15 mL) equipped with a magnetic stirrer. Polymerization was initiated by adding of Grubbs first generation catalyst (PCy₃)₂Cl₂Ru=C(H)Ph (1.87 × 10^{–3} mmol, 1.95 mL). After 6 h the inhibitor (2,2'-methylenebis(6-*tert*-butyl-4-methylphenol)) and vinyl ethyl ether were added and the mixture was allowed to stay for 10 min. Then the polymer solution was precipitated by ethanol with the inhibitor, separated, washed by several portions of ethanol, and dried in vacuum. The polymer was twice reprecipitated by ethanol from the toluene solution and dried in vacuum at 50 °C up to a constant weight. Yield = 1.4 g (70%), *M*_w = 950000, *M*_w/*M*_n = 1.2, and *T*_g = 236 °C.

¹H NMR (CDCl₃, ppm): 5.47–4.76 (2H, m, H-7, H-8), 3.02–2.45 (3.2H, m), 2.20–1.66 (2.6H, m), 1.34–0.89 (2.2H, m), +0.34 to –0.21 (54H, m, Si(CH₃)₃).

²⁹Si NMR (CDCl₃, ppm): 6.88–6.58 (m), –65.59 (m), –68.21 (m).

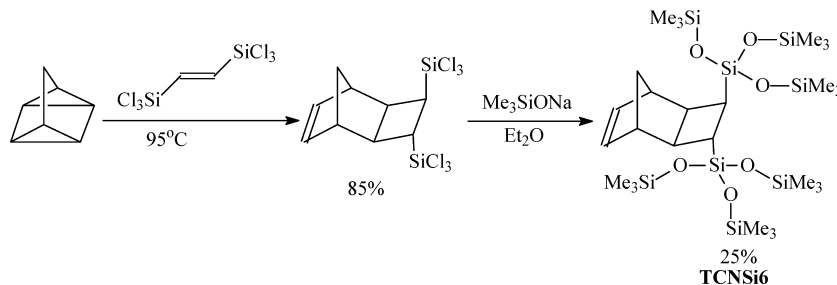
Hydrogenation of Metathesis PTCNSi6. PTCNSi6 (0.90 g), *p*-toluenesulfonylhydrazide (1.5 g) and 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) (the inhibitor, 20 mg) were placed into a round-bottom two-necked flask (*V* = 50 mL) equipped with a magnetic stirrer and a backflow condenser. Then absolute *o*-xylene (25 mL) was added and the resulting mixture was refluxed for 12 h. After that the reaction mixture was precipitated by ethanol, separated, washed by several portions of ethanol and dried in vacuum. The polymer was twice reprecipitated by ethanol from the toluene solution and dried in vacuum at 50 °C up to a constant weight. Yield = 0.81 g (90%), *M*_w = 1.32 × 10⁶, *M*_w/*M*_n = 1.2, and *T*_g = 225 °C.

¹H NMR (CDCl₃, ppm): 2.66–0.65 (12H, m), +0.62 to –0.30 (54H, m, Si(CH₃)₃).

²⁹Si NMR (CDCl₃, ppm): 6.68–6.41 (m), –65.42 (m), –67.98 (m).

Permeability Coefficients. These were determined using a setup with gas chromatographic analysis of permeates. In the experiments a feed (upstream) pressure was 1 bar, while the downstream pressure was also 1 bar but it comprised mainly the pressure of sweep gases (He in most the cases and N₂ in the cases of He and H₂ as penetrants). The partial pressure of penetrants in the downstream part of the cell was negligible, so the penetrants' pressure drops were virtually 1 bar. More details of the experimental procedure can be found in ref 22.

Scheme 2. Synthesis of New Monomer: 3,4-Bis[tris(trimethylsiloxy)silyl]tricyclononene-7



RESULTS AND DISCUSSION

Recently, we accomplished the synthesis of glassy metathesis poly[3-tris(trimethylsiloxy)silyl]tricyclononene-7 and found¹⁷ for the first time that for this polymer the solubility controlled gas permeation is observed in contrast to other metathesis polynorbornenes. It was shown that replacement of Me₃Si-side group by bulkier substituent containing three Me₃Si-groups in tricyclononenes based metathesis polymers results in a strong increase of permeability in respect to all studied gases (from $P(\text{CH}_4) = 14$ Barrer for Me₃Si-containing polymers to $P(\text{CH}_4) = 180$ Barrer for novel polynorbornene with Si(OSiMe₃)₃ side groups).

In the present paper, we demonstrate a general character of the proposed approach to affect purposefully the gas separation properties of glassy polymers by introducing Si–O–Si-containing substituents. This approach will supply a new tool for macromolecular design of polymers with high and controlled gas separation characteristics.

With this aim, we, for the first time, synthesized and studied gas permeation properties of a series of new polymers containing in each repeat unit several Me₃Si-groups bonded to the carbocycle via flexible Si–O–Si bonds. The initial corresponding monomer was obtained according to Scheme 2. The synthetic method was based on a stereospecific $[2\sigma+2\sigma+2\pi]$ -cycloaddition reaction of quadricyclane and *trans*-1,2-bis(trichlorosilyl)ethylene followed by the step of siloxanation with Me₃SiONa.

This new monomer 3,4-bis[tris(trimethylsiloxy)silyl]tricyclononene-7 (TCNSi6) was isolated as a crystalline solid and its structure fully agreed with NMR data and the results of X-ray analysis. From the results of X-ray analysis (Figure 1), it is obviously the cyclobutane ring is in a preferable for polymerization *exo*-position, while two bulky (Me₃SiO)₃Si-groups are in *syn*- and *anti*-positions correspondingly.

The obtained monomer (TCNSi6) was successfully polymerized by ring-opening metathesis mechanism in the presence of the first generation Grubbs catalyst (Scheme 3). As a result the first metathesis polymer with six Me₃Si-groups per a monomer unit (PTCNSi6) was synthesized ($M_w \sim 9.5 \times 10^5$, $M_w/M_n = 1.2$, $T_g = 236$ °C (DMA)) in a high yield. In order to have a fully saturated polymer of such kind the hydrogenation was carried out with *p*-toluenesulfonylhydrazide in *o*-xylene at 130 °C.

According to ¹H and ²⁹Si NMR data the hydrogenation was performed quantitatively and selectively without a cleavage of the side groups during the reaction. The T_g value of the hydrogenated polymer (PTCNSi6H) was lower (225 °C (DMA)) and the molecular weight increased a little ($M_w \sim 1.32 \times 10^6$, $M_w/M_n = 1.2$) than the initial polymer possesses. The temperatures of 5% weight loss (TGA) for all these polymers

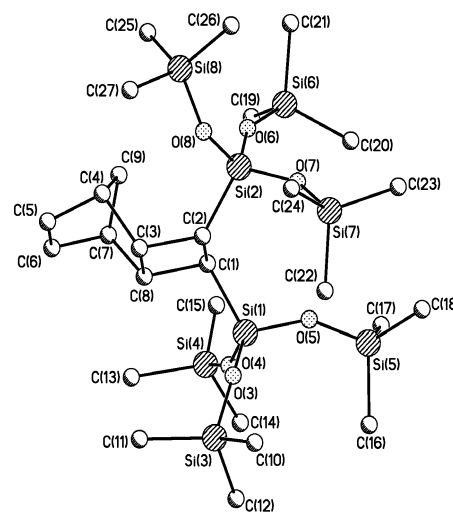


Figure 1. General view of TCNSi6 in representation of atoms via thermal ellipsoids at 50% probability level.

were very high (310 (Air) /380 °C (Ar) for PTCNSi6 and 325 (Air) /400 °C (Ar) for PTCNSi6H). It should be noted that both polymers PTCNSi6 and PTCNSi6H demonstrated good film-forming properties and their films were transparent (Figure 2).

The study of gas permeability of the synthesized polymers provided new interesting data. In Table 1 we compared the permeability coefficients P (Barrer) of novel metathesis norbornene polymers with Me₃Si-groups and Si–O linkages in substituents (entries 3–6) and two other Si-containing metathesis polymers with Me₃Si-groups attached directly to norbornene and tricyclononene cycles, i.e. via Si–C bonds (entries 1 and 2). It should be noted that new polymers (entries 3–6) can be considered as the most permeable among common metathesis polynorbornenes. An analysis of the data for light gases indicates that the appearance of bulky Si(OSiMe₃)₃ side groups results in increases of permeability. More specifically, if we compare two metathesis polytricyclononenes with one substituent in the monomer unit (Table 1, entries 1 and 3) we see that the presence of a siloxy-substituent containing three Me₃Si groups gives rise of helium permeability coefficients by the factor 2.7, while methane permeability has risen almost by a factor nearly 13. Further increase in the number of Me₃Si groups up to six in the monomer results in 1.5–2 times increase in the permeability coefficients in comparison with a polytricyclononene containing only three Me₃Si groups in each unit (Table 1, entries 3 and 4). As can be judged by the glass transition temperatures T_g given in Table 1 all the polymers studied are glassy. An appearance of two bulky Si(OSiMe₃)₃ side groups in the main chain results in much

Scheme 3. Synthesis of New Polymers PTCNSi6 and PTCNSi6H

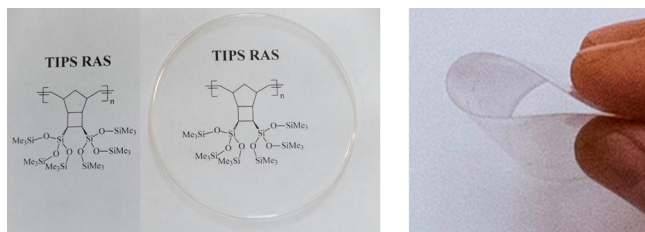
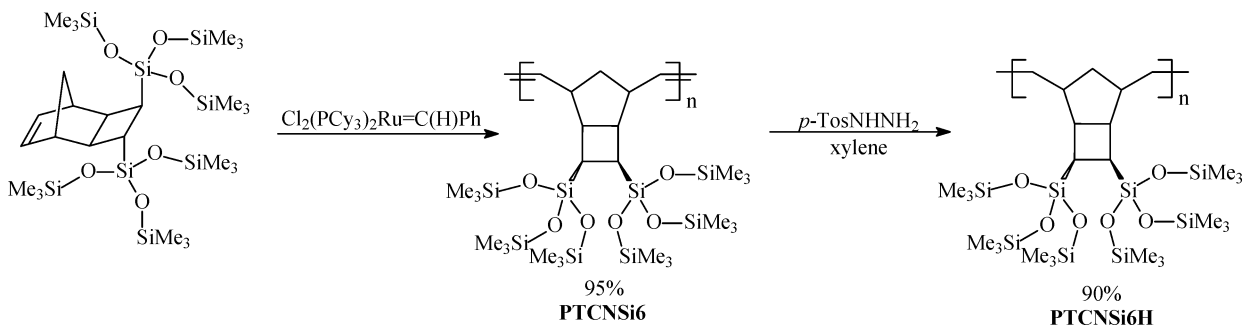


Figure 2. Pictures of PTCNSi6.

higher rigidity of polymer chain and higher T_g . If we compare two polymers with the same substituent but somewhat different rigidity of the main chain (or T_g) (entries 4 and 5 in Table 1) we see that the polymer with somewhat higher T_g is distinguished by larger P values. For comparison, Table 1, as well as Tables 2 and 3, show also the gas permeation parameters of poly(dimethylsiloxane) (PDMS).

It is of interest to compare the fractional free volume (FFV) of the novel polymers described in this work with those of conventional glassy polymers. For the polymers 3–6 from

Table 1. Permeability Coefficients (P)^{5,17,23–25} for Light Gases of Metathesis Si-Containing Polynorbornenes^a

No	Structure	T_g , °C	P , Barrer						Ref.
			He	H ₂	O ₂	N ₂	CO ₂	CH ₄	
1		104	80	120	28	7	110	14	23
2		129	230	330	90	24	400	55	24
3		110	220	360	170	55	830	180	17
4		236	420	690	295	100	1160	300	this work
PTCNSi6									
5		225	300	460	220	75	840	215	this work
PTCNSi6H									
6		101	290	430	290	93	910	-	25
		-	-	-	270	88	1140	280	this work
7	PDMS	-123	350	650	600	280	3250	950	5

^aTemperature 22 ± 1 °C.

Table 2. Separation Factors $\alpha_{ij} = P_i/P_j$ of Metathesis Si-Containing Polynorbornenes^{5,17,23–25}

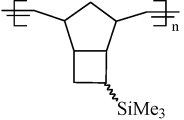
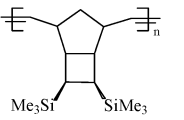
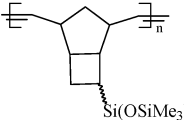
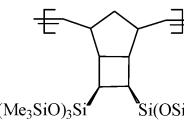
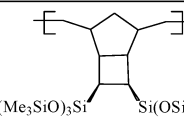
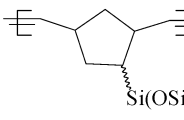
No	Structure	$\alpha_{ij} = P_i/P_j$				Ref.
		O ₂ /N ₂	CO ₂ /N ₂	He/N ₂	CO ₂ /CH ₄	
1		4.0	15.7	11.4	7.9	23
2		3.8	16.7	9.6	7.3	24
3		3.1	15.1	4.0	4.6	17
4		3.0	11.6	4.2	3.9	this work
PTCNSi6						
5		2.9	11.2	4.0	3.9	this work
PTCNSi6H						
6		3.1	9.8	3.1	-	25
		3.1	13.0	-	4.1	this work
7	PDMS	2.1	11.6	1.2	3.4	5

Table 1 the FFV values are in the range 22–25%. This is somewhat higher than FFV values reported e.g. for various polycarbonates and polysulfones having FFV in the range 13–20%.²⁶ On the other hand, for high free volume polymers that have gas permeability much greater (e.g., $P(\text{O}_2) = 6000\text{--}12000$ Barrer for PTMSP²⁷), the reported values are about 30% or even greater.

Meanwhile, increases in permeability for light gases are accompanied by decreases in permselectivity $\alpha_{ij} = P_i/P_j$ as is seen from Tables 1 and 2, and the values of the separation factors approach the corresponding values of rubbers. Though for some gas pairs (for example He/N₂) PDMS is much less permselective (Table 2).

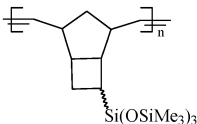
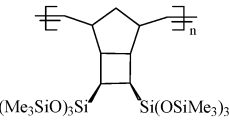
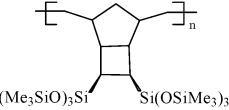
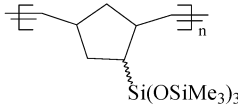
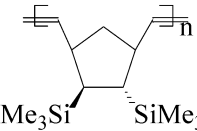
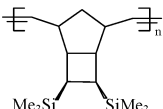
It is known that high permeability of siloxane polymers is caused by great flexibility of their main chains as revealed by low glass transition temperature.²⁷ However the results of our and some other works indicate that small scale mobility (flexibility) of side groups as well as their shape can also affect the observed permeability, permselectivity and glass transition temperature. Thus, Kawakami and Imae²⁸ investigated several polystyrenes *p*-substituted by Si–O–Si containing groups. The functionalized polymers became more “rubber-like”, because the observed α (O₂/N₂) moved to those of polydimethylsiloxane and other rubbers. As for the glass transition temperatures T_g , they decreased but the quantitative effects depended on the form of side groups; more elongated substituents prone to self-

plasticization resulted in lower T_g and α . Similar effects were demonstrated recently for metathesis polymers.²⁵ Introduction of linear siloxane chains resulted in formation of polymers with T_g as low as -115 °C, whereas a more bulky substituent led to the increase in T_g up to 101 °C. But in the works on the polymers with Si–O bonds in side groups^{25,29,30} only permeability coefficients for light gases were measured.

An unexpected result that can be noted for novel glassy metathesis norbornene polymers was an observation that they exhibit solubility controlled permeation of light hydrocarbons (Table 3), that is, an increase in P values for a series of hydrocarbons from methane to *n*-butane.

As has been mentioned in Introduction such trend is characteristic either for rubbers or for large free volume, highly permeable glassy polymers like PTMSP or addition type Si-containing norbornene polymers. The polymers studied in this work do not belong to either of these groups; still they systematically show such a trend. So we demonstrate here a novel group of polymers with so-called reversed, solubility controlled permeation. Numerous studies of metathesis polynorbornenes have never showed permeation of this type. For making a more substantiated comparison of Si–O containing metathesis polynorbornenes with other polymers of this group we tested early synthesized metathesis polynorbornenes—poly[3,4-bis(trimethylsilyl)tricyclononene]²⁴ (entry 6 in Table 3) and poly[5,6-bis(trimethylsilyl)-

Table 3. Permeability Coefficients (P , Barrer)^{5,17,29–} of Hydrocarbons for Metathesis Si-Containing Polynorbornenes^a

Entry	Structure	P , Barrer				$P(C_4)/P(C_1)$	Ref.
		CH ₄	C ₂ H ₆	C ₃ H ₈	<i>n</i> -C ₄ H ₁₀		
1		180	270	290	1940	10.8	17
2		300	480	520	2120	7.1	This work
PTCNSi6							
3		215	305	300	1140	5.3	This work
PTCNSi6H							
4		280	440	390	1970	7.0	This work
5		45	30	-	-	-	29
6		57	52	18	61	1.1	This work
7	PDMS	950	2500	4100	9000	9.5	5

^aTemperature 22 ± 1 °C.

norbornene]²⁹ (entry 5 in Table 3). They contain two Me₃Si groups but are devoid of Si–O bonds. Their permeability coefficients for gaseous hydrocarbons were compared with the P values of Si–O containing polymers presented in Table 3. It is seen that neither of these two polymers exhibits solubility controlled permeation of hydrocarbons C₁–C₄. The ratio $P(C_4)/P(C_1)$ that is slightly higher than unity of the polymer 6 from Table 3 does not contradict to the latter statement. The permeability coefficients for all hydrocarbons were measured at upstream pressure of 1 atm. For methane and ethane permeability coefficients usually does not depend on pressure. For propane some dependence can be expected, however, the activity of propane vapor at 1 atm is relatively low ($p/p_s = 0.13$). Meanwhile, for butane p/p_s at 1 atm corresponds to a much higher value (0.4), so a not negligible contribution into $P(C_4H_{10})$ is caused by pressure dependence, so even in this case no increase in the permeability coefficient with molecular weight of penetrants is observed.

No doubt, the reason for the phenomena described is the presence of numerous flexible Si–O bonds in side groups. It is intriguing that these polymers show a contradictory combination of properties. They are glassy by their mechanical and thermal properties having rather high T_g (sometimes up to 240 °C). On the other hand, their trend in permeation of hydrocarbons is akin to that of rubbers.^{5,6,31} It can be assumed that the reasons for solubility controlled permeation in them are decreased energy barriers of gas diffusion due to easy small scale movements of Si–O linkages and induced by this weak dependence of the diffusion coefficients D versus the size of penetrants.

The novel norbornene polymers can be compared with the state-of-the-art materials such as PDMS,⁵ PTMSP,^{2,9} Si-substituted norbornene polymers,² or PIM-1^{32,33} that reveal solubility controlled permeation/separation of hydrocarbons. In a wider context, they are similar to many other membrane materials that can be characterized by reverse-selective polymers for gas separation (see, e.g., ref 34. where however

mainly CO₂ containing mixtures are considered). The main peculiarity of the described metathesis polynorbornenes is that the reason for their reverse-selective behavior is neither the flexibility of main chains nor very large excess free volume, but local, small scale mobility of side groups that contain Si–O bonds.

A detailed elucidation of unusual properties of novel Si–O–SiMe₃-containing metathesis polynorbornenes requires independent measurements of the diffusion coefficients of different gases, determination of the gas and vapor solubility coefficients and sorption isotherms, investigation of their physical properties (free volume, smaller scale (sub-*T_g*) chain motion). This research is now in progress.

CONCLUSIONS

In this work we demonstrated a new chemical class of glassy polymers, Si–O–SiMe₃-containing metathesis polynorbornenes, which is distinguished by very rare feature—solubility controlled permeation. It was shown that introduction of bulky (Me₃SiO)₃Si-substituents in polynorbornene backbone not only increased polymer's gas permeability but supplied polynorbornenes solubility controlled permeation. This work shows that quite different chemical structures of membrane materials can possess such properties very important for creation of membrane materials capable for separation of hydrocarbons of natural and associated petroleum gases.

ASSOCIATED CONTENT

Supporting Information

¹H, ¹³C, and ²⁹Si NMR spectra of monomers and polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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