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Synthesis of High Molecular Weight Poly[3-{tris(trimethylsiloxy)silyl}tricyclononenes-7] and Their Gas Permeation Properties

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S Supporting Information

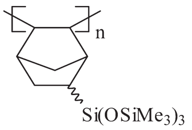
Norbornene and its derivatives can be polymerized, producing high molecular weight products of entirely different structure of the main chain depending on the choice of the catalysts. In the presence of the catalysts such as WCl_6, $RuCl_3$, Re_2O_7/Al_2O_3, or Grubbs Ru−carbene complexes, ring-opening metathesis polymerization (ROMP) proceeds leading to formation of cyclolinear unsaturated polymers.[1,2] On the other hand, norbornenes can be also polymerized via opening of double bonds like vinyl monomers in the presence of Ni and Pd catalysts. This addition-type polymerization leads to bulky bicyclic repeat units that do not contain unsaturated bonds.[3,4]

Most of the ROMP polynorbornenes are glassy polymers (T_g in the range ca. 40−100 °C) with relatively small gas permeability ($P(O_2)$ = 1−100 barrer).[5,6] However, introduction of silicon-containing substituents in monomer units significantly increases this parameter.[5,7] Addition-type polynorbornenes have rigid main chains, their glass transition temperatures in most cases are above the onset of thermal decomposition (>400 °C), and those that contain bulky Me_3Si groups are characterized by much higher gas permeability ($P(O_2)$ = 900−2400 barrer) and large free volume.[8] An interesting feature of these polymers is so-called solubility controlled permeation of gaseous hydrocarbons, that is, an increase in permeability coefficients in the series from methane to *n*-butane. Earlier such behavior among glassy polymers has been reported only for polyacetylenes.[9]

The outcome of the numerous studies discussed in refs 5 and 6 is that a substantial increase in gas permeability and free volume can be achieved by introduction of more than one bulky Me_3Si substituent into repeat units of the polymers. The increases in permeability due to the introduction of Me_3Si groups are also valid for polymers of different classes.[10] In this regard, an interesting result was obtained recently by preparation of ROMP norbornene material containing three bulky Me_3Si groups in each monomer unit (Scheme 1).[11]

The obtained high molecular weight polymer showed very high (for ROMP polymers) permeability ($P(O_2)$ = 290 barrer).

Attempts to realize addition polymerization of the same monomer with formation of high molecular weight polymer[12] failed: only low molecular weight product having the structure was achieved in the presence of Ni-containing catalyst. Low molecular weight did not allow measurement of gas permeability of this material.



Earlier it has been observed that there is a hindrance for addition polymerization of norbornenes containing one or more Me_3Si groups. The presence of Me_3Si groups markedly decreased polymerization activity of the monomer in comparison with nonsubstituted norbornene.[13,14] Also, it was demonstrated that *endo*-isomer was less active than *exo*-one.[13] An introduction of the second Me_3Si group led to full disappearance of monomer activity in addition polymerization in the presence of both Ni- and Pd-containing catalyst systems (the right side of Scheme 2), keeping its high activity in ROMP (the left side of Scheme 2).

The aim of this work was the synthesis of high molecular weight polynorbornenes of both types containing three pendant Me_3Si-O groups and study their gas permeation properties.

The idea of our synthetic strategy was in shift of hindered Me_3Si groups further from the double bond.[15] In such a way a synthesis of a novel 3-{tris(trimethylsiloxy)silyl}tricyclo[$4.2.1.0^{2,5}$]non-7-ene (**III**) on the basis of thermal condensation of vinyltrichlorosilane with quadricyclane was accomplished (Scheme 3).

The monomer **III** was successfully polymerized by ROMP mechanism in the presence of first generation Grubbs catalyst (Scheme 4, left side).

The assumption of reactivation of norbornene double bond by removal of bulky $-Si(OSiMe_3)_3$ groups was confirmed by successful addition polymerization of **III** in the presence of Pd-containing catalyst systems (Scheme 4, right side). It should be noted that the catalysts on the basis of Ni complexes ($Ni(acac)_2/B(C_6F_5)_3$) turned out to be inactive.

The results of the polymerization experiments are given in Table 1.

It is seen that in the presence of both catalysts high molecular weight glassy polymers can be prepared. The ROMP poly(**III**) has relatively high glass transition temperature close to that of ROMP poly(trimethylsilyltricyclononene) (104 °C).[5] The addition-type polymer like its analogue containing Me_3Si group has a very high glass transition temperature.

Gas permeability coefficients of the two novel polymers were measured using chromatographic technique described elsewhere.[8,16] Measurements were performed for nine gases: He, H_2, O_2, N_2, CO_2, CH_4, C_2H_6, C_3H_8, *n*-C_4H_{10}. A motivation for

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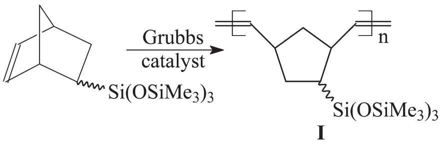
an inclusion of gaseous alkanes into the standard list of light gases was caused by observation of solubility controlled permeation of hydrocarbons in addition-type Si-containing norbornene polymers.[8,14]

The permeability coefficients of the polymers studied are presented in Table 2. The corresponding ideal separation factors $\alpha = P_i/P_j$ are given in Table 3.

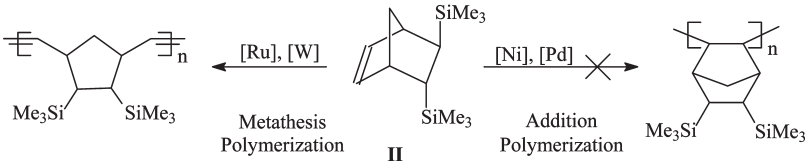
Let us consider the transport parameters of ROMP poly(**III**). It shows relatively high (for a ROMP norbornene polymer) gas permeability. Only siloxane containing polymer (PNBSi-$(OSiMe_3)_3$) described in ref 11 reveals greater permeability coefficients; however, it is less selective (Table 3). An unexpected result obtained in the study of ROMP poly(**III**) is the observed solubility controlled permeation, i.e., increase of the *P* values for the series from CH_4 to C_4H_{10}. Even one of the most permeable ROMP polynorbornene studied so far, namely the polymer containing two Me_3Si groups, revealed diffusivity-controlled permeation of lower alkanes.[17] Solubility-controlled permeation is usually attributed to the polymers with large free volume and high permeability (polyacetylenes with branched side groups,[9] addition-type Si-containing norbornene polymers,[8] the polymer with intrinsic microporosity PIM-1[18]). On the other hand, conventional glassy polymers such as polycarbonate, polysulfone, or polyvinyltrimethylsilane[18−20] show diffusivity-controlled permeation (i.e., the *P* values decrease for the series from CH_4 to C_4H_{10}). It is tempting to assume that diffusivity-controlled permeation is characteristic for polymers with lower permeability. So ROMP poly(**III**) would be considered as a noticeable exception. As we know, only some glassy polyacetylenes with alkyl side groups reveal solubility controlled permeation in spite of rather low gas permeability ($P(O_2)$ = 39−71 barrer).[21] It means that it is not average size of free volume elements which determines the level of gas permeability of a polymer, but some other quality of free volume; namely, its connectivity should be considered as a criterion for solubility or diffusivity-controlled permeation of hydrocarbons.

Addition-type poly(**III**) is distinguished by greater permeability as compared to ROMP poly(**III**). In this regard the same

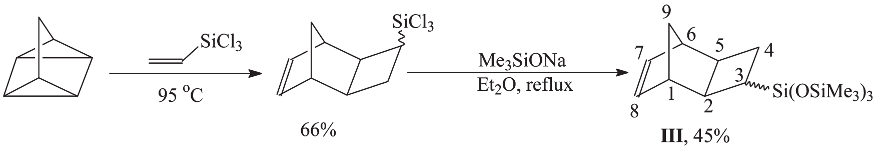
Scheme 1. Metathesis Polymerization of 5-Tris(trimethylsiloxy)silylnorbornene-2



Scheme 2. Metathesis and Addition Polymerization of 5,6-Bis(trimethylsilyl)norbornene



Scheme 3. Synthesis of 3-{Tris(trimethylsiloxy)silyl}tricyclo[4.2.1.0^{2,5}]non-7-ene



Scheme 4. Metathesis and Addition Polymerization of 3-{Tris(trimethylsiloxy)silyl}tricyclo[4.2.1.0^{2,5}]non-7-ene

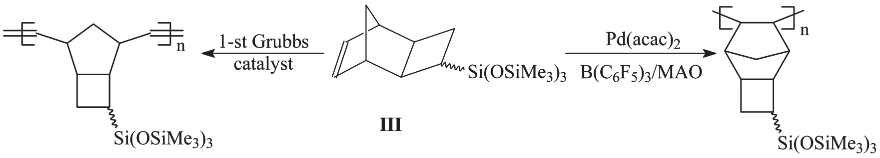


Table 1. Polymerization of 3-{Tris(trimethylsiloxy)silyl}tricyclononene-7

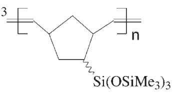
catalyst	[M]/[Cat.]/[B]/[MAO]	yield, %	M_w	M_w/M_n	T_g, °C
		Metathesis Polymerization			
$(PCy_3)_2Cl_2RuC(H)Ph$	1000/1/0/0	95	6.1×10^5	3.8	110
	3000/1/0/0	95	9.2×10^5	3.5	
		Addition Polymerization			
$Pd(acac)_2/B(C_6F_5)_3/MAO$	3000/1/300/0	36	3.3×10^5	3.9	–[a]
	3000/1/300/600	40	5.5×10^5	3.6	–[a]

[a] T_g is higher than the onset of thermal decomposition.

Table 2. Permeability Coefficients *P*, barrer, of ROMP Poly(III), Addition-Type Poly(III), and Some Other Polymers for Comparison

Gas	Polymer			
	ROMP poly(III)	Addition type poly(III)	ROMP PNBSi(OSiMe$_3$)$_3$*[11]	Addition type PTCN-Si**[8]
He	220	1110	290	930
H_2	360	2040	430	2060
O_2	170	960	290	990
N_2	55	420	93	390
CO_2	830	4020	910	5300
CH_4	180	1250	260	1010
C_2H_6	270	2370	-	1360
C_3H_8	290	3490	-	1470
C_4H_{10}	1940	22200	-	13030

* PNBSi(OSiMe$_3$)$_3$



** PTCN-Si

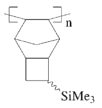


Table 3. Separation Factors $\alpha_{ij} = P_i/P_j$ of ROMP Poly(III), Addition-Type Poly(III), and Some Other Polymers for Comparison

gas pair	polymer			
	ROMP poly(**III**)	addition-type poly(**III**)	ROMP PNBSi(OSiMe$_3$)$_3$[11]	addition-type PTCN-Si[8]
O_2/N_2	3.1	2.3	3.1	2.1
H_2/N_2	6.5	4.9	4.6	2.3
CO_2/CH_4	4.6	3.2	3.5	3.4
CO_2/N_2	15.1	9.6	9.8	11.6
C_2/C_1	1.5	1.9		2.6
C_4/C_1	10.8	17.8		9.5

effects were observed earlier for other addition-type norbornene polymers with SiMe$_3$ side groups.[8,13] In Table 2, the permeability coefficients of addition-type poly(**III**) can be compared with those of another addition-type polymer containing a single Me$_3$Si group instead of Si(OSiMe$_3$)$_3$ substituent.[8] It is evident that for light gases permeability coefficients of the two polymers are very similar; however, the differences appear for hydrocarbons C_{2+}. This is reflected in higher selectivity of separation factors $\alpha(C_2/C_1)$ and $\alpha(C_4/C_1)$ as seen from Table 3.

Different interpretations of this result can be made. An introduction of such bulky side group attached directly to the main chain can make difficult dense packing of the chains, thus increasing free volume and the transport parameters that depend on it. On the other hand, such substituent includes flexible Si−O bonds. It is known that the appearance of flexible Si−O bonds not only in the backbone chains but also in the side groups results in significant decrease in the glass transition temperature and increase in permeability, though reduction of permselectivity. Thus, it has been shown that some polystyrenes having oligodimethylsiloxanyl substituents in the para-position of phenylene group has T_g as low as about 260 K (that is, are rubbery) and are characterized by permeability much higher than that of polystyrene and substantially reduced permselectivity.[22−24] Since no significant reduction of T_g and separation factors are observed for ROMP poly(**III**) and addition-type poly(**III**) (Tables 1 and 3), it is likely that the main factors that determine the transport parameters of the two novel polymers are the big size and the presence of siloxy fragments in the introduced Si-containing side groups. Hence, it is worthwhile to continue studies of the effects of Si−O containing side groups on the properties of norbornene polymers of both types.

Thus, in this work we succeeded to polymerize the tricyclononene monomer with Si(OSiMe$_3$)$_3$ substituent according to ROMP and addition-type schemes with obtaining high molecular weight products with good film-forming properties. Gas permeation properties of the two polymers were studied, and both revealed distinct solubility controlled permeation of hydrocarbons C_1-C_4. A general problem that is advanced by the results obtained for ROMP poly(**III**) is the search for explanation why low permeable glassy polymer materials like this show solubility controlled permeation, which is important for separation of hydrocarbons of natural and associated petroleum gases. Atomistic modeling of the nanostructure of this material using molecular dynamics is apparently the way for solving this intriguing problem.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic details, ^{1}H and ^{13}C NMR spectra for compounds **III**, ROMP poly(**III**), addition-type poly(**III**), and EA for compounds **III**, addition-type poly(**III**), and MS for compound **III**. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: London, 1997; p 472.
(2) Grubbs, R. H. *Handbook of Metathesis*; Wiley-VCH: Weinheim, 2003; Vol. 3, p 442.
(3) Makovetskii, K. L. *Polym. Sci., Ser. C* **2008**, *50*, 22–38.
(4) Blank, F.; Janiak, Ch. *Coord. Chem. Rev.* **2009**, *253*, 827–861.
(5) Finkelshtein, E. Sh.; Bermeshev, M. V.; Gringolts, M. L.; Starannikova, L. E.; Yampolskii, Yu. P. *Russ. Chem. Rev.* **2011**, *80* (4), 341–361.
(6) Yampolskii, Yu. In *Comprehensive Membrane Science and Technology*; Drioli, E., Giorno, L., Eds.; Elsevier: Amsterdam, 2010; Vol. 1, p 131.
(7) Finkelshtein, E. Sh.; Ushakov, N. V.; Gringolts, M. L. In *Silicon Polymers Series: Advances in Polymer Science*, 1st ed.; Muzafarov, A. M., Ed.; Springer: Heidelberg, 2011; Vol. 235, p 111.
(8) Gringolts, M.; Bermeshev, M.; Yampolskii, Yu.; Starannikova, L.; Shantarovich, V.; Finkelshtein, E. *Macromolecules* **2010**, *43*, 7165–7162.
(9) Nagai, K.; Masuda, T.; Nakagawa, T.; Freeman, B. D.; Pinnau, I. *Prog. Polym. Sci.* **2001**, *26*, 721–798.
(10) Plate, N.; Yampolskii, Yu. In *Polymeric Gas Separation Membranes*; CRC Press: Boca Raton, FL, 1994; p 155.
(11) Katsumata, T.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Polymer* **2009**, *50*, 1389–1394.
(12) Tetsuka, H.; Isobe, K.; Hagiwara, M. *Polym. J.* **2009**, *41*, 643–649.
(13) Finkelshtein, E. Sh.; Makovetsky, K. L.; Gringolts, M. L.; Rogan, Y. V.; Golenko, T. G.; Lakhtin, V. G.; Filatova, M. P. *J. Mol. Catal.: A* **2006**, *257*, 9–13.
(14) Finkelshtein, E.; Makovetskii, K.; Gringolts, M.; Rogan, Yu.; Golenko, T.; Starannikova, L.; Yampolskii, Yu.; Shantarovich, V.; Suzuki, T. *Macromolecules* **2006**, *39*, 7022–7029.
(15) Gringolts, M. L.; Bermeshev, M. V.; Makovetsky, K. L.; Finkelshtein, E. Sh. *Eur. Polym. J.* **2009**, *45*, 2142–2149.
(16) Teplyakov, V. V.; Evseenko, A. L.; Novitskii, E. G.; Durgaryan, S. G. *Plast. Massy* **1978**, *5*, 49–51.
(17) Finkelshtein, E. Sh.; Gringolts, M. L.; Ushakov, N. V.; Lakhtin, V. G.; Soloviev, S. A.; Yampol'skii, Yu. P. *Polymer* **2003**, *44*, 2843–2851.
(18) Thomas, S.; Pinnau, I.; Du, N.; Guiver, M. D. *J. Membr. Sci.* **2009**, *333*, 125–131.
(19) Freeman, B.; Pinnau, I. *Trends Polym. Sci.* **1997**, *5*, 167–173.
(20) Yampolskii, Yu.; Durgaryan, S.; Nametkin, N. *Vysokomol. Soed., B* **1979**, *21*, 616–621.
(21) Pinnau, I.; Morisato, A.; He, Z. *Macromolecules* **2004**, *37*, 2823–2828.
(22) Kawakami, Y.; Karasawa, H.; Aoki, T.; Yamamura, Y.; Hisada, H.; Yamashita, Y. *Polym. J.* **1985**, *17*, 1159–1172.
(23) Kawakami, Y.; Sugisaka, T.; Yamashita, Y. *Polym. J.* **1988**, *20*, 685–692.
(24) Kawakami, Y.; Imae, I. *Macromol. Chem. Phys.* **1999**, *200*, 1245–1256.