Synthesis and Gas Permeation Parameters of Metathesis Polytricyclononenes with Pendant Me₃E-groups (E = C, Si, Ge)

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ABSTRACT: Metathesis polytricyclononenes were synthesized via ROMP polymerization in the presence of the 1-st generation Grubbs catalyst and their gas-transport properties were studied for the first time. The aim of this work was to evaluate the influence of Me₃E-groups (E = C, Si, Ge) on gas permeation parameters of ROMP materials. New metathesis poly(3-*tert*-butyltricyclononene-7) and poly(3-trimethylgermyltricyclononene-7) were obtained with high yields (up to 95%) and high-molecular weights ($M_w \sim 3$–7×10^5 g mol^{-1}). The glass transition temperatures of the ROMP polytricyclononenes with Me₃E-groups decreased when E was changed from C to Si and then to Ge. It was shown that the polytricyclononene containing Me₃Si-groups has the highest gas permeability while the polytricyclononene containing Me₃C-substituents has the lowest gas permeability. In addition, the gas permeation parameters were estimated for ROMP Me₃Si- and Me₃Ge-substituted polytricyclonona-3,7-dienes. So the influence of the second double bond in the monomer units on the permeability of the polymers obtained was studied. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41395.
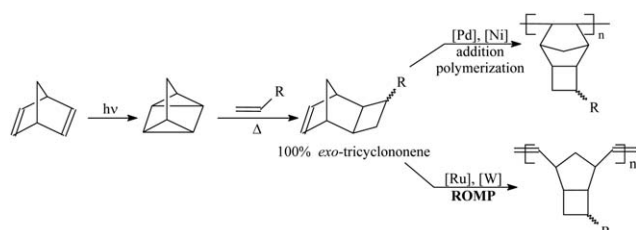
INTRODUCTION

The discovery of poly(vinyltrimethylsilane) and the effects of Me₃Si-group on the transport and sorption properties of different glassy polymers played an important role in membrane materials science.[1,2] It was shown that an introduction of this group resulted in a significant increase in gas permeability, diffusivity, and solubility, as well as in the enhancement of free volume of the materials. These works demonstrated that not only rubbery materials, but also some glassy polymers can reveal high permeability. Subsequently, the same group was introduced in various main chains: in polyacetylenes,[3] polynorbornenes,[4] polystyrene,[5] polyphenylene oxide,[6] and others. In this regard an important stride was a discovery of poly(trimethylsilylpropyne).[3] It turned out to be the most permeable polymer among both glassy and rubbery materials. It also exhibited numerous unusual and interesting membrane properties.[7] It was shown that not only the introduction of several Me₃Si-groups in different main chains usually results in higher permeability,[8] but also the position of groups is of a great importance.[8–10] On the basis of these and other studies, one can ask a natural question: is the strong effect of Me₃Si-group caused by its bulky and symmetric shape or by the presence of silicon atom in it? Some

studies were performed to answer this question, i.e., several glassy polymers with Me₃C- and Me₃Ge-side groups were studied.[11–13] Usually, comparisons of gas permeability were made only between Me₃Si- and Me₃Ge-substituted polymers which were synthesized by the similar scheme. However, so far no attempts were made to investigate gas permeation parameters of the whole series of polymers containing Me₃C-, Me₃Si-, and Me₃Ge-substituents.

In previous work, we have demonstrated that norbornene derivatives are very attractive monomers for macromolecular design and searched for correlations between gas permeation parameters of polymers and the structure of their repeat units.[4] Among norbornenes, *exo*-tricyclononenes are the most active monomers in polymerization.[14–16] Furthermore, in some cases polynorbornene derivatives with bulky or electron-withdrawing groups can be obtained only from tricyclononenes while the synthesis of the analogues polymers from norbornenes are not possible.[14,16] *Exo*-tricyclononenes can be obtained by the thermal [2+2+2]-condensation of quadricyclane and a substituted ethylene/acetylene[14–18] (Scheme 1). Although the synthesis of *exo*-tricyclononenes with different substituents has been reported in many papers,[18–22] their polymerization and the properties of the

Scheme 1. Synthesis of *exo*-tricyclononenes and the ways of their polymerization.

obtained polymers were not studied sufficiently.[4,14,20] Being derivatives of norbornene, tricyclononenes can be polymerized according to metathesis (ROMP) and addition schemes (Scheme 1).

Addition polynorbornenes are more permeable than their ROMP isomers.[4,21,23] However, the metathesis polymers are more convenient objects for investigation of structure-property correlations due to the very high driving force of metathesis polymerization. This allows polymerizing monomers with desired hindrance or functional groups and to achieve fine film-forming properties of the obtained polymers. Therefore, taking into consideration the above, metathesis polytricyclononenes were chosen for the investigation of relations between the nature of Me₃E-side substituents (E = C, Si, Ge) and gas permeation parameters of the corresponding polymers. It should be noted that so far the investigation of the gas permeation properties was limited to metathesis polytricyclononenes with Me₃Si-substituents (Figure 1, **poly2**, **poly7-poly9**). In this work we first study gas permeation properties of a series of metathesis polytricyclononenes and polytricyclonondienes with different Me₃E-groups (E = C, Si, Ge) in the polymer unit. This series of polymers along with the earlier studied metathesis polytricyclononenes forms an extended family of polymers with analogous structures for systematical examination of the structure–permeability relations (Figure 1).

EXPERIMENTAL

Materials

All manipulations involving air- and moisture-sensitive compounds were carried out under dried and purified argon using standard Schlenk and vacuum-line techniques. Toluene was

dried over sodium metal and then distilled under argon. All monomers were stored under argon. The 1st generation Grubbs catalyst was received from Aldrich and used as 0.004–0.005M solution in toluene. 2,2'-Methylene-bis(6-*tert*-butyl-4-methyl-phenol) was received from Aldrich and used without any purification. Monomers 3-*tert*-butyltricyclononene-7 and 3-trimethylgermyltricyclononene-7,[22] **poly2**,[10] **poly4**,[13] **poly5**,[9] **poly6**,[13] and **poly7**[9] were obtained as described earlier.

ROMP Polymerization

In the typical procedure (the example is given for **poly1** synthesis), the monomer (0.55 g, 3.1 mmol), toluene (2.5 mL) and the 0.005M toluene solution of the 1-st generation Grubbs catalyst (0.21 mL, 1.05·10⁻³ mmol) were charged into a round bottom glass ampoule (10 mL) equipped with a magnetic stirrer under an inert atmosphere. Polymerization was stopped by addition of 0.05 mL of ethylvinyl ether after 2 h. The polymers were precipitated into 0.1% ethanol solution of antioxidant [2,2'-methylenebis(6-*tert*-butyl-4-methylphenol)], decanted, washed with several portions of the same fresh solution, and dried under reduced pressure. The polymer was twice reprecipitated into ethanol from toluene solution and dried under reduced pressure at 50°C until a constant weight. Yield 95%, $M_w = 6.25·10^5$, $M_w/M_n = 2.3$.

Poly[3-(tert-butyl)tricyclononene-7] (poly1)

¹HNMR (CDCl₃): δ = 5.40–5.00 (m, 2H, $HC=CH$), 2.90–2.60 (m, 0.5H), 2.50–2.25 (m, 1.5H), 2.15–1.74 (m, 5H), 1.60–1.47 (m, 1H), 1.33-1.17 (m, 1H), 0.76 (bs, 9H, C(CH_3)₃);

¹³CNMR (CDCl₃): δ = 134.50–131.40 (m, $C=C$), 53.90-49.90 (m), 49.12–40.09 (m, C(1), C(2), C(3), C(5), C(6), C(9)), 31.49 (m, C(CH₃)₃), 26.46 (m, C(CH_3)₃), 24.84 (m, C(4)).
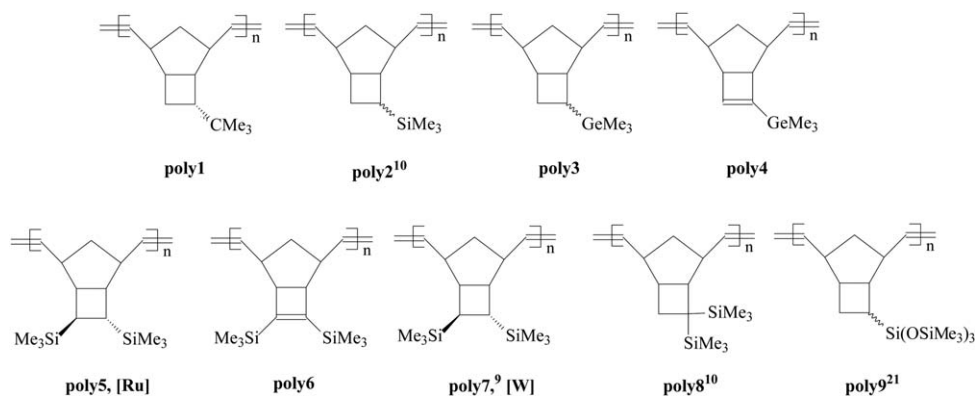
Anal. calcd. for (C₁₃H₂₀): C 88.57%, H 11.43%. Found: C 88.91%, H 11.02%.
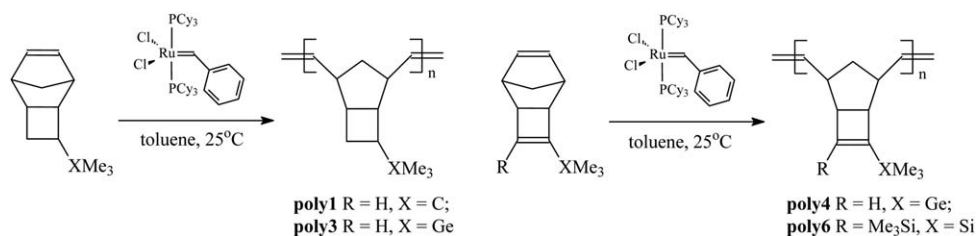
Poly[3-(trimethylgermyl)tricyclononene-7] (poly3)

The polymer was obtained according to the procedure described above from 0.55 g (2.3 mmol) of the monomer and 0.15 mL of the catalyst solution (0.005M).

Yield 90%, $M_w = 7.3·10^5$, $M_w/M_n = 2.5$.

¹HNMR (CDCl₃): δ = 5.31–5.04 (m, 2H, C(7)H, C(8)H), 2.93–1.12 (m, 9H), 0.04 (bs, 9H, Ge(CH₃)₃);

Figure 1. The family of metathesis polytricyclononenes studied in this work and earlier.

Scheme 2. ROMP polymerization of tricyclononenes and tricyclononadienes.

Anal. calcd. for $(C_{12}H_{20}Ge)$: C 60.83%, H 8.51%. Found: C 60.32%, H 8.31%.

Characterization

NMR spectra were recorded on a Bruker MSL-300 spectrometer operating at 300 MHz for ^1H and on a Varian Unity Inova AS500 spectrometer operating at 125 MHz for ^{13}C. Each polymer sample was dissolved in $CDCl_3$ up to a concentration of 10%. Cis/trans ratio of double bonds of ROMP polymers was established based on ^1HNMR spectra by the integration of olefinic protons at cis- and trans-double bonds. Deconvolution of the corresponding signals was performed with Win NMR and Win FIT software.

Gel-permeation chromatography (GPC) analysis of the polymers was performed on a Waters system with a differential refractometer (ChromatopackMicrogel-5, toluene as the effluent, the flow rate 1 mL/min). Molecular weight and polydispersity were calculated by standard procedure relative to monodispersed polystyrene standards.

Differential scanning calorimetry (DSC) was performed on a Mettler TA4000 system at a heating rate 20 K/min. Thermal

gravimetric measurements (TGA) were carried out using a Perkin-Elmer TGA-7 instrument at a heating rate 20 K/min.

Density of polymers was determined as the ratio of polymer film mass to the film volume. The film volume was measured directly (from the geometry of the film).

Film Casting

The films of the polymers studied were cast from the 1.5 to 2 wt % solution in toluene. The solution was poured into a steel cylinder with a stretched cellophane bottom. The solvent was allowed to evaporate slowly to yield the desired polymer films. After the films formation, cellophane was wetted to detach the films from it. Before testing, the films were kept under vacuum until the constant weight is achieved. The thickness of the films was in the range of 80–100 μm.
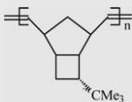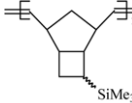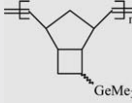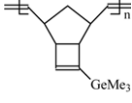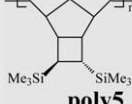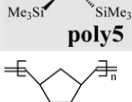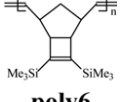
Measurement of Gas Permeability

Permeability coefficients of polymers were determined using the gas chromatographic method.[24] A steady stream of penetrant gases under atmospheric pressure was directed along the upstream part of the cell, while the downstream part was flown around by gas-carrier: helium or nitrogen (the latter in the measurement of H_2 and He permeation). The permeability

Table I. ROMP Polymerization of the Monomers Having Me_3E-Substituents (E = C, Si, Ge)[a]

Polymer	Yield, %	$M_w \cdot 10^3$, g mol^{-1}	M_w/M_n	cis/trans ratio	Ref.
poly1	95	625	2.3	25/75	This work
poly2	98	634	1.5	26/74	10
poly3	90	730	2.5	21/79	This work
poly4	94	400	1.4	35/65	13

[a] Molar ratio of a monomer to the catalyst was 3000/1. The polymerization was performed at 25°C in toluene.

Table II. Gas Permeability and Density of the ROMP Polytricyclononenes and Polytricyclononadienes Containing Me$_3$E-Groups (E = C, Si, Ge)

Polymer	ρ, g/cm^3	T_g, °C	P, Barrer[a]						Ref.
			He	H$_2$	O$_2$	N$_2$	CO$_2$	CH$_4$	
poly1	0.973	125	51	63	14	3.8	51	6	This work
poly2	0.903	104	81	120	28	6.8	112	14.3	10
poly3	1.191	79	67	90.0	22	5.2	100	14	This work
poly4	1.141	100	90	120	28	8	114	26	This work
poly5 **poly5**	0.930	123	250	350	91	25	400	57	This work, Ru-catalyst
poly7	–	129	227	332	89	24	396	55	9, W-catalyst
poly6	0.945	125	218	317	91	24	416	69.8	This work

[a] 1 Barrer = $10^{-10} \cdot$cm$^3 \cdot$(STP)$\cdot$cm cm^{-2} s$^{-1} \cdot$(cm Hg)$^{-1}$.

coefficients were determined by measuring the penetrant concentration in the gas-carrier (permeate) and the total flow rate of the permeate. Partial pressure of the penetrants was close to zero in the downstream part of the cell. The gas permeation parameters were obtained at 20–22°C.
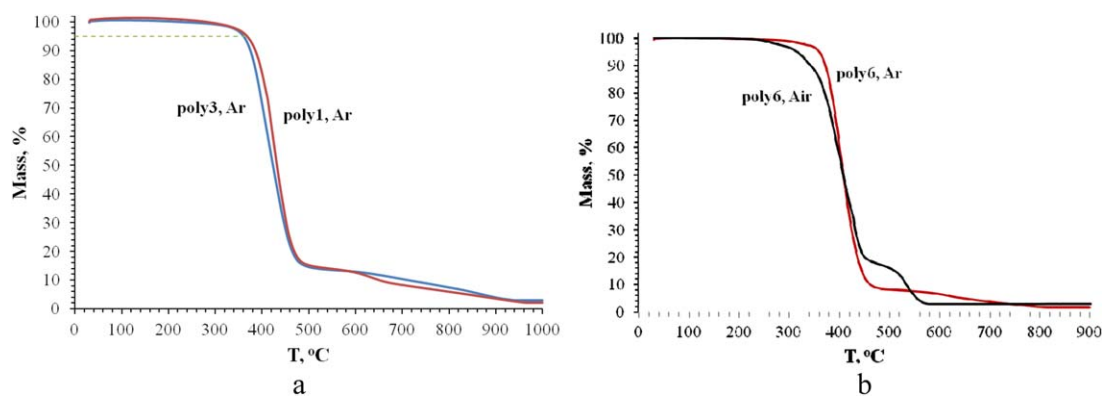
RESULTS AND DISCUSSION

Polymer Synthesis

In general, ROMP polymerization of tricyclononenes proceeds readily due to a high strain energy of the norbornene fragment and the *exo*-orientation of cyclobutane ring.[9,10,20] Earlier[9,13] we have demonstrated that ROMP polymerization of tricyclononenes and tricyclononadienes proceeds effectively in the presence of the 1st generation Grubbs catalyst at high monomer/catalyst ratios resulting in high molecular weight polymers. This process is characterized by a good reproducibility and tolerance to the strain cyclobutene ring in the case of polymerization of tricyclononadienes.[4,13] So all the polymers studied in this work were synthesized on the above catalyst according to Scheme 2 (Table I).

As it is seen from Table I, we first successfully polymerized 3-*tert*-butyltricyclononene-7 and 3-trimethylgermyltricyclononene-7

according to metathesis pathway. The polymers were obtained with good yields and with high molecular weights ($M_w > 6 \cdot 10^5$ g mol^{-1}) even when the high monomer/catalyst ratios were used. It was found that T_g of ROMP polytricyclononenes containing one group per monomer unit decreased when a central atom (E) in the substituent was changed from C to Ge (Table II). Thus, **poly1** has the highest T_g (125°C) and **poly3** possesses the lowest T_g (79°C). This could be explained by an increase in bond length E-C (where E = C, Si, Ge) while going down from C to Ge and, thereby, by an increase of flexibility of a Me$_3$E-substituent.

All the studied ROMP polymers, even substituted polytricyclonondiene-3,7 (**poly6**) containing a highly strained cyclobutene ring demonstrated a very high thermal stability (Figure 2). The temperatures of 5% weight loss (TGA) for all these polymers were very high (300–310°C (Air)/>350°C (Ar)).

Thus, **poly1**, **poly2**, and **poly3** form a systematic series of polymers containing Me$_3$E-substituents (where E = C, Si, Ge). It should be noted that such regular series of polymers has not been described before to the best of our knowledge. Although the syntheses of **poly4−6** have been described earlier[9,13] their

Figure 2. TGA curves of ROMP polytricyclononenes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

properties have not been studied. So the investigation of the properties of this extended family of polymers seems attractive and may allow finding new relationships between polymer structure and gas permeability of the corresponding polymer.
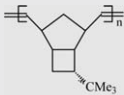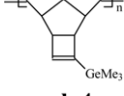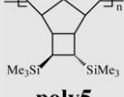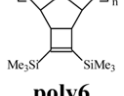
Gas Permeation Properties

The permeability coefficients of **poly1**-**poly7** are shown in Table II. The most interesting results were obtained for the series of polytricyclononenes with Me$_3$C-, Me$_3$Si-, and Me$_3$Ge-substituents. Based on the data of Table II one can conclude that the polytricyclononene containing one Me$_3$Si-group in each repeat unit (**poly2**) is more permeable than the analogous polytricyclononenes (**poly1** and **poly3**) with Me$_3$C- or Me$_3$Ge-substituents. At the same time, **poly3** containing Me$_3$Ge-side groups is more permeable than **poly1**. So for the macromolecular design of high permeable polymers the presence of side Me$_3$Si-substituents in a polymer is more preferable than Me$_3$C- and Me$_3$Ge-groups. The possible explanations of the above observations are in the size and the flexibility of Me$_3$E-substituent. It should be noted that for glassy polymers in comparison with rubbery ones an opposite relationship between gas permeability and the flexibility of the main chain or a substituent is usually observed. An increase in main chain flexibility or a substituent flexibility as a rule results in a decrease of gas permeability for light gases. The relationship between gas permeability of a polymer and its main chain flexibility can be illustrated for polymers of different classes: polyphenylacetylenes[7,25] and polystyrenes,[5] ROMP polynorbornenes[4,21,23] and addition polynorbornenes.[4,21] The influence of the flexibility of a substituent on gas permeability of polymers was demonstrated for polymers containing -SiMe$_3$/SiMe$_2$CH$_2$SiMe$_3$/SiMe$_2$CH$_2$CH$_2$SiMe$_3$[3,26,28] and by the example of alkyl substituents in polyacetylenes[26,28] and addition polynorbornenes.[29] Therefore, the presence of more bulky groups or less flexible substituents could provide a less dense packing of polymer chains resulting in higher gas-permeability. The size of a Me$_3$E-side group (E = C, Si, Ge) rises from C to Ge as well as the flexibility of Me$_3$E-substituent. A confirmation of the increase of Me$_3$E-substituent flexibility from C to Ge is in the decrease of glass transition temperatures of polymers having the same main chain (**poly1**-**poly3**), when E in Me$_3$E-substituent changes from C to Ge (Table II). An additional evidence also might be the decrease of the cone angle of Me$_3$E-group moving

from C (98–100°) to Si (91–93°) and Ge (91–93°) which were calculated based on X-Ray data for compounds containing Me$_3$E-C(sp^3)-fragments.[30] The higher value of cone angle for Me$_3$C-group indicates that the structure containing this group has less degree of conformational flexibility[31] than the analogous molecules with Me$_3$Si- and Me$_3$Ge-side groups. It seems that in the case of E = Si an optimum relationship between the size and the flexibility of Me$_3$E-substituents in the series C-Si-Ge takes place. Indeed, **poly2** possessed the lowest density among the series of **poly1**-**poly3** (Table II).

For the pairs **poly1** versus **poly2** and **poly2** versus **poly3** some comparisons can be made with published properties of the polymers having the same side groups but different structure of the main chains. According to the literature data[13] Ge-containing addition polytricyclononene has lower permeability than Si-containing one. The same was observed for polyacetylenes: poly(trimetylsilylpropyne) has permeability coefficient higher by a factor of 2.5 than poly(trimetylgermylpropyne).[7,12,32] As to the pair of the polymers containing Me$_3$C- and Me$_3$Si-substituents to the best of our knowledge such comparison is only possible for properties of substituted polystyrenes.[5,11] It indicated that Me$_3$C-containing polystyrene has markedly lower gas permeability than the polymer containing Me$_3$Si-side group. So the comparisons with earlier published data for gas-permeability of different C-, Si-, and Ge-containing polymers also confirmed our observations.

The gas permeation parameters were investigated for the polymers with one and two double bonds in the repeat unit (Table II, **poly3**-**poly4**, **poly5**-**poly6**). It was found that the effects depended on the number of substituents. For the pair **poly3**–**poly4**, the appearance of the double bond in the four-member ring resulted in some increases in permeability, especially for the larger size gases. On the other hand, the behavior of another pair of polymers (**poly5**–**poly6**) did not show any effects. A possible reason of the phenomena observed for **poly3** and **poly4** is a more rigid polymer chain in the case of polytricyclononadienes due to the presence of an additional double C═C bond in the repeat unit. As a result, the **poly4** possesses a less dense structure. This effect is smeared out in the case of more permeable polymers **poly5** and **poly6** because of stronger influence of the second Me$_3$Si-group in a monomer unit which gave an increase in gas permeability in 2–3 times (**poly2**-**poly5** pair).
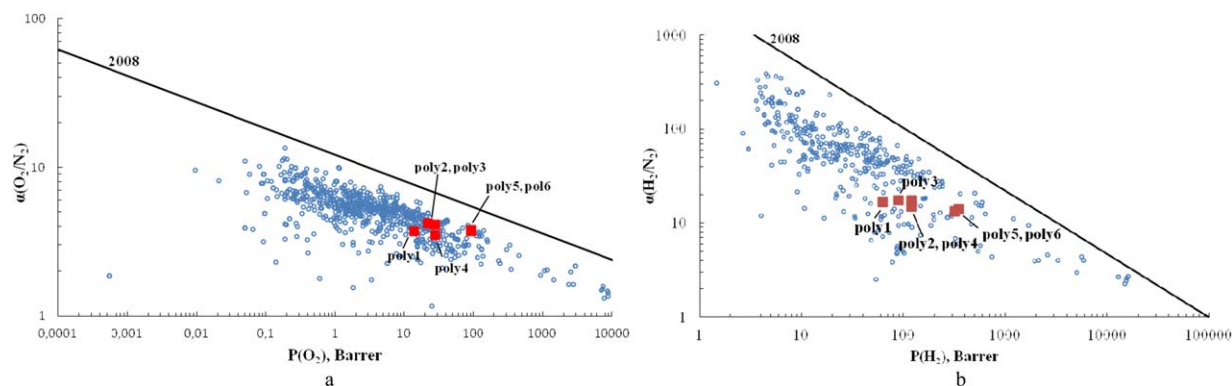
Table III. The Ideal Gas-Separation Factors for the Metathesis Polytricyclononenes and Polytricyclononadienes Containing Me_3E-Groups (E = C, Si, Ge)

Polymer	$\alpha = P_i/P_j$						Ref.
	H_2/N_2	He/N_2	O_2/N_2	CO_2/N_2	He/CH_4	CO_2/CH_4	
poly1	16.6	13.4	3.7	13.4	8.5	8.5	This work
poly2	17.5	11.9	4.1	16.5	5.7	7.8	10
poly3	17.3	12.9	4.2	19	4.7	7.1	This work
poly4	15.0	11.2	3.5	14.3	3.5	4.4	This work
poly5	14.0	10.0	3.7	16.5	4.1	7.0	This work
poly6	13.2	9.1	3.8	17.3	3.1	5.9	This work

The metathesis polymers obtained in the presence of Ru and W-catalyst had a different microstructure, namely *cis/trans* ratio of double bonds (22/78 for **poly5** and 47/53 for **poly7**, correspondingly). Despite it, **poly5** and **poly7** possessed similar values of permeability. That can be explained by the weak influence of the polymer microstructure on gas-transport parameters in comparison with the effect of a substituent nature. At the same time all the polymers with two side groups (**poly5**, **poly6**, and **poly7**) were certainly more permeable than other studied polymers with a single substituent.

Using the measured density of the prepared polymers and the van der Waals volume of the repeat units[33] it was possible to calculate the fraction free volume (FFV) of the polymer. The FFV values were in the range of 17–27%, which were typical for the polymers having similar gas permeability. No distinct correlation between FFV and the permeability coefficients could be observed.

Table III presents the separation factors P_i/P_j of the polymers studied. On the Robeson diagrams, the data points for the more permeably **poly5** and **poly6** are located relatively close to the

Figure 3. The correlations of permeability and permselectivity for the O_2/N_2 (a) and H_2/N_2 (b) gas pairs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Upper bounds (2008[34]). For other studied polymers they located inside the cloud of the data points for numerous glassy polymers (Figure 3). It is interesting that higher permeability of **poly2** in comparison with **poly1** and **poly3** is not accompanied by notable decreases in permselectivity as compared with two other polymers of this series (no trade-off behavior) as it is seen from Table III. The selectivities of **poly1**-**poly3** are little higher than that of more permeable **poly5** and **poly6**. Thus for these polymers the trade-off behavior between permeability and selectivity took place.

CONCLUSIONS

In this work we first studied the influence of side Me$_3$E-groups (E = C, Si, Ge) on gas permeation parameters of metathesis polytricyclononenes and polytricyclononadienes. With this aim, we successfully synthesized new high molecular weight polymers - poly(3-*tert*-butyltricyclononene-7) and poly(3-trimethylgermyl-tricyclononene-7) and investigated gas permeation properties of such type of polymers. It was shown that namely Me$_3$Si-substituted polymer shows the highest gas permeability among Me$_3$C- and Me$_3$Ge-containig polymers. Also the influence of the presence of an additional double bond in metathesis polymers and the number of side groups were investigated.

ACKNOWLEDGMENTS

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