

# Effects of cis-trans-Configurations of the Main Chains of Poly(trimethylsilyl Norbornene) on its Transport and Sorption Properties as well as Free Volume

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## SYNOPSIS

Samples of poly(trimethylsilyl norbornene) having different content of cis configurations of double bonds in the main chains were prepared by ring opening metathesis polymerization in the presence of the catalysts characterized by different stereoselectivity ( $\text{Re}_2\text{O}_7$ ,  $\text{RuCl}_3$ ,  $\text{WCl}_6$ ). It was shown that the polymer obtained in the presence of the  $\text{WCl}_6$  catalysts having the closest content of the cis- and trans-configurations is distinguished by largest gas permeability, diffusion, and solubility coefficients. Determination of the parameters of gas sorption isotherms and estimation of free volume using group contribution and positron annihilation methods allowed to conclude that microstructure of this polymer (cis/trans ratio) affects its free volume and, therefore, its transport and thermodynamic properties.

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## INTRODUCTION

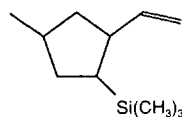
It can be considered as a proven fact today that the whole complex of transport and thermodynamic properties of polymers is determined by the chemical structure of their repeat unit.<sup>1,2</sup> This can make more or less successful predictions of these properties using graph theory<sup>3,4</sup> or the group contribution method.<sup>5</sup> However, there are some peculiarities of polymer chains structure, which cannot be interpreted within the frames of these approaches. Namely, the symmetry and features of spatial arrangement of backbone and side chains should influence mutual orientation of the chains, a density of their packing, and, possibly, their supermolecular organization. For example, it is known<sup>6</sup> that isotactic-, syndiotactic-, and atactic vinylic-type polymers are distinguished by strongly different gas permeability and diffusion coefficients. Some differences in the transport properties were noted for polymers

with aromatic backbones having varying symmetry (meta or para) of phenylene ring substitution.<sup>2</sup>

Cis-trans isomerism of double bonds in the main chains is another, although less investigated, element of molecular design of polymers. A single systematic study of the effects of this factor on sorption and diffusion parameters is, to the best of our knowledge, the investigation of propane sorption in poly(tert-butyl acetylene) (PTBA).<sup>7</sup> The first and preliminary report on transport properties of this polymer has appeared much earlier.<sup>8</sup> An assumption was made that the transport properties of the most permeable among all the polymers—poly(trimethylsilyl propyne)—were affected by cis-trans-configuration of its main chains.<sup>9</sup> This makes further studies of this problem quite desirable, especially for polymers of other classes. Characterization of a wider set of different transport and physicochemical parameters is also very relevant.

This article reports the effects of cis-trans configurations of substitution around double bonds in the main chains of poly(trimethylsilyl norbornene) (PTMSNB), the chemical structure of which is shown below:

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Norbornene polymers prepared by ring opening metathesis polymerization can have different microstructure or stereoregularity depending on the stereospecific properties of the catalysts used (Re, W, and Ru compounds). A transition from predominantly trans-stereocontrol to cis-stereocontrol is observed when Ru catalysts are replaced by Re catalysts. W catalysts usually give norbornene polymers with mixed microstructure.<sup>10</sup> Because of it, the following catalytic systems were chosen for obtaining PTMSNB with widely varying range of cis/trans ratio of repeat units:  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  modified by tetra-*n*-butyltin,<sup>11</sup>  $\text{WCl}_6$ -phenylacetylene,<sup>12</sup> and  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ .<sup>13</sup> The effects of microstructure or cis-content on the glass transition temperature, density, permeability coefficients in respect to different gases, diffusion coefficients, solubility coefficients and the parameters of sorption isotherms, and free volume estimated by means of positron annihilation method were studied.

## EXPERIMENTAL

### Materials

5-Trimethylsilylnorbornene was prepared from trimethylvinylsilane and dicyclopentadiene using the technique described previously,<sup>14</sup> which was slightly modified. Trimethylvinylsilane (Redkino Chemical Plant) was distilled over metallic sodium and had a purity 98.5% according to gas-liquid chromatography. Dicyclopentadiene (Reakhim) was dried over  $\text{CaCl}_2$  and distilled in vacuum. The reactants were charged into a steel autoclave at optimal mole ratio diene/silane = 2, the apparatus was purged with dry argon, and the reaction proceeded for 3 h at 205°C. The reaction product was fractionated in vacuum. The yield of the fraction with boiling point 67–68°C/14 mm Hg was equal to 71% at quantitative conversion of the diene. The content of 5-trimethylsilylnorbornene was 99.5% according to gas chromatography (GC) analysis. It consisted of equal amounts of exo- and endo-conformers (according to GC analysis and  $^1\text{H-NMR}$ ) and had  $n_D^{20} = 1.4677$  and  $d_4^{20} = 0.8853$ . The monomer was dissolved in dry toluene and stored in a Schlenk vessel before polymerization. The solvents were purified according

to usual methods and redistilled under argon. Chlorobenzene was distilled under Ar over  $\text{P}_2\text{O}_5$ .

### Polymerization

The experiments on polymerization in the presence of different catalyst were performed in a different manner. Heterogeneous  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst ( $\text{Re}_2\text{O}_7$  content 10%,  $\text{Sn}(\text{C}_4\text{H}_9)_4$  content 3%) was activated before the run as it had been described by Finkelshtein et al.<sup>11</sup> and charged into a thermostated glassy reactor with magnetic stirrer and reflux condenser. The monomer solution in toluene was introduced directly from a Schlenk vessel. After reaction completion, liquid products were decanted, whereas the catalyst was washed several times with toluene to remove all polymer. The polymer was precipitated by methanol from combined solutions, redissolved in benzene, once again precipitated by methanol, which contained small amounts of Irganox 1076, and dried in vacuum at 20°C.

The polymerization in the presence of Ru catalyst was realized in a similar experimental setup. Solid  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  was dissolved in ethanol under stirring, then chlorobenzene was added (vol. ratio  $\text{C}_6\text{H}_5\text{Cl}/\text{EtOH} = 1/1$ ), and finally toluene solution of the monomer (concentration 7.6 M) was introduced. The further procedure was the same as it was indicated above.

The polymerization in the presence of homogeneous W catalyst was performed in sealed ampules at ambient temperature. First, the solutions of  $\text{WCl}_6$  and phenylacetylene (mole ratio 1 : 1) were charged, and then after 1 h the solution of the monomer was introduced from the Schlenk vessel, and the ampule was sealed.

### Analysis

Liquid products were analyzed using a gas chromatograph LKhM-8MD (capillary column with the liquid phase OV-17 having the length 25 m, flame ionization detector, gas carrier hydrogen, temperature programmed with the rate 5 K/min up to 250°C).

### Characterization of Polymers

Intrinsic viscosities of the polymers in toluene solutions were determined using Ubbelode viscometers at 30°C. A density was determined using the technique of hydrostatic weighing, isopropanol being used as a liquid with known density. The glass transition temperatures were measured by means of dif-

**Table I** Polymerization of 5-Trimethylsilylnorbornene in the Presence of Ring-Opening Metathesis Catalysts

Catalyst	Conditions			Time (h)	Polymer Yield (%)	[ $\eta$ ] (dL/g)
	[M] (mol/L)	[M]/[Cat] (mol)	$T$ ( $^{\circ}$ C)			
RuCl <sub>3</sub>	1.9	180	70	15	76	2.4
WCl <sub>6</sub> -PhC=CH	2	1000	20	2	92	2.2
Re <sub>2</sub> O <sub>7</sub> /Al <sub>2</sub> O <sub>3</sub>	3.5	400	40	5	45	2.1

ferential scanning calorimetry method in the range 0–200 $^{\circ}$ C in a Mettler instrument.

An NMR spectrometer Bruker MSL-300 having a working frequency 300 MHz CH was used to characterize the structure of PTMSNB. <sup>1</sup>H-NMR (CCl<sub>4</sub>):  $\delta$  = 5.0–5.4 (m, 2H, CH=CH), 0.7–3.2 (m, 7H, protons of cyclopentylene ring), –0.3 – 0.2 (m, 9H, SiMe<sub>3</sub>). <sup>13</sup>C-NMR spectrum of the polymer (CDCl<sub>3</sub>):  $\delta$  = –2.33–1.02 [Si(CH<sub>3</sub>)<sub>3</sub>]; 31.6–45.09 (C<sub>1</sub>, C<sub>4</sub>, C<sub>5</sub>, C<sub>6</sub>, C<sub>7</sub>); 131.75–134.30 (C<sub>2</sub> and C<sub>3</sub>).

Microstructure of different samples of PTMSNB was determined by their IR spectra using a Specord 82 instrument. The fraction of trans-double bonds was estimated by the ratio of optical densities of the bands at 970 cm<sup>–1</sup> (trans-CH=CH) and 1250 cm<sup>–1</sup> ( $\delta$ -Si-CH<sub>3</sub>), which served as an inner standard. This ratio increases in the series 0.25 (Re), 0.33 (W), and 0.69 (Ru). These ratios allowed to calculate the cis-content, which is given in Table I. It should be noted that this estimate was supported by a coincidence of cis-content of the polymer obtained in the presence of W catalyst and measured using both IR spectra (this work) and <sup>13</sup>C-NMR (previous paper<sup>15</sup>).

Permeability of PTMSNB was studied using a mass-spectrometric method. The measurements were performed in a setup with Balzers QMG-400 instrument at 22 $^{\circ}$ C. Gas pressure of 100–400 mm Hg over the film and about 0.001 mm Hg below the film were kept during the measurement. Diffusion coefficients were determined using Daines-Barrer or

time-lag method. The films having thickness 50–200  $\mu$ m were obtained by pouring a 1–2% toluene solutions onto a horizontal cellophane surface with subsequent slow evaporation of the solvent first at ambient conditions and then in vacuum until constant weight was achieved. The thickness of the films was chosen in such a way to have time lag larger than 100 s, when it was possible to neglect inertia of the mass-spectrometric system.

Gas sorption isotherms and solubility coefficients were measured by means of a Sartorius electrobalance (Model 4436 MP6) at 25 $^{\circ}$ C and pressures up to 30 atm. Lifetime spectra of positron annihilation were obtained in an ORTEC instrument. The details of the technique can be found elsewhere.<sup>16</sup>

## RESULTS AND DISCUSSIONS

Conditions of the polymerization experiments, the yields, and some characteristics of the polymers obtained are presented in Tables I and II. It can be seen that high molecular mass polymers of 5-trimethylsilylnorbornene are formed in the presence of all the catalysts with reasonable yields. The highest activity is observed in the case of W catalyst, which permits to obtain the largest yield at shortest time. According to spectral data, all the polymers contained the concentration of double bonds close to the theoretical one, i.e., the polymerization proceeded completely according metathesis mechanism.

**Table II** Structure and Physical Properties of PTMSNB

Catalyst	Cis-content	$T_g$ ( $^{\circ}$ C)	$\rho$ (g/cm <sup>3</sup> )	FFV <sup>a</sup>
Re	0.75	59	0.934	0.188
W	0.67	101	0.918	0.202
Ru	0.31	85	0.920	0.200

<sup>a</sup> FFV, free volume fraction, i.e. the ratio of free volume  $v_f$  (cm<sup>3</sup>/g) and specific volume  $v_o = 1/\rho$  (cm<sup>3</sup>/g).

**Table III Permeability Coefficients  $P$ , Ba of PTMSNB**

Cis-content	H <sub>2</sub>	He	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>
0.75	50.5	56.0	18.1	4.4	72.3	9.2
0.67	76.8	58.4	20.9	6.2	79.3	17
0.31	66.8	51.2	16.5	4.8	65.7	4.8

1 Ba =  $10^{-10}$  cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cm Hg.

As can be assumed, the fraction of cis-C=C bonds ( $\sigma_c$ ) in the chains of PTMSNB increased in the sequence of the polymers obtained in the presence of the catalysts Ru < W < Re.

The glass transition temperatures and densities of the PTMSNB samples distinguished by different cis/trans ratio are given in Table II. Interestingly, the glass transition temperature is a strong function of the cis-trans-configuration of PTMSNB main chain. The highest  $T_g$  value is observed in the case of the polymer prepared in the presence of W catalyst. This  $T_g$  value is in a reasonable agreement with the results of the previous study of a similar specimen of PTMSNB.<sup>15</sup> When cis- or trans-configurations prevail in the main chain, the glass transition temperature decreases. Densities of the PTMSNB samples depend on the cis/trans ratio less drastically. However, the minimum value of a density and, accordingly, maximum fractional free volume can be noted for the polymer obtained in the presence of W catalyst.

Permeability coefficients of the polymers studied, in respect to various gases, are presented in Table III. It is seen that maximum permeability coefficients are observed for the polymer with the distribution of cis-trans-configurations closest to random ( $\sigma_c = 0.5$ ), i.e., the one prepared in the presence of W catalyst. Although this effect is not strong, it is certainly larger than the statistical error of the determination of the permeability coefficients, which was equal to  $\pm 2-3\%$ .

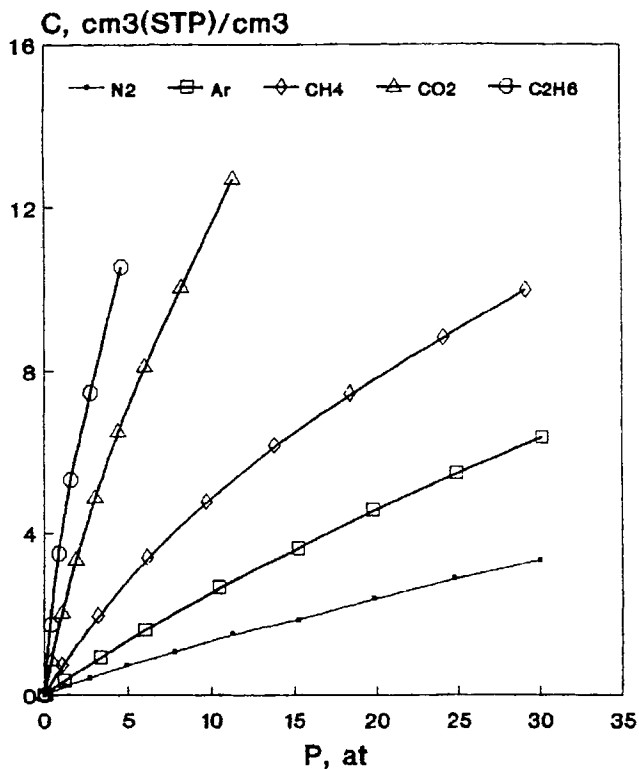
Permeability coefficients of the PTMSNB samples obtained in the presence of Re and Ru catalysts vary in a different manner for different gases. Therefore, a conclusion that cis-PTMSNB is characterized by enhanced (in comparison with trans-PTMSNB) permeability can be made only with a big caution and better reserved until the samples with  $\sigma_c$  closer to 1 and zero are available for the investigation. As it will be shown below rather weak effects of  $\sigma_c$  on the  $P$  values are caused by opposite dependencies of diffusion and solubility coefficients of the cis/trans ratio.

**Table IV Diffusion Coefficients  $D \cdot 10^7$ , cm<sup>2</sup>/s in PTMSNB**

Cis-content	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>
0.75	6.0	2.2	3.2	1.3
0.67	6.0	2.6	3.2	1.5
0.31	4.2	1.7	2.2	0.90

The kinetic and thermodynamic contributions can be separated in the permeability coefficients, i.e., diffusion and solubility coefficients. It is desirable that the  $D$  and  $S$  values be determined independently, rather than via relationship  $P = DS$ . Diffusion coefficients in the PTMSNB samples obtained in the presence of different catalysts are given in Table IV. It can be seen that the same behavior is observed as the one noted for permeability coefficients: the largest  $D$  values are characteristic for the polymer obtained in the presence of W catalyst. trans-PTMSNB (Ru catalyst) is distinguished by minimum diffusion coefficients as compared with two other polymers.

Somewhat different results were obtained in sorption studies. Figure 1 shows, as an example,

**Figure 1** Sorption isotherms in PTMSNB prepared in the presence of Ru catalyst.

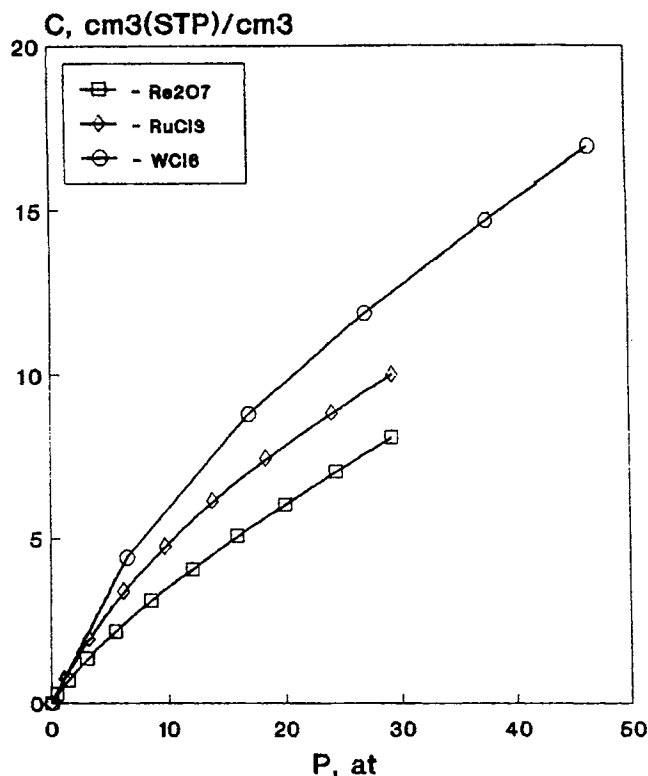


Figure 2 Sorption isotherms of methane in PTMSNB samples with different cis/trans ratios.

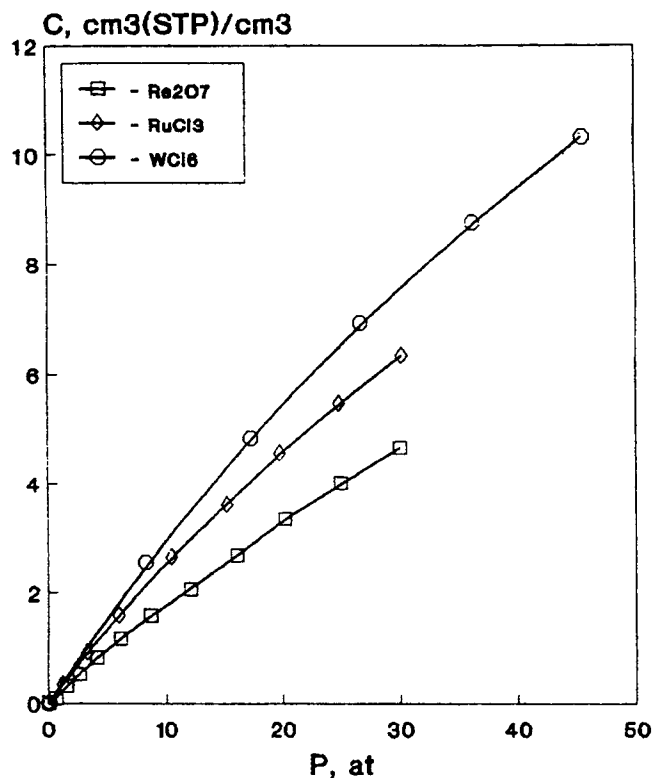


Figure 3 Sorption isotherms of argon in PTMSNB samples with different cis/trans ratios.

sorption isotherms of different gases in PTMSNB with predominant trans-character (prepared in the presence of Ru catalyst). The shape of the isotherms is typical for sorption in glassy polymers—the curves are concave to the pressure axis. Therefore, solubility coefficients can be found not only by initial slope of the curve, which is not very accurate, but via treatment of the whole curve using the dual-mode sorption equation

$$C = k_D p + C'_H b p / (1 + b p)$$

where  $k_D$  is Henry's law solubility coefficient,  $C'_H$  is Langmuir sorption capacity parameter, and  $b$  is affinity constant. Additionally, the analysis of these parameters in the series of the polymers studied can afford also some useful information.

Figures 2 and 3 show sorption isotherms of methane and argon in the PTMSNB samples distinguished by different microstructure. It can be concluded that sorption isotherms in the polymer with random cis/trans distribution (obtained in the presence of W catalyst) are situated above the isotherms found for two other polymers. The same behavior was observed for sorption isotherms of other

gases. Solubility coefficients can be calculated using the formula

$$S = k_D + C'_H b$$

The model parameters were found by least-squares treatment of the isotherms, and then the solubility coefficients were determined and are presented in Table V. Once again, the largest  $S$  values are observed in the case of the polymer prepared in the presence of W catalyst. On the other hand, the ratio of the  $S$  values characteristic for the polymers obtained in the presence of Re and Ru catalyst (i.e., with prevailing of cis- or trans-configuration of the chains) is less than 1. Thus, microstructure of the polymers influences diffusion and sorption proper-

Table V Solubility Coefficients  $S$ ,  $\text{cm}^3$  (STP)/ $\text{cm}^3$  atm in PTMSNB

Cis-content	N <sub>2</sub>	Ar	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
0.75	0.12	0.22	1.6	0.53	3.8
0.67	0.19	0.35	3.1	0.91	10.8
0.31	0.16	0.29	2.2	0.72	6.7

**Table VI Dual-Mode Sorption Parameters of PTMSNB**

Cis-content	$k_D$	$C'_H$	$b$
Argon			
0.75	0.129	1.18	0.076
0.67	0.106	11.4	0.021
0.31	0.106	7.19	0.026
Carbon dioxide			
0.75	0.721	3.32	0.255
0.67	0.686	13.1	0.181
0.31	0.618	8.44	0.184

$k_D$  cm<sup>3</sup> (STP)/cm<sup>3</sup> atm,  $C'_H$  cm<sup>3</sup> (STP)/cm<sup>3</sup>,  $b$  atm<sup>-1</sup>.

ties of the polymer differently. It explains rather weak effects of stereoregularity of the chains on polymer permeability.

Table VI shows the dual mode sorption parameters found for the isotherms of argon and carbon dioxide. Behavior of other gases studied in this article was very much similar. It can be seen that spatial arrangement of the chains strongly affects the Langmuir capacity parameter  $C'_H$ : the maximum values of this parameter are found for the polymer synthesized in the presence of W catalyst. A variation of two other parameters  $k_D$  and  $b$  is less regular, perhaps due to relatively narrow pressure range studied in the present work.

The  $C'_H$  value is often interpreted as a measure of nonequilibrium free volume in a glassy polymer.<sup>17</sup> This view is supported by a possibility to estimate  $C'_H$  via dilatometric data as well as by the correlations of  $C'_H$  in different polymers with their glass transition temperatures.<sup>18</sup> A comparison of the data given in Tables II and VI indicates that, for the polymers studied, the  $C'_H$  parameters correlate with the glass transition temperatures of the isomeric PTMSNB. Therefore, it can be assumed that the PTMSNB sample with the distribution close to random one (prepared in the presence of W catalyst) should be distinguished by largest free volume. It is in agreement with a minimum density found for this sample (Table II) and with the results of the investigation using positron annihilation methods as will be shown below.

Several methods are available now for estimation of free volume  $v_f$  in polymers. The most widely used approach is based on an assumption that  $v_f$  can be presented as a difference of total or specific volume and occupied volume. The former is defined as a reciprocal density, whereas the latter can be calcu-

lated via group contributions into van der Waals volume. This approach gives reasonable results when low and high permeable polymers are compared, e.g., poly(vinyl chloride) and poly(trimethylsilyl propyne). When polymers of similar structure and properties are compared (e.g., some polyimides), the correlations obtained often exhibit large scatter.

In the present work, positron annihilation lifetimes method was used for free volume characterization. As it has been shown for different polymers, including norbornene polymers,<sup>16,19-21</sup> this method gives free volume values, which correlate with gas diffusion coefficients in polymers. It is based on the fact that lifetimes of positrons in a material depend on the mechanism of their behavior and free volume in the polymer. If positrons get into a polymer, they can exist there as free positrons  $e^+$  and in a form of a bound state—a Positronium atom or an electron-positron pair  $Ps$ . Usually, lifetimes distribution of positron annihilation can be approximated by three components spectrum (lifetimes  $\tau$  and corresponding statistical weights  $I_i$ ). The short-lived component ( $\tau_1, I_1$ ) is due to the annihilation of positrons in several states and brings no particular information on free volume. The second component  $\tau_2, I_2$  is due to the annihilation of free positrons in microcavities, and according to Alexanyan et al.,<sup>22</sup> these events happen predominantly in more ordered regions within the material. At last, the third component  $\tau_3, I_3$  is due to the annihilation of Positronium atoms and happens in less ordered regions within the medium, which contain free volume elements, voids, and holes. Information on free volume of a material can be obtained either by the analysis of lifetimes spectrum itself or by interpreting some structural parameters, which can be deduced from them.<sup>16,19</sup>

Positron annihilation lifetimes parameters (times  $\tau_i$  and statistical weights  $I_i$ ) are given in Table VII. It is evident that a variation of cis-trans-ratio of the PTMSNB chains does not result in substantial changes in the spectra.

Earlier, the model that had been developed by Alexanyan et al.<sup>22</sup> was used to calculate, on the basis the lifetimes spectra, the parameters of size distri-

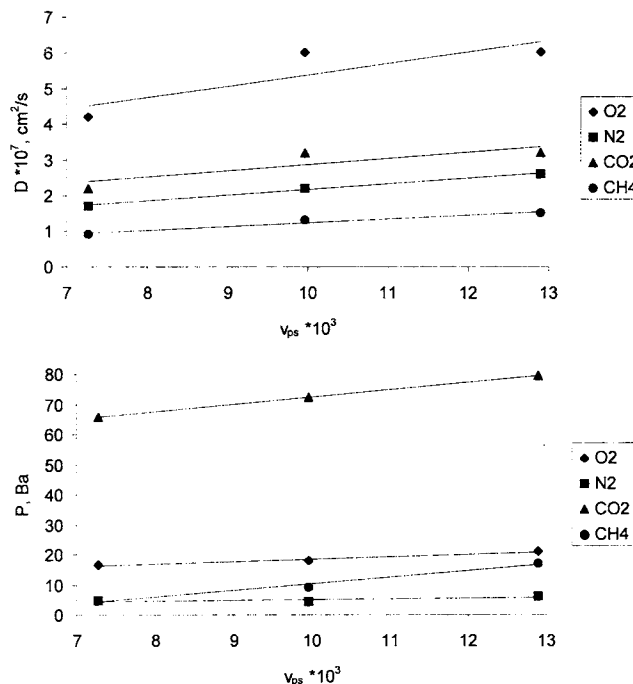
**Table VII Positron Annihilation Lifetime Parameters  $\tau_i$ , ns, and  $I_i$ , %, in PTMSNB**

Cis-content	$\tau_1$	$I_1$	$\tau_2$	$I_2$	$\tau_3$	$I_3$
0.75	0.208	39.2	0.697	28.9	2.74	31.9
0.67	0.193	35.9	0.640	32.0	2.70	32.2
0.31	0.255	53.7	0.798	23.1	2.74	23.2

bution of free volume elements.<sup>16</sup> Therefore, the results of the positron annihilation method can be correlated with permeation and sorption parameters of the PTMSNB samples studied. Table VIII presents characteristic radii ( $R_+$ ,  $R_{P_s}$ ) of free volume elements and their respective concentrations ( $N_+$ ,  $N_{P_s}$ ) and free volume ( $V_+$ ,  $V_{P_s}$ ) in ordered (+) and disordered ( $P_s$ ) regions in the polymer. It can be assumed that the  $V_{P_s}$  values characterize the free volume, via which gas diffusion takes place. It is seen from Table VIII that the  $N_{P_s}$  and  $V_{P_s}$  values pass through maximum for the polymer obtained in the presence of W catalyst. Maximum  $N_+$  value is also typical for this polymer. On the other hand, the  $R_+$ ,  $R_{P_s}$ , and  $V_+$  values increase monotonously when cis-content is decreased.

Free volume in disordered regions  $V_{P_s}$ , which can be estimated by positron annihilation method, has been shown to correlate with diffusivity of rubbers.<sup>16</sup> For glassy polymers, the situation is more controversial: however, correlations with lifetimes spectrum parameters were reported<sup>21,23,24</sup> for diffusion and permeability coefficients. Figure 4 shows that permeability and diffusion coefficients for different gases in the PTMSNB samples, which are distinguished by different cis/trans ratio, correlate with free volume  $V_{P_s}$  in disordered regions with the polymer. The larger  $V_{P_s}$  values the higher are diffusivity and permeability of the polymers.

It would be of interest to compare the effects of cis/trans ratio in the main chains of different polymers. Now it can be done by using the results of this work and the investigation of PTBA.<sup>7</sup> Morisato et al.<sup>7</sup> studied diffusion of propane in this polymer by means of sorption method. In the present work, the diffusion coefficients in PTMSNB were determined by means of time-lag method. The dependencies of the diffusion coefficients on cis-content in the main chains of these polymers are shown in Figure 5. It also shows corresponding dependencies for polynorbornenes with different cis/trans ratio according to our recent paper.<sup>26</sup> The most striking feature is the appearance of maxima for all three polymers and for different gases in the vicinity of cis-content equal to 50%. Another feature of the results obtained

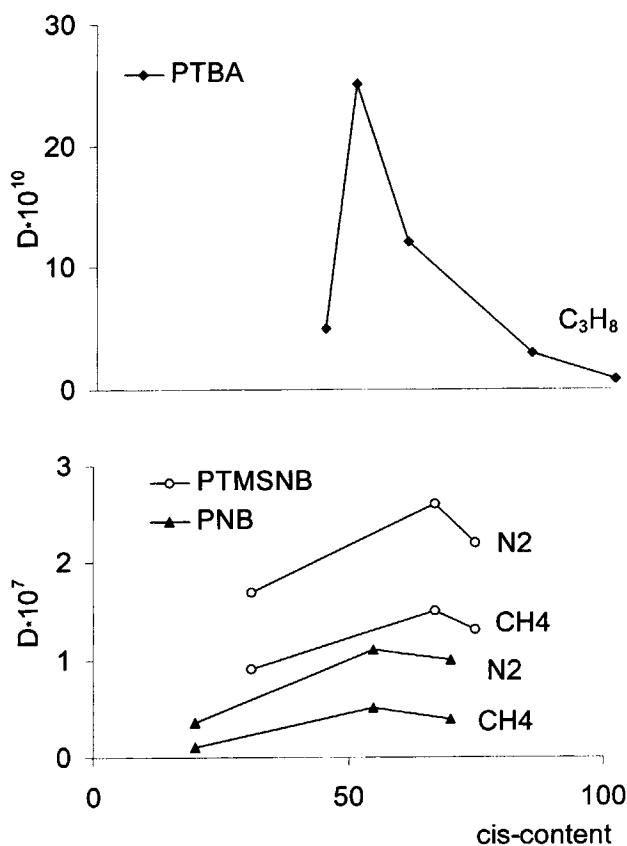


**Figure 4** Dependences of diffusion and permeability coefficients in PTMSNB with different cis/trans ratios on free volume in disordered regions of the material.

for PTBA<sup>7</sup> and PTMSNB are the effects of cis-content on solubility coefficients (initial slopes of sorption isotherms) and the Langmuir capacity parameters  $C'_H$ . In both polymers, independently of the nature of sorbed gas, maximum values of  $S$  and  $C'_H$  are observed for the polymers with cis/trans ratio close to 1. This is in agreement with the assumption that nonequilibrium free volume decreases when stereoregularity of the chains is increased resulting in less random sequence of cis- or trans-double bonds in the chain that, therefore, can be tightly packed with more ease. It is noteworthy that other quantities, which characterize free volume or chain packing, namely positron annihilation parameters  $N_{P_s}$  and  $V_{P_s}$ ,  $v_f$  values estimated via densities of PTMSNB samples as well as  $d$ -spacing measured by wide-angle X-ray diffraction<sup>7</sup> in PTBA also have maximum values for the polymers having comparable concentration of cis- and trans-configurations.

**Table VIII** Free Volume Size Distribution Parameters in PTMSNB According to Positron Annihilation Method

Cis-content	$N_+$ $10^{-18}$	$N_{P_s}$ $10^{-22}$	$V_+$ $10^7$	$V_{P_s}$ $10^3$	$R_+$ , A	$R_{P_s}$ , A
0.75	0.42	0.32	7.06	9.96	3.4	4.2
0.67	0.52	0.37	8.58	12.9	3.4	4.4
0.31	0.41	0.19	11.0	7.27	4.0	4.5



**Figure 5** Dependence of the diffusivity of polymers on cis-content of double bonds in their main chains: top, poly(tert-butyl acetylene)<sup>7</sup>; bottom, polynorbornene,<sup>25</sup> PTMSNB (this work).

Apparently, it is more difficult to pack tightly the chains with equal concentrations of cis- and trans-double bonds, what is manifested therefore in the volumetric, transport, and sorption properties of the materials.

## CONCLUSIONS

The content of cis-double bonds of PTMSNB can be varied by use of stereoselective catalysts for ring-opening metathesis polymerization. We have shown that the largest gas permeability, diffusion and solubility coefficients, Langmuir capacity parameters  $C'_H$ , and positron annihilation parameters  $N_{Ps}$ , and  $V_{Ps}$ , which characterize free volume elements in disordered areas of the polymer, are characteristic for the polymer obtained in the presence of the W catalyst with lower stereoselectivity, resulting in close concentrations of cis- and trans-chain configurations. The PTMSNB samples with higher or lower cis-content are distinguished by smaller val-

ues of these parameters. This behavior is consistent with the hypothesis that the chains of different chemical structure (cycloliner chains of norbornene polymers and alternating double bonds of PTBA) form the most loosely packed matrix that is characterized by largest free volume and transport and sorption parameters, provided a random sequence of cis- and trans-double bonds in the main chain takes place.

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