

Synthesis, Transport, and Sorption Properties and Free Volume of Polystyrene Derivatives Containing Si and F

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ABSTRACT: Gas permeation, sorption, and free volume was studied in a series of glassy vinylic type Si-containing polymers. They included p-substituted derivatives of polystyrene, which were compared with polystyrene, and poly(vinylphenyldimethyl silane). The strongest increase in permeability and diffusion coefficients were observed for the polymer containing the Si(CH₃)₃ group directly attached to phenylene ring. An introduction of spacers between phenylene ring and Si(CH₃)₃ group results in much lower gas permeability. Positron annihilation study of free volume in these polymers showed that lifetime spectra are composed of four components. It implies that size distribution of free volume in these polymers, which are characterized by a modest level of gas permeability, is bimodal, a feature previously observed only for extra large free volume and permeability materials such as poly(trimethylsilyl propyne). © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1612–1620, 2000

Key words: gas permeability; sorption isotherms; positron annihilation; glassy polymers

INTRODUCTION

Relationship between structure and transport properties of polymers, potential materials for separation membranes, is a field of permanent interest in membrane material science. It provides the basis for prediction of the gas permeation parameters and directed search for advanced membrane materials.¹ Investigation of series of polymers that belong to the same class or have common structural features often gives more insight in the problem (see e.g., Paul and

Yampolskii²). Substituted polystyrenes (PS) provide an interesting class for such studies.^{3–8} Many of the monomers are commercially available, others can be prepared using well developed procedures. However, only limited information on transport and sorption properties of these polymers has been reported. Thus, Kawakami et al.^{3–6} described many p-substituted PS derivatives containing silicon and fluorine in side chains. However, the transport parameters have been reported only for oxygen and nitrogen. The aim of the present work is to fill this gap. In this paper we describe preparation and properties (permeability, diffusion, solubility coefficients, sorption isotherms for several simple gases) as well as positron annihilation lifetime (PAL) pa-

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Table I Conditions of the Performance of Polymerization Reactions and the Characteristics of the Polymers Obtained

Monomer	Initiator ^a	[M], mol/L	[I]10 ³ , mol/L	Time (h)	Yield, (%)	T, °C	M _w 10 ⁻³ , D	M _n 10 ⁻³ , D	M _w /M _n
TMSS	AIBN	5.0	5.0	10.0	50.0	60	758	229	3.7
TMSMS	AIBN	4.0	1.3	100.0	43.4	60	669	140	4.7
FPDMSS	AIBN	4.1	4.1	27.0	59.5	60	368	173	2.1
VPDMS	sec.BuLi	3.9	2.7	2.0	77.0	25	425	201	2.1

^a 2,2-Azobisisobutyronitrile or sec-Butyllithium.

rameters and free volume deduced from them for several PS derivatives, containing Si and F atoms in side chains.

EXPERIMENTAL

Materials

Commercial organochloride compounds: trimethylsilyl chloride, vinyldimethylsilyl chloride, γ -trifluorostyrene and chloromethylstyrene (Aldrich Chem., Milwaukee, WI, USA) were distilled before use. Tetrahydrofuran (THF) and benzene were purified by conventional methods.⁹ 2,2-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. p-Trimethylsilylstyrene (TMSS), γ -trifluoropropyl dimethylsilylstyrene (FPDMSS), and trimethylsilylmethylstyrene (TMSMS) were prepared using the organomagnesium synthesis by the reaction of p-chlorostyrene (or chloromethylstyrene) and corresponding silicon chlorides, as described by Petrov et al.¹⁰ Vinylphenyldimethylsilane (VPDMS) was synthesized by reaction of phenylmagnesium bromide and vinyl dimethylsilyl chloride according to the method used for TMSS. Monomers were dried over CaH₂ and distilled under reduced pressure.

Polymerization

The polymerization experiments were carried out in a glass sealed ampoules. The ampoule that contained the required amounts of reagents was degassed several times by freeze-thaw method, then sealed under vacuum and placed in a thermostat at 60°C.

VPDMS, which cannot be polymerized by radical process, was polymerized in benzene solution by sec.-BuLi as a catalyst at 25°C. Polymerization and introduction of reactants was performed in conditions excluding the contact with air.

When the reaction was complete, the ampoule was opened and polymer was dissolved in toluene and precipitated into methanol. Each sample was re-precipitated two times. The precipitated polymer was filtered and dried at 30°C until a constant weight was achieved. Polymerization conditions and characteristics of polymers obtained are shown in Table I. The X-ray analysis showed amorphous high molecular mass polymers, which can be dissolved in aliphatic and aromatic hydrocarbons, and chlorine-containing organic solvents.

Polymer Characterization

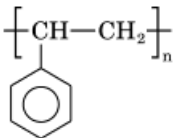
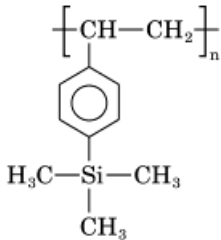
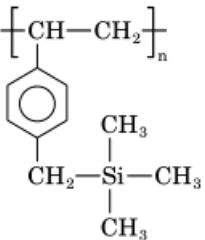
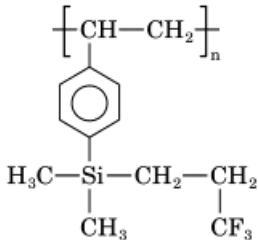
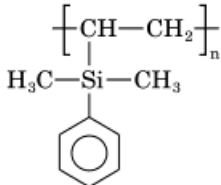
Molecular masses of polymers were determined using gel permeation chromatography (GPC) method (a Waters instrument with differential refractometer R-401 as a detector). The separation was carried out at 30°C using four columns (Ultrastayragel of Waters Co., Milford, MA, USA) having the pore sizes of 500, 1000, 10 000, and 100 000 Å. Polystyrenes standards were used for calibration. Tetrahydrofuran was employed as an effluent, the rate of elution being equal to 1 mL/min.

The glass transition temperatures were determined using differential scanning calorimetry on a TA-3000 (DSC-30) instrument of Mettler Co., Paris, France. The T_g values were read from the middle points of heat capacity curves measured with the error of ± 10 K; the error of ΔC_p determination was $\pm 10\%$. The heating rate was 10 K per min.

Nuclear magnetic resonance (NMR) spectra were obtained on a MSL-300 instrument (Bruker, Bzemen, Germany) in solutions of CCl₄ using an external standard at 300 MHz frequency.

The polymer films were cast over horizontal surface of cellophane from the toluene solutions containing about 5% of polymers. Evaporation of the solvent was performed for 3 days at ambient

Table II Physical Properties of the Polymers of the General Formula $-\text{[CH}_2\text{-CH(R)]}_n-$

Polymer	Formula	Density, g/cm ³	FFV (%)	T_g , °C
PS		1.048	13.5	93
PTMSS		0.965	19.1	135 (136)
PTMSMS		0.962	18.1	85 (85)
PFPMSS		1.127	18.6	62 (52)
PVPDMS		1.043	13.4	120

temperature. The films were dried in vacuum also at room temperature for 24 h. The thickness of the films was in the range 50–150 μm .

Permeability coefficients of the polymers were measured using either volumetric or gas chromatographic methods at 25°C. A partial pressure drop across the film was 1 atm.

Measurement of gas sorption was carried out with a Sartorius electrobalance (Model 4436 MP6) at 25°C and pressure range 0–30 atm.

Usual corrections for buoyancy of the films were introduced.

The PAL decay curves were measured at room temperature with an Ortec “fast-fast” lifetime spectrometer. The time resolution was 230 ps full width at half maximum (FWHM). We used a nickel-foil-supported [²²Na] sodium chloride radioactive source of positrons. The contribution from the annihilation in the source and instrumental resolution were taken into account in the PATFIT

Table III Permeability of Phenyl-Containing Polymers

Polymer	He	H ₂	O ₂	N ₂	CO ₂	CH ₄
PS ^a	22.4	27.7 ⁷	2.90	0.53	12.4	0.79
PTMSS	117.0	182.0	56.0	16.0	227.0	34.0
PTMSMS	46.0	54.0	14.0	45.0	56.0	7.8
PFPDMSS	95.0	109.0	38.10	11.8	284.0	22.0
PVPDMS	—	—	2.47	0.45	12.3	—
PtBS ^a	104.1	—	35.50	8.4	140.1	16.7

^a At 308 K; the values from ref. 7.

and CONTIN computing programs. The integral statistics for each spectrum was equal to $(1.5-2.0) \times 10^7$ coincidences. CONTIN program determined the chosen solution, corresponding to regularization parameter $\alpha \sim 10^{-4}$. This is a solution having a Fisher F-probability closest to 0.5. Each final PAL spectrum was obtained by summing up the results of some cycles of measurements (10^6 counts in each cycle). Application of the PATFIT program to the results of one cycle gave satisfactory variance of the fit ($\varphi \approx 1.05$) providing the number of the components (three or four) was determined correctly. The results of one cycle measurements were used to discriminate between three or four components PAL spectrum. In order to perform measurements in inert (nitrogen) atmosphere, the samples were placed in rubber glove, and dry nitrogen was allowed inside it.

RESULTS AND DISCUSSION

Gas Permeation Parameters

Table II presents chemical structures and some physical properties of the polymers obtained. The values of T_g of poly(p-trimethylsilyl styrene) (PTMSS) and poly(γ -trifluoropropyl dimethylsilyl styrene) (PFPDMSS) are consistent with the ones reported earlier.³ The results show that an introduction of a bulky substituent in the PS structure leads to an increase in T_g . However, if a spacer appears between the phenylene ring and bulky Si(CH₃)₃ group, the effect is opposite: the glass transition of poly(trimethylsilylmethyl styrene) (PTMSMS) is lower than that of PS. Even more pronounced effect can be noted for PFPDMSS having a long aliphatic group that terminates the side chain. All this can be explained by self-plasticization by flexible aliphatic side chains. Similar effects have been observed in many cases, for example for substituted norbornene polymers.¹¹

One of the polymers included in consideration, poly(vinylphenyldimethylsilane) (PVPDMS), is a phenyl-containing polymer that is not a derivative of PS. Its properties should be compared with those of poly(vinyltrimethyl silane) (PVTMS) studied in much detail.¹ The former has markedly higher density, smaller fractional free volume, and somewhat lower glass transition temperature.

The permeability coefficients in respect of various gases are shown in Table III, where two other PS derivatives were included for a comparison: poly(p-tert-butylstyrene) (PtBS) and PS itself. Table III indicates that an introduction of substituents in p-position of PS increases gas permeability significantly. However, the magnitude of this effect depends strongly on a structure of side group and on the nature of gas. Thus, for the most permeable polymer among the studied, PTMSS, the ratio P(PTMSS)/P(PS) is about 5 for helium, but 46 for oxygen, and 18 for carbon dioxide. Similar effects can be noted in comparison of other polymers with PS. If CH₂ spacer is inserted between the bulky Si(CH₃)₃ group and phenylene ring, as in the case of PTMSMS, permeability decreases as compared with that of PTMSS. A similar behavior can be noted for the polymers of other classes: vinylic, acetylenic, and norbornenic ones.¹

It should be noted that gas permeability of PTMSS for oxygen and nitrogen has been reported by Kawakami et al.⁶ They found the P(O₂) value of 14 Barrer, whereas a much higher value was obtained in this work. The difference in molecular mass (210 000 in ref. 6 and 760 000 in the present work) can hardly explain the differences in permeabilities observed. No explanation of this discrepancy can be proposed now.

In the studies of structure-properties relations in silicon-containing polymers, carbon structural analogue is often absent. It is, however, available

Table IV Permselectivity $\alpha = P_i/P_j$ of the Polymers Studied for Various Gas Pairs

Polymer	He/N ₂	H ₂ /CH ₄	O ₂ /N ₂	CO ₂ /CH ₄
PS ⁷	42.0	25.5 ^a	5.5	15.7
PTMSS	7.3	5.3	3.5	6.7
PTMSMS	10.2	6.9	3.1	7.2
PFPDMSS	8.1	5.0	3.2	12.9
PVPDMS	6.1 ^a	18.5 ^a	5.5	8.1 ^a
PtBS ⁷	12.4		4.2	8.4

^a Estimated using the group contribution method.

in the present case. A comparison of PTMSS and PtBS⁷ indicates that an appearance of Si atom in a bulky Si(CH₃)₃ group results in larger permeability than in the case tert-butyl group of purely hydrocarbon polymer, in spite of the fact that PtBS is also fairly high-permeable material.

As has been mentioned, PVPDMS is a structural analogue of PVTMS. In the group of the polymers considered in this work, this is a relatively low-permeable polymer. Its permeability is smaller by an order of magnitude than that of PVTMS. It can be assumed that here we encounter with the effect of nonsymmetrically substituted side group, well demonstrated by Masuda et al. for polyacetylenes.¹²

A comparison of the data presented in Tables II and III shows the correlation between permeability coefficients in respect of various gases and the fractional free volume of polymers.

Ideal separation factors $\alpha_{ij} = P_i/P_j$ of the polymers studied are given in Table IV. An usual tradeoff behavior is obvious: more permeable polystyrene derivatives exhibit less selectivity. However, no polymers studied in this work had permselectivity really attractive for membrane separation.

A possibility to consider a big group of polymers having a common element of molecular design, polystyrene main chain, and varying by the structures of side groups in the same position of phenylene ring makes it desirable to analyze structure-property relationship within a single polymer class. Robeson's permeability-permselectivity diagrams¹³ is a convenient way for such an analysis. These diagrams were plotted for various derivatives of PS using the data taken from refs. 3–8 and from the present work. As an example, Figure 1 shows such diagram for O₂/N₂ gas pair. It can be seen from Figure 1 that all the data points are located substantially lower than the upper bound, according to Robeson.¹³ Within the set of substituted polystyrenes, the correlation of $\alpha(O_2/N_2)$ and $P(O_2)$ is not better than for various polymers with different structures. It indicates that the structure of side chains exerts at least not less effects on α and P values than the structure of main chains.

Gas Sorption

Sorption isotherms were obtained for the following gases: He, Ar, O₂, N₂, CO₂, CH₄. All the isotherms, except those of He, are nonlinear. The

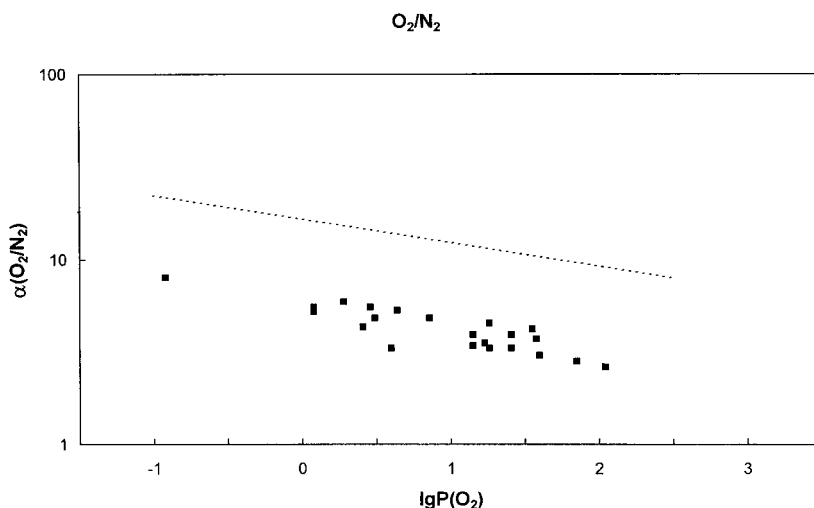


Figure 1 Correlation for O₂/N₂ separation factor with oxygen permeability coefficients P , Barrer, for substituted polysulfones: dashed line is upper bound according to Robeson.¹³

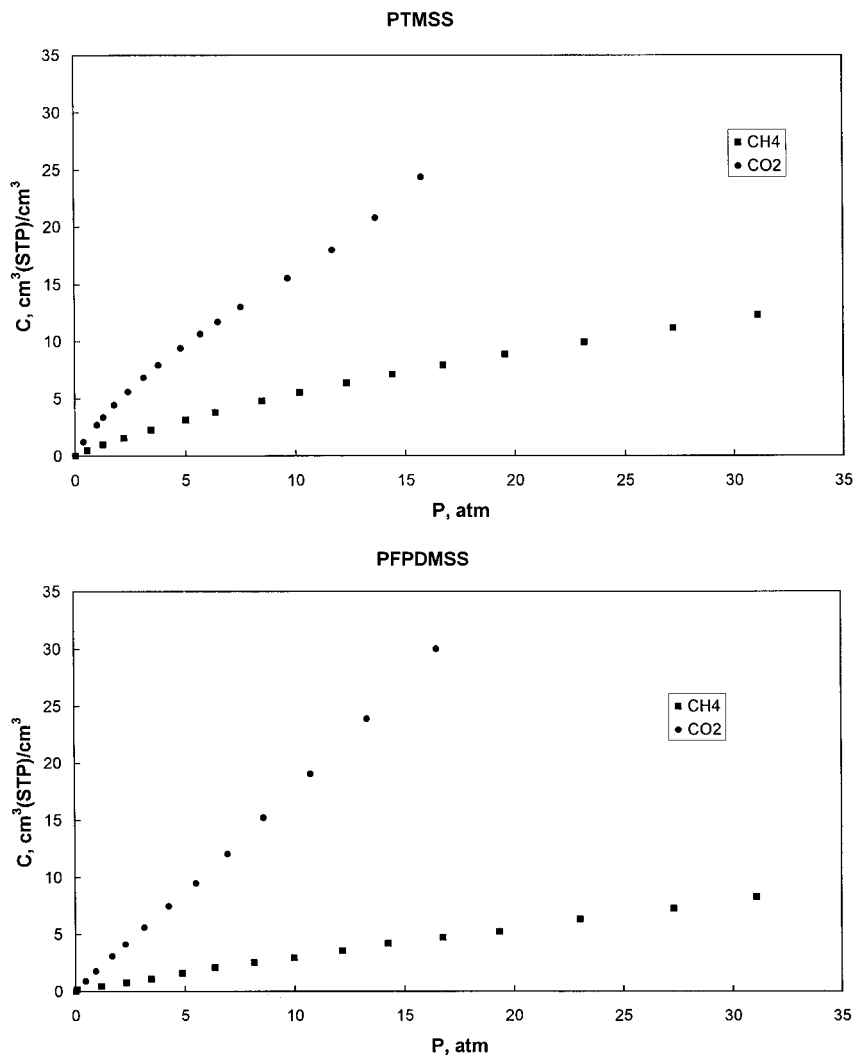


Figure 2 Sorption isotherms of CO₂ and CH₄ in (a) PTMSS and (b) PFPDMSS.

isotherms of sorption of Ar, O₂, N₂, CH₄ have the form of curves concave to the pressure axis, that is, are consistent with the dual mode sorption (DMS) model for gases in glassy polymers (see Fig. 2). As is usually the case for glassy polymers, a sorption-desorption hysteresis takes place: sorption isotherms are located below the desorption isotherms. Bearing in mind a relatively narrow pressure range studied (0–30 atm) and the effects of this range on the parameters of the DMS model,¹⁴ no attempt was made to calculate them for the polymers studied. Sorption isotherms of carbon dioxide reveal S-shaped form at larger pressures. Figure 2 shows examples of this behavior for PTMSS and PFPDMSS. Noteworthy, the inflection points of the isotherms in two polymers occur at different pressures: in the case of PFPDMSS it is located at much lower pressure

than in the isotherm of PTMSS. This difference is consistent with the results of analysis of S-shaped isotherms for other polymers.¹⁵ The pressure at which the inflection point at the isotherm occurs is lower for the glassy polymers having lower glass transition point. Since T_g of PFPDMSS is lower than that of PTMSS by 73°, no wonder that the conditions for a decrease the T_g values of the system “polymer-sorbed gas” due to the effect of plasticization down to the temperature of measurement (25°C) are satisfied at much lower pressure and concentration of the sorbed gas.

The initial slopes of the isotherms were used for estimation of the solubility coefficients S . Then using the formula $P = DS$, the diffusion coefficients D were found. All these parameters are displayed in Table V. It can be noted that there is no strong structural effects on the solubility

Table V Solubility (S)^a and Diffusion (D)^b Coefficients (25°C)

Polymer	He		Ar	O ₂		N ₂		CO ₂		CH ₄	
	S	D10 ⁷	S	S	D10 ⁷	S	D10 ⁷	S	D10 ⁷	S	D10 ⁷
PS ⁷ (308 K)	—	—	—	0.140	1.65	0.081	0.12	1.1	0.88	0.38	0.16
PTMSS	0.025	355	0.325	0.275	15.5	0.175	7.00	2.6	6.60	0.68	3.80
PFPDMSS	0.023	317	0.198	0.147	20.0	0.089	10.00	1.9	11.40	0.32	5.20
PVPDMS	0.005	—	0.109	0.076	2.5	0.040	0.86	—	3.2 ^c	—	0.57 ^c
PtBS ⁷ (308 K)	—	—	—	—	2.9 ^c	—	—	1.9	5.60	0.84	1.50

^a S in cm³(STP)/cm³ atm.^b D in cm²/s.^c Estimated using the group contribution method.

coefficients. On the other hand, the *D* values are much more sensitive to the structure of p-substituents in polystyrenes.

Nagasaki et al.⁸ noted a correlation of the solubility coefficients of oxygen with the content of Si in a series of silyl substituted polystyrenes. According to these authors, enhanced solubility selectivity $S(\text{O}_2)/S(\text{N}_2)$ can be anticipated in the polymers with large Si content. In Table VI, this possibility is analyzed for silicon-containing and other polystyrenes. Obviously, an appearance of Si and F atoms in side groups of polystyrenes does not influence solubility selectivity. However, diffusivity selectivity $D(\text{O}_2)/D(\text{N}_2)$ for the polymers studied in the present work and having more open structure as revealed in large gas permeability is markedly smaller than for those polystyrenes, which have —H, —CH₃, and —F groups as p-substituents in phenylene rings of PS.

Positron Annihilation Study

Traditionally, it was accepted that positronium component of PAL spectroscopy in conventional

Table VI Solubility Selectivity S_i/S_j and Diffusivity Selectivity D_i/D_j of Substituted Polystyrenes and PVPDMS

Polymer	S_i/S_j		D_i/D_j	
	O ₂ /N ₂	CO ₂ /CH ₄	O ₂ /N ₂	CO ₂ /CH ₄
PTMSS	1.57	3.8	2.2	1.7
PFPDMSS	1.65	5.9	2.0	2.2
PVPDMS	1.90	—	2.9	—
PS ⁷	1.70	2.9	3.3	5.5
PMS ⁷	1.80	3.8	2.7	3.4
PFS ⁷	1.60	4.2	3.2	3.6

PMS, poly(p-methylstyrene); PFS, poly(p-fluorostyrene).

glassy polymers (e.g., PMMA, PC) consist of one component (the PATFIT τ_3 and I_3 parameters or monomodal CONTIN distribution).¹⁶ Bimodal lifetimes distribution of the positronium component (or two lifetimes τ_3 and τ_4) has been reported for a high free volume polymer-poly(trimethylsilyl propyne) (PTMSP).¹⁷ It means that size distribution of free volume elements in this polymer should also be bimodal. One may, however, assume that the presence of two positronium lifetimes is a regular behavior of glassy polymers and that, in the case of conventional glassy polymers like PMMA or PC, resolving of two positronium lifetimes is complicated only because the longest lifetime τ_4 is too short (≈ 2 ns). Hence it is interesting to find examples where $\tau_4 > 2$ ns but not as long as in PTMSP (5–6 ns). The polymers considered in this work provide this opportunity: their permeability and diffusivity are intermediate between those of high free volume and conventional glassy polymers.

It has been shown that in porous sorbents¹⁸ and high free volume polymers¹⁹ the τ_4 lifetime depends on the concentration of sorbed oxygen $[\text{O}_2]_s$ if the sample during the measurements is in contact with air. Because of it, measurements of lifetimes were performed both in air and in nitrogen atmosphere.

PAL spectra of studied p-substituted PS measured in air atmosphere are presented in Table VII. For comparison, PVTMS is also considered. Although these polymers do not exhibit extremely large gas permeability [$P(\text{O}_2)$ values 2–50 Barrer], their PAL spectra consist of four components. For positronium lifetimes in the range 2.6–4.0 ns, it is possible to resolve both components using discrete PATFIT analysis, so this type of PAL spectrum is not a feature of high free volume polymers like PTMSP. The spectra of all substituted polystyrene are rather similar: the τ_3

Table VII Positron Annihilation Lifetime Spectra of Si-substituted Polystyrenes and PVPDMS According to PATFIT Analysis (Measurements in Air Atmosphere)

Parameter	Polymers				
	PTMSS	FPDMS	PTSMS	PVPDMS	PVTMS
τ_1 , ns	0.171 ± 0.004	0.183 ± 0.004	0.179 ± 0.004	0.176 ± 0.003	0.187 ± 0.003
I_1 , %	25.82 ± 1.09	29.81 ± 1.22	29.16 ± 1.38	28.60 ± 0.95	30.5 ± 0.9
τ_2 , ns	0.401 ± 0.008	0.408 ± 0.008	0.401 ± 0.010	0.408 ± 0.007	0.44 ± 0.07
I_2 , %	35.45 ± 0.90	35.48 ± 1.01	33.29 ± 1.08	33.98 ± 0.77	28.4 ± 0.7
τ_3 , ns	1.80 ± 0.11	1.73 ± 0.11	1.57 ± 0.12	1.78 ± 0.08	2.31 ± 0.07
I_3 , %	10.16 ± 1.14	8.44 ± 0.83	10.00 ± 1.47	16.66 ± 2.17	14.6 ± 1.0
τ_4 , ns	3.14 ± 0.03	3.11 ± 0.03	2.61 ± 0.03	2.72 ± 0.05	4.11 ± 0.04
I_4 , %	28.57 ± 1.34	26.26 ± 1.03	27.55 ± 1.78	20.76 ± 2.37	26.4 ± 1.1

values nearly coincide, the longer lifetime τ_4 of more permeable polymers (PTMSS and PFPDMS) are somewhat larger. But nevertheless those τ_4 values are in the range of longer lifetimes reported for conventional glassy polymers.¹⁶ Therefore one can assume that bimodal size distribution of free volume elements is characteristic for much wider range of polymers than has been accepted.

The results of studies of high gas permeability polymers¹⁹ might imply that the effect of oxygen sorbed during experiments in the sample can affect the longer lifetimes in four components PAL spectrum. More specifically, the larger the longest lifetime and $[O_2]_s$ during the measurement the stronger shift should be observed from τ_4 measured in air to τ_4 determined in nitrogen. Because of this reason, PAL spectra of the polymers were also obtained in inert (nitrogen) atmosphere. The results obtained in the present work indicate that the situation is somewhat more complicated.

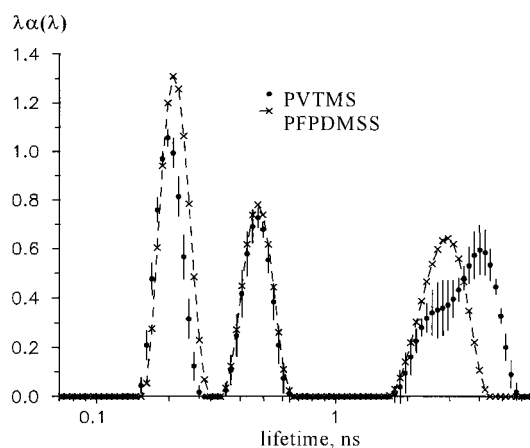
Although four components spectra were obtained for Si- and F-substituted PS, sorbed oxy-

gen does not exert noticeable effects on τ_3 and τ_4 values, as Table VIII illustrates. It is obvious that PAL spectra measured in air and nitrogen atmosphere are virtually identical. One can assume that relatively small free volume elements of the polystyrene derivatives studied in this work (2.8–4.3 Å, according to Tao-Eldrup equation^{20,21}) are not sufficient to accommodate sorbed oxygen molecules and enable them to react with Ps atom.

Examples of continuous lifetimes spectra are given in Figure 3. It is seen that for PFPDMS the longest lifetime component is displayed as a nonresolved peak. The same was true for other substituted PS. On the other hand, the lifetime component of the spectrum obtained for PVTMS exhibits a shoulder. Besides the maximum of this peak in the PVTMS spectrum is shifted to larger lifetimes. The maxima of the peaks are consistent with τ_4 values presented in Table VII. It can be noted, τ_4 lifetime of PVTMS is markedly longer

Table VIII Positron Annihilation Lifetime Spectra of PTMSS and PVPDMS According to PATFIT Analysis (Measurements in Nitrogen Atmosphere)

Parameter	PTMSS	PVPDMS
τ_1 , ns	0.19 ± 0.06	0.20 ± 0.05
I_1 , %	29.0 ± 1.9	31.0 ± 1.8
τ_2 , ns	0.42 ± 0.01	0.43 ± 0.01
I_2 , %	31.6 ± 1.6	32.7 ± 1.4
τ_3 , ns	1.85 ± 0.20	1.78 ± 0.16
I_3 , %	8.11 ± 1.73	14.83 ± 3.79
τ_4 , ns	3.16 ± 0.04	2.69 ± 0.08
I_4 , %	31.31 ± 2.01	21.50 ± 4.10

**Figure 3** Continuous positron annihilation lifetime distribution in PVTMS and PFPDMS.

than that of PFPDMSS, as Table VII shows. All this implies that free volume microstructure of PVTMS is just at the border of free volume sizes, where bimodal continuous PAL spectrum can be resolved. For the polymers having smaller τ_4 values (or smaller free volume sizes), the positronium spectrum is displayed as one broad component. Apparently, this is true for all substituted PS studied in this work.

CONCLUSIONS

A series of structurally related Si-containing PS has been prepared via radical polymerization. Their study resulted in formulation of various structure-property relations, where gas permeability, diffusion, and solubility coefficients are considered as polymer properties. Introduction of different Si-containing side groups in the p-position of phenylene ring is accompanied by an increase in P and, especially, D values for all gases. The changes of the solubility coefficients are much weaker. Simultaneously, separation factors P_i/P_j and diffusivity selectivity D_i/D_j decrease markedly. A comparison of PTMSS with its hydrocarbon analogues, PtBS, indicates that the $\text{Si}(\text{CH}_3)_3$ group exerts much stronger effects on gas permeability and diffusivity of polymers than tert-butyl group. Again, the role of spacers was demonstrated: they make an increase in gas permeability in corresponding structures much weaker in spite of the fact that the size of the side chain is increased. One may assume that an appearance of relatively flexible spacers in the side chains enables them to align along the main chains, thus partly filling free volume elements located between main chains.

Obtained via anionic polymerization, PVPDMS is a structural analog of PVTMS. One difference between these two polymers is asymmetric design of the side group in the former. A conclusion can be made that symmetrically substituted silyl group results in significantly larger values of permeability and diffusion coefficients.

Unexpected results were obtained in the study of vinylic type polymers using lifetime positron annihilation technique. It was shown that lifetime spectra consist of four components. Previously such behavior was observed only for high free volume glassy polymers like poly(trimethylsilyl propyne) or amorphous teflons AF. The following conclusion can be made on this basis: bimodal size distribution of free volume elements is not an unusual feature of only highly permeable polymers but is realized in conventional glassy

polymers too. Recently four component spectra have been reported for polyethylene and polytetrafluoroethylene both below and above their glass transition temperature.²²

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