Gas Transport Properties in a Novel Poly(trimethylsilylpropyne) Composite Membrane with Nanosized Organic Filler Trimethylsilylglucose

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ABSTRACT: We report a novel composite membrane made from the high free volume polymer poly(trimethylsilylpropyne) and the small organic filler trimethylsilylglucose (TMSG). The permeabilities, diffusivities, and solubilities of six gases (He, H_2, CO_2, O_2, N_2, CH_4) were determined in these PTMSP/TMSG composites with a series of TMSG loads using the time-lag method. Increasing TMSG content in PTMSP resulted in substantial reduction of all gas permeabilities. The observed decrease in permeability was much larger than predicted by the Maxwell model for the incorporation of impermeable fillers. In addition, the permeability loss varied significantly from gas to gas, leading to increased selectivities for some gas pairs. For example, nitrogen permeability (9.6×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg)) in PTMSP containing 56.8 vol % TMSG decreased by more than 600-fold compared to that of unfilled PTMSP (5490×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg)). Simultaneously, the O_2/N_2 selectivity increased from 1.5 up to 3.4. The varying permeability behavior in PTMSP/TMSG composites is in good agreement with the diffusivity change. In addition, a parallel reduction in solubility for all tested gases was observed. In these composites, the natural logarithms of the diffusivities and solubilities are well linearly related to the square of penetrants diameter and their condensability, respectively. It was observed that the activation energy of permeation increased with TMSG content. From the analysis of the temperature dependence of the gas permeability, we conclude that the gas transport in pure PTMSP and PTMSP/TMSG composites follows different mechanisms. Our results indicate that the PTMSP/TMSG composite membranes offer a readily accessible means to physically modify the FFV in PTMSP polymer and to achieve the desired gas permeability and permselectivity compared to the pure polyacetylene polymers.

Introduction

PTMSP has the highest gas permeability of all known polymers and has been synthesized and described first by Masuda et al.[1] For example, the oxygen permeability in PTMSP is nearly 4 orders of magnitude higher than that of low FFV, conventional glassy polymers such as polysulfone.[2] However, PTMSP exhibits very low gas selectivities; for example, the oxygen/nitrogen selectivity is only about 1.5. These unusual transport properties are predominantly attributed to the extremely high FFV (0.29),[3−5] which constructs an interconnected network making up to about 20−25% of total volume in the PTMSP polymer. Hence, PTMSP may be regarded as a polymer with an intrinsic microporosity.[4,5] Srinivasan et al.[4] and Pinnau et al.[5] supposed that gas permeation takes place in this microporous network. As we can see from the chemical structure of PTMSP shown in Figure 1, the high FFV primarily results from the rigid −C═C− backbone containing the bulky trimethylsilyl pending group, which prevents the polymer chains from effectively packing.[3]

It is well recognized now that the free volume element (FVE) size and its size distribution both play an important role for gas transport properties.[6] It has been shown by positron annihilation lifetime spectroscopy (PALS) that the size distribution of free volume in PTMSP is bimodal with two sorts of microcavities with radii in the ranges 2.5−4.0 and 5−7.5 Å, respectively.[7]

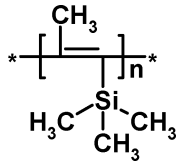

Figure 1. Chemical structure of PTMSP.

Additionally, the simulation work by Hofmann et al.[8] also revealed a wide range distribution of FFV in PTMSP (radii: from 1.1 to 9 Å); this broad FFV in PTMSP had an asymmetric distribution with at least two peaks, one at about 3−4 Å and the other at about 6−8 Å.

The distinctive gas transport properties and unusual FFV in PTMSP have evoked large interest in synthesizing numerous derivates of polyacetylenes by modifying the bisubstitutes attached to the double bond.[9] Noticeably, the polyacetylene family exhibits a wide range of difference in permeability.[9] Some polyacetylenes even display 3 orders of magnitude lower permeability compared to that of PTMSP. For example, oxygen permeability is just 3.8 barrers in 1-phenyl-2-[4-(triphenylsilyl)-phenyl]acetylene (*p*Ph_3SiDPA) reported by Teraguchi et al.[10] The extremely large differences in gas permeability for the polyacetylene family result from varied polymer chain packing, which leads to the corresponding various size of FFV, interchain spacing, and connection behavior of FVE.[9]

Efforts were also made to modify the FFV in PTMSP through physical means (e.g., particle filling). For example, an increased FFV in the PTMSP composite system by incorporating nonporous fumed silica (FS), thereby resulting in an increased gas

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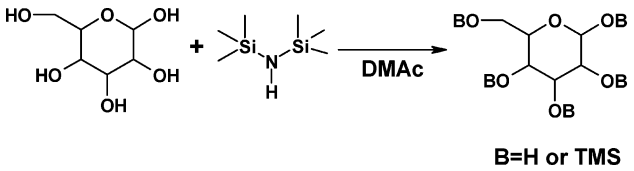

Figure 2. Synthesis of trimethylsilylglucose (TMSG).

permeability, was reported by Merkel et al.[11] and Gomes et al.[12] On the other hand, a decreased FFV in fullerene filled PTMSP matrix causing a decreased permeability was described by Higuchi et al.[13] Li and Freeman also observed a drastically decreased permeability in PTMSP containing 1.5 nm POSS particles.[14] In practice, Langsam et al.[15] have also reported a decreased permeability accompanied by an increased selectivity in PTMSP with a large number of additives such as silicon oils, nonionic surfactants, hydrocarbon oils, flame-retardant additives, and so on. But, the systemic investigation for PTMSP with organic fillers is still missing. In addition, the commonly used fillers are inorganic particles, which have a notorious problem in compatibility with the polymer matrix, therefore frequently producing defects.[16] In this paper, we report a novel PTMSP composite membrane with the compatible organic filler trimethylsilylglucose (TMSG). The effect of TMSG addition on the FFV modification and the corresponding gas transport properties in PTMSP are discussed.

Experimental Section

Synthesis and Characterization of Trimethylsilylglucose (TMSG). The synthesis of TMSG using the silyl agent hexamethyldisilazane (HMDS) and glucose has been performed in *N*,*N*-dimethylacetamide (DMAc) at 80 °C under a nitrogen atmosphere for 12 h. The method is similar to that reported by Mormann et al.[17] and Nouvel et al.[18] Figure 2 shows the synthesis formula.

Glucose was obtained from Aldrich, and HMDS and all solvents were purchased from Merck. The glucose was dried in a vacuum at 100 °C overnight before use. 3 g of glucose was mixed with 120 mL of DMAc in a 250 mL round flask and stirred at 80 °C under nitrogen gas protection. 50 mL of HMDS was added dropwise through a drop funnel over 3 h, and then the mixture was continuously stirred for 9 h in order to maximize the silylation degree. The mixture was allowed to slowly cool to room temperature. Afterward, the mixture was poured into a separation funnel, and 400 mL of ice water was added. Then 150 mL of hexane was added to extract the product. The extracted product in hexane was dried with anhydrous sodium sulfate and subjected to a rotation evaporator for removing the solvent. The crude product was dried under vacuum at room temperature for 24 h. The transparent liquid product was characterized by proton nuclear magnetic resonance (^{1}H NMR) and thermogravimetry analysis (TGA). The overall silylation degree was 83% with a good reproducibility, which was estimated from ^{1}H NMR spectra according to Nouvel et al.[18] The thermal stability of TMSG is up to 110 °C measured by TGA. TMSG is soluble in polar solvents like methanol as well as in unpolar solvents like cyclohexane.

PTMSP/TMSG Composite Film Preparation and Characterization. PTMSP was purchased from Gelest (Lot: 5I-7401). Before film preparation, PTMSP was purified via reprecipitation with methanol. 1% (w/v) PTMSP polymer solution in dry cyclohexane was prepared in a glass bottle at room temperature. Various amounts of TMSG were added to the PTMSP polymer solution. The transparent homogeneous solution was filtered and poured into an aluminum ring, which was supported by a dust-free, dry, flat glass plate. Subsequently, the solvent was allowed to evaporate slowly for 2 days by covering a glass dish at room temperature. After solvent evaporation the film was further dried under an oil-free vacuum overnight to completely remove residual solvent. The film was removed from the glass plate by immersion in water and dried under an oil-free vacuum overnight again. All PTMSP/TMSG composite films are transparent, featureless via optical observation, indicating an excellent miscibility between PTMSP and the filler TMSG. The miscibility behavior of composite material via the optical observation has been discussed elsewhere.[19] Film thickness varied from 140 to 230 μm, which was measured by a digital micrometer with a precision of ± 2 μm. Finally, the film was cut into a round disk with diameter of 4.6 cm for a time-lag test cell. The freshly prepared film was directly analyzed by time-lag in order to reduce the influence of aging as much as possible.

Time-Lag Measurements. Gas permeation data were measured at 30 °C with six pure gases (helium, hydrogen, carbon dioxide, oxygen, nitrogen, methane) by a pressure increase time-lag apparatus, which has been described elsewhere.[20] The feed pressure used was between 200 and 400 mbar for the larger gases (carbon dioxide, oxygen, nitrogen, methane) and around 100 mbar for smaller gases (helium and hydrogen). The permeate pressure was maintained at less than 10^{-7} bar with an oil-free vacuum pump. The gas permeability P was calculated under steady state by eq 1

$$P = \frac{Vl}{At(P_f - P_p)} \tag{1}$$

where V is permeate chamber volume (cm^3), l is the film thickness (cm), A is the effective film area (cm^2), t is the time (s), P_f is the feed pressure, and P_p is the permeate pressure. The unit of permeability P is barrer, which is 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg).

The solution−diffusion transport model is applied for gas transport process through dense polymer film. It means that the permeability coefficient P can be defined as

$$P = DS \tag{2}$$

where D is the steady diffusion coefficient (cm^2/s) and S is the solution coefficient (cm^3 (STP)/(cm^3 cmHg). The diffusion coefficient D can be directly obtained by the time-lag method under the assumption of a constant diffusion coefficient. As the gas transport through the film reaches a steady state, the diffusion coefficient D can be calculated by eq 3

$$D = \frac{l^2}{6\theta} \tag{3}$$

where θ is the time lag (s). The solution coefficient can then be derived from eq 2.

The permselectivity of a polymer film for component A relative to component B is the ratio of their permeation coefficients.

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{4}$$

Since the permeation coefficient is the product of the diffusion coefficient and solubility coefficient, the permselectivity for two gases can be expressed (eq 5) as the combination of diffusion selectivity and solubility selectivity.

$$\alpha_{A/B} = \frac{D_A}{D_B}\frac{S_A}{S_B} \tag{5}$$

Results and Discussion

Permeability and Permselectivity. In Table 1 the effect of TMSG filler in PTMSP on the permeability coefficients of six light gases (He, H_2, CO_2, O_2, N_2, CH_4) is illustrated. The incorporation of TMSG in PTMSP leads to a drastic decrease in gas permeability. For instance, in PTMSP loaded with 5 vol % TMSG all gas permeability coefficients decreased by nearly 50% compared to pure PTMSP. As PTMSP is loaded with 56.8 vol % TMSG, the nitrogen permeability even reduces by more than 600-fold. On the basis of the data in Table 1, the normalized

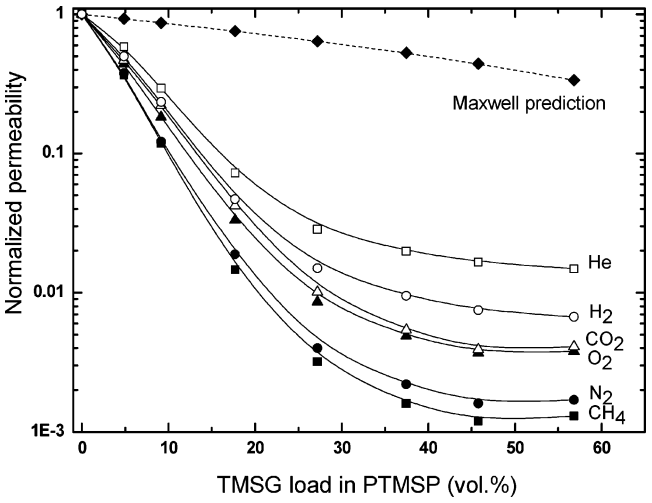

Figure 3. Normalized gas permeability coefficients for six gases [He (□), H_2 (○), CO_2 (△), O_2 (▲), N_2 (●), CH_4 (■)] and Maxwell model prediction (◆) as a function of loading amount of TMSG in PTMSP.

Table 1. Gas Permeability of the PTMSP/TMSG Composite Membranes at 30 °C

load of TMSG in PTMSP (vol %)	permeability (cm^3 (STP) cm/(cm^2 s cmHg)) × 10^{-10}					
	He	H_2	CO_2	O_2	N_2	CH_4
0.0	5690	15850	31333	8120	5490	14833
4.9	3223	7910	14600	3580	2070	5430
9.2	1680	3713	6923	1480	668	1760
17.7	413	743	1320	270	104	218
27.2	162	238	316	70	22	48
37.4	113	151	168	40	12	24
45.8	94	119	123	30	9	18
56.8	85	106	129	31	9	19

Table 2. Estimated Volume of Spherical TMSG and PTMSP FFV[a]

	volume (Å^3)
TMSG	811
PTMSP FFV	5.6−3052

[a] The diameter of the TMSG molecule is about 10 Å; the PTMSP FFV radii expand from 1 to 9 Å from Hofmann et al.[8]

gas permeability (calculated as the ratio of the permeability in the various amount TMSG filled PTMSP to the unfilled PTMSP) as a function of the loading content of TMSG is plotted in Figure 3, where the prediction of the classical Maxwell model can be used to describe the decrease of permeability of a homogeneous polymer phase containing an impermeable filler.[21] Figure 3 demonstrates that a significantly negative deviation of the gas permeability is observed relative to the Maxwell model. It means the gas permeability reduction in PTMSP/TMSG composites cannot be explained by the simple tortuous effect.

This strongly reduced permeability is seemingly related to the reduced accessible free volume caused by the TMSG occupation of partial FFV in PTMSP. We speculate that the organic filler TMSG can enter the interconnected FVE[6−8] and to some extent occupy the "micropores"[4] in PTMSP. Such behavior was also reported in the study of PTMSP filled with low molecular weight poly(dimethylsiloxane) (PDMS) by Nakagawa and co-workers.[22] In this study, the "pore-filling" hypothesis can be reasonably supported by the direct size comparison between the volume of the presumably spherical FVE in PTMSP[7,8] and the spherical TMSG molecule. Table 2 presents the estimated size for both, which indicates that TMSG may be allowed to enter the partial FFV elements in PTMSP without disruption of polymer chain packing.

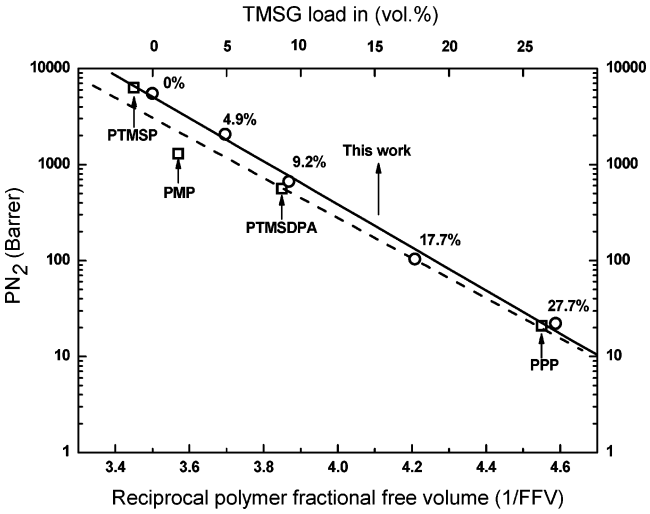

Figure 4. Nitrogen permeability ($P(N_2)$) in four disubstituted acetylene polymers (□) (PTMSP, PMP, PTMSDPA, PPP)[23] and in PTMSP/TMSG composites (○) as a function of reciprocal fractional free volume (1/FFV) of the polymer [23] and the loaded amounts of TMSG in vol %, respectively [1 barrer = 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg)].

The analysis of the permeability decrease with TMSG content can further validate the assumption of the "pore filling" in PTMSP with TMSG. In Figure 3, the decline in permeability for all six gases can be obviously divided into two stages. In the first stage, the permeability decreases radically with increasing TMSG loading, followed by a smooth decrease in permeability in the second stage. The turning point lies at the loading of around 27 vol % TMSG. For example, about 250-fold loss in nitrogen permeability is observed at the loading of TMSG from 0 to 27 vol %. In contrast, a relatively small decrease for nitrogen permeability (2.5-fold) takes place from 27 to 57 vol % TMSG load. A reasonable explanation for such behavior can be based on our hypothesis as well that TMSG may first fill the larger interconnected FVE,[4,5] which contributes to the fast gas transport. After the available large free volume is occupied, the additional loaded TMSG may just reside between polymer chains, leading to an increased tortuosity for gas transport; this behavior is in line with the prediction of the Maxwell model.[21] Srinivasan et al.[4] and Pinnau et al.[5] assumed about 20−25% connected free volume is in PTMSP and suggested most gas permeates through this interconnected FVE. In contrast, the other 75−80% dense polymer matrix contributes insignificantly to the gas permeation. This statement is consistent with our experimental results: around 27 vol % loading TMSG can block the fast gas transport passage in PTMSP.

Such behavior further indicates that addition of TMSG can readily modify the FFV in PTMSP. To discuss this physical modification of FFV in PTMSP, we compare the nitrogen permeability behavior in PTMSP/TMSG composite membranes with that of four representative polyacetylene derivatives with declined FFV (poly(1-trimethylsilyl-1-propyne) [PTMSP] (FFV = 0.29), poly(4-methyl-2-pentyne) [PMP] (FFV = 0.28), poly-[1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene] [PTMSDPA] (FFV= 0.26), and poly(1-phenyl-1-propyne) [PPP] (FFV = 0.22), which were reported by Toy and co-workers.[23] In Figure 4, the nitrogen permeability is plotted as a function of the TMSG loading in PTMSP/TMSG composites. For comparison, the nitrogen permeability in four polyacetylenes as a function of the corresponding reciprocal FFV is also presented. Obviously, the simple process of filling PTMSP with TMSG leads to similar nitrogen permeabilities, which were obtained with the different polyacetylenes. In the polyacetylenes, the decrease in the

Table 3. Selectivities of Various Gases over Nitrogen in PTMSP with Various Amounts of TMSG at 30 °C

load of TMSG in PTMSP (vol %)	gas/N_2 selectivity				
	He	H_2	CO_2	O_2	CH_4
0.0	1.0	2.9	5.7	1.5	2.7
4.9	1.6	3.8	7.1	1.7	2.6
9.2	2.5	5.6	10.4	2.2	2.6
17.7	4.0	7.2	12.7	2.6	2.1
27.2	7.3	10.8	14.3	3.1	2.2
37.4	9.5	12.7	14.1	3.3	2.0
45.8	10.7	13.5	13.9	3.4	2.0
56.8	9.2	11.5	14.0	3.4	2.1

nitrogen permeability is well correlated to the decrease in FFV.[23] In PTMSP/TMSG composites, a similar relationship between the nitrogen permeability and the content of TMSG is observed as well. By analogy, it is reasonable to speculate that the loading with TMSG can systemically reduce the FFV in PTMSP, consequently reducing the permeability.

Besides a radical decrease in gas permeability in the PTMSP/TMSG composites, as clearly shown in Figure 3, the permeability decrease varies significantly from gas to gas. For instance, at the content of 27.2 vol % TMSG in PTMSP, compared to the unfilled PTMSP, the permeability reduction is 35-fold for helium, 66-fold for hydrogen, 99-fold for carbon dioxide, 117-fold for oxygen, 248-fold for nitrogen, and 312-fold for methane. The permeability decrease is apparently gas size dependent. The rank of the permeability decrease of the gases is He < H_2 < CO_2 < O_2 < N_2 < CH_4, which is in a good agreement with the effective gas diameter order:[24] He (0.178 nm) < H_2 (0.214 nm) < O_2 (0.289 nm) ≈ CO_2 (0.302 nm) < N_2 (0.304 nm) < CH_4 (0.318 nm). Moreover, a consistent increase in permselectivity is observed for gas/N_2 pairs (except methane/nitrogen because methane is larger than nitrogen) with increasing amount of TMSG in PTMSP, which is summarized in Table 3. It can be seen that PTMSP has almost no selectivity for He/N_2, but PTMSP with 45.8 vol % TMSG displays almost a selectivity of 9. To visibly express the permselectivity change in the PTMSP/TMSG composites, the normalized permselectivity of the other five gases over nitrogen as a function of TMSG loading in PTMSP is plotted in Figure 5. The larger the size difference of the permeating gas pair, the higher the increased permselectivity of the gas pair with increased load of TMSG in PTMSP. Such behavior can be explained by the increased size selectivity in PTMSP/TMSG composites.

As generally observed, the size selectivity increases as permeability decreases in the PTMSP/TMSG membranes, which is in accordance with the well-known permeability/selectivity tradeoff relationship.[25] This behavior may be rationalized from free volume consideration.[11] The decreased permeability and enhanced permselectivity exhibited by filling PTMSP with TMSG are believed to arise from the reduced, less selective interconnected FFV. Therefore, the small "conventional" free volume in PTMSP contributes to increase the size selectivity in the composites. Such behavior is typical for the low volume, conventional glassy polymers.[2,5]

More specifically, we compare the oxygen permeability and oxygen/nitrogen selectivity in PTMSP/TMSG composite membranes. Figure 6 compares the correlation between oxygen permeability and oxygen/nitrogen selectivity for the substituted polyacetylenes[9] and the PTMSP/TMSG composite membranes in this study. It clearly shows that the physical loading of TMSG in PTMSP can readily improve the selectivity of oxygen over nitrogen from 1.5 up to 3.5. The selectivity improvement, though, is along with a permeability decrease for O_2 from 8120 to 30 barrers, which complies with the tradeoff behavior

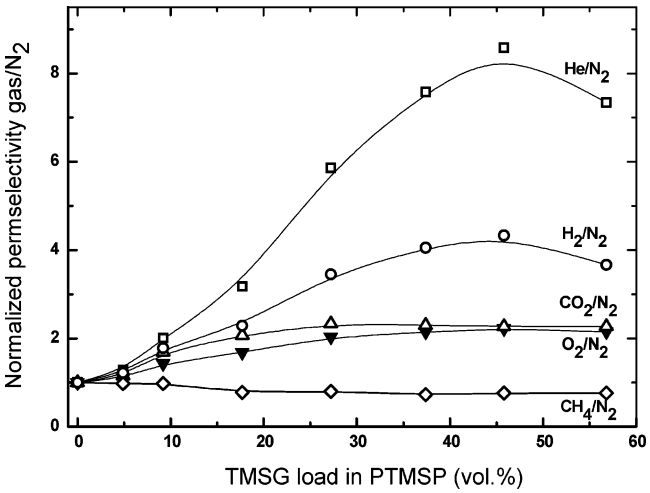

Figure 5. Normalized selectivities for five gases [He (□), H_2 (○), CO_2 (△), O_2 (▼), CH_4 (◇)] over nitrogen in PTMSP/TMSG composites as a function of loading amount of TMSG.

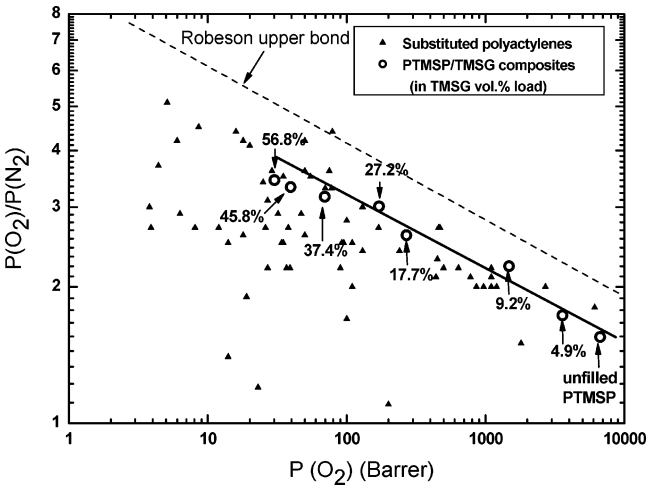

Figure 6. Relationship between oxygen permeability and its selectivity over nitrogen for substituted polyacetylenes (▲)[9] and PTMSP/TMSG composite membranes in this study (○). The upper bound line comes from Robeson.[25]

relationship between the gas permeability and selectivity.[25] Interestingly, in comparison with more than 50 synthesized polyacetylene polymers,[9] PTMSP with various amount of TMSG exhibits a relatively good performance in terms of permeability and selectivity. Moreover, the optimal, tailored performance can be readily obtained via control of the TMSG load compared to the time-consuming synthesis.

Diffusivity. Since the permeation coefficient is a product of the diffusion and the solution coefficient, it is worthwhile to study both coefficients in order to get more insight into transport behavior of the PTMSP/TMSG composites. Table 4 presents the diffusion coefficients for He, H_2, CO_2, O_2, N_2, and CH_4 in PTMSP as a function of various contents of TMSG and the effective molecular diameter for each gas. The systematic decrease in diffusivity for all six gases is observed with increased contents of TMSG in PTMSP. Simultaneously, the diffusivity decrease is strongly related to the gas size difference. The small gas helium experiences the least loss in diffusivity; in contrast, the largest methane exhibits the largest loss. For example, in the PTMSP with 37 vol % TMSG, helium diffusivity reduces by 5-fold compared to that in unfilled PTMSP; however, methane diffusivity reduces more than 100-fold. The gas diffusivity decline is well related to the gas size, which is ranked in the order CH_4 > N_2 > CO_2 ≈ O_2 > H_2 > He. In addition, the

Table 4. Gas Diffusion Coefficients in a Series of PTMSP/TMSG Composite Membranes at 30 °C in Terms of the Effective Molecular Diameter for Six Gases

gas	He	H_2	CO_2	O_2	N_2	CH_4
d_{eff} (nm)	0.178	0.214	0.302	0.289	0.304	0.318
load of TMSG in PTMSP (vol %)	diffusivity (cm^2/s) $\times 10^{-5}$					
0.0	25.2	29.4	3.2	4.5	3.5	3.02
4.9	19.9	16.4	1.65	2.24	1.47	1.21
9.2	14.1	10.5	0.83	1.07	0.68	0.46
17.7	5.9	3.7	0.22	0.3	0.16	0.09
27.2	4.3	2.0	0.09	0.15	0.08	0.04
37.4	3.6	1.5	0.06	0.11	0.06	0.03
45.8	3.2	1.4	0.05	0.1	0.05	0.02
56.8	3.4	1.5	0.07	0.13	0.07	0.03

diffusivity change behavior is very similar to the permeability change in PTMSP/TMSG composites, which clearly indicates that the diffusivity plays a dominant role in the transport.

It has been reported that major physicochemical factors, which control the gas diffusivity and selectivity of polymers, are (1) cohesive energy density (CED) and (2) FFV, FVE size, and size distribution, and (3) gas−polymer interaction.[26] However, it is well-known that there are hardly any specific interactions of light gases with polymers at low gas pressures (<10 bar). It is also supposed that the CED of PTMSP/TMSG composites do not vary much by the physical addition of TMSG because the special interactions between the hydrophobic filler TMSG and the hydrophobic polymer chains of PTMSP are absent. Thus, the gas diffusivity in the PTMSP/TMSG composite membranes depends mainly on the FFV. Theoretically, the diffusion coefficients straightforwardly reflect the mobility of molecular transport through the polymer.[27] Cohen and Turnbull first formulated the mathematical relationship between the gas diffusion coefficient and the penetrate size combined with the polymer FFV.[27] Equation 6 expresses this correlation.

$$D = A \exp\left(-\frac{\gamma}{V_f} v^*\right) \tag{6}$$

where D is the diffusion coefficient, A is a preexponential factor slightly dependent on temperature, γ is an overlap parameter, v^* is the size of permeate, and V_f is the fractional free volume. Equation 6 obviously suggests that the decreased FFV will result in the diffusivity decrease.

In PTMSP, the extremely high FFV contributes to the high gas diffusivity.[3−5] The decreased diffusivity in the PTMSP/TMSG composites obviously suggests less accessible FFV for gas transport, indicating that the filler TMSG occupies partial FFV in PTMSP. The observed improved diffusivity selectivity is mainly ascribed to the blocked interconnected FFV elements in PTMSP by TMSG. As a result, gas was forced to diffuse through the conventional FVE, where the size selectivity occurs as a conventional glassy, low free volume polymer.

Teplyakov and Meares[24] formulated an empirical correlation between molecular effective diameter and its diffusion coefficients for more than 50 polymeric materials. Equation 7 expresses the mathematical relationship

$$\ln D = k_1 + k_2 d_{eff}^{\ 2} \tag{7}$$

where D is the diffusion coefficient, k_1 and k_2 are fitting parameters which are polymer type dependent, and d_{eff} is the effective molecular diameter. From this equation, we can see the diffusion selectivity for any chosen gas pair in a polymer is determined by the parameter k_2. A higher k_2 value indicates higher diffusion selectivity.

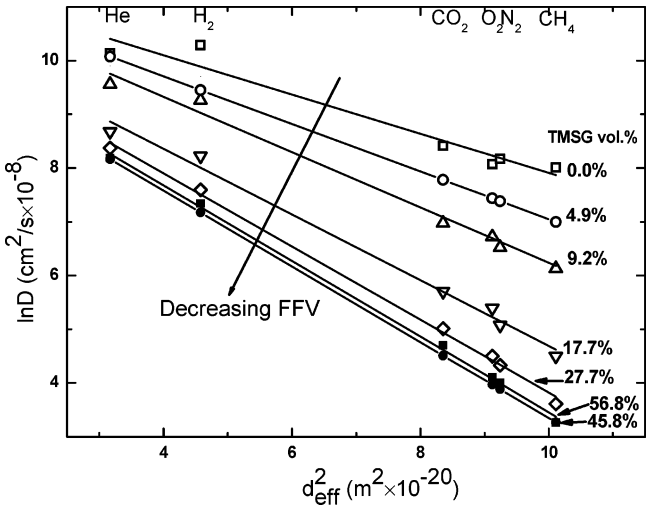

Figure 7. Plots of the natural logarithm of gas diffusivity as a function of square of its effective diameter in a series of PTMSP/TMSG composite membranes [TMSG load in PTMSP: 0.0% (□), 4.9% (○), 9.2% (△), 17.7% (▽), 27.7% (◇), 45.8% (●), 56.8% (■)].

Table 5. Linear Fitting Parameters of k_1, k_2, and Regression R in the Plots of the Natural Logarithm of Gas Diffusivity as a Function of Square of Its Effective Diameter[24] in a Series of PTMSP/TMSG Composite Membranes

load of TMSG in PTMSP (vol %)	k_1	k_2	R
0	11.5573	0.3647	0.9744
4.9	11.4756	0.4427	0.9925
9.2	11.3866	0.5149	0.9949
17.7	10.8034	0.6113	0.9956
27.2	10.6268	0.6806	0.9988
37.4	10.4938	0.7035	0.9992
45.8	10.4017	0.7053	0.9991

According to eq 7, Figure 7 presents the plots of the gas diffusivity as a function of the square of the effective diameter in the PTMSP/TMSG composites. The intercept k_1, slope k_2, and linear regression R parameters are summarized in Table 5. The linear relationship between the natural logarithm of gas diffusion coefficient and corresponding square of effective molecular size is proven (regression value $R > 0.98$). As expected, we can see that the value of the slope (k_2) progressively increases with increase of TMSG loading, indicating the enhanced diffusivity selectivity. On the other hand, it is interesting to find that the intercept (k_1) systemically decreases with an increased content of TMSG, which is consistent with the gas diffusivity decrease. In other words, a large k_2 value always accompanies with a small value of k_1 and vice verse.

Solubility. From the permeability and diffusivity, the solubility is estimated according to eq 2. Table 6 exhibits the solubility coefficients for all six gases (He, H_2, CO_2, O_2, N_2, and CH_4) in PTMSP with various amounts of TMSG. With an increased TMSG content in PTMSP, a systematic decrease in gas solubility is observed. More than 50% loading TMSG causes the solubility capacity of PTMSP to reduce by almost 1 order of magnitude for each gas. This solubility capacity is getting close to that of conventional glassy polymers.[5] In addition, the solubility selectivity is almost unchanged. The gas solubility in a polymer/filler composite is simply estimated by the additive model,[29] described by eq 8

$$S_f = S_0(1 - \phi) \tag{8}$$

where S_f is the solubility in polymer composite, ϕ is the filler

Table 6. Effective Force Constants for Six Gases[24] and Their Solubility Coefficients in a Series of PTMSP/TMSG Composite Membranes at 30 °C

	He	H_2	CO_2	O_2	N_2	CH_4
effective force constants $(e/k)_{eff}$ (K)	9.5	62.2	213.4	112.7	83	154.7
load of TMSG in PTMSP (vol %)	solubility (cm^3 (STP)/cm^3 $cmHg^{-1}$) × 10^{-2}					
0.0	0.226	0.541	9.773	1.805	1.555	4.913
4.9	0.072	0.483	8.843	1.6	1.41	4.483
9.2	0.12	0.354	8.35	1.387	0.989	3.83
17.7	0.07	0.202	5.95	0.888	0.651	2.535
27.2	0.037	0.119	3.523	0.469	0.291	1.265
37.4	0.032	0.098	2.77	0.356	0.126	0.904
45.8	0.03	0.083	2.295	0.297	0.18	0.745
56.8	0.025	0.072	1.9	0.238	0.137	0.584

volume fraction, and S_0 is the gas solubility in the unfilled polymer. Figure 8 presents the nitrogen solubility coefficient in PTMSP/TMSG composites vs the TMSG loading. The prediction of the additive model is shown as comparison. The figure clearly displays the negative departure for nitrogen solubility in comparison with the prediction of this model. The sorption coefficient depends primarily on three factors: (1) the penetrant condensability, (2) the polymer−penetrant interactions, and (3) the free volume in glassy polymer matrix.[30] The penetrant condensability is an intrinsic property of each gas. Moreover, the interaction between the composite matrix and gas molecules is unaffected by the TMSG load in PTMSP, supported by the unchanged solubility selectivity. Therefore, it is reasonable to suppose that a negative departure from the prediction of the additive model in solubility for PTMSP/TMSG composites can be explained in terms of a reduction of free volume. PTMSP has an interconnected free volume ("microvoids"), which offer the high Langmuir solubility capacity for gas molecular in contrast to that of other conventional polymers.[4] The "pore filling" by TMSG leads to greatly reduced Langmuir sorption capacity in nonequilibrium excess free volume in PTMSP.

The solubility capacity of light gases (He, H_2, CO_2, O_2, N_2, CH_4) in the polymer is strongly correlated to the gas condensability (expressed in terms of critical temperature, boiling point, or Lennard-Jones temperature).[2] Teplyakov et al.[24] have also put forward eq 9 for the linear correlation between the gas solubility coefficients and the Lennard-Jones temperature (ϵ/k).

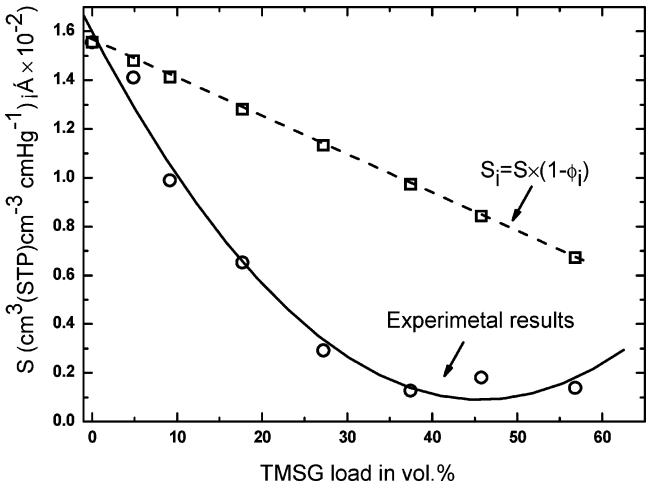

Figure 8. Nitrogen solubility coefficient (○) in PTMSP/TMSG composites as a function of TMSG loading amount at 30 °C as comparison of the additive model (□).

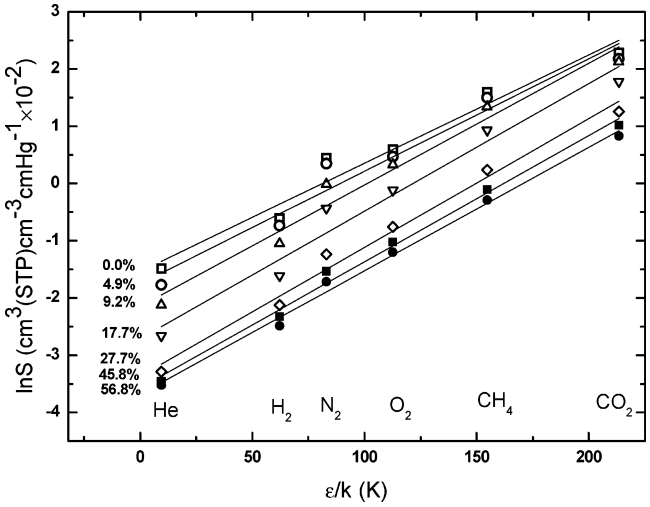

Figure 9. Plots of the natural logarithm of gas solubilities at 30 °C as a function of their effective force constants in a series of PTMSP/TMSG composite membranes [TMSG load in PTMSP: 0.0% (□), 4.9% (○), 9.2% (△), 17.7% (▽), 27.7% (◇), 45.8% (■), 56.8% (●)].

Table 7. Linear Fitting Parameters of k_3, k_4, and Regression R in Plots of the Natural Logarithm of Gas Solubility at 30 °C as a Function of Its Effective Force Constant[24] in a Series of PTMSP/TMSG Composite Membranes

load of TMSG in PTMSP (vol %)	k_3	k_4	R
0	−1.5385	0.018 93	0.9822
4.9	−1.7508	0.019 67	0.9796
9.2	−2.1485	0.021 25	0.9857
17.7	−2.7105	0.022 29	0.9845
27.2	−3.3725	0.022 55	0.9938
37.4	−3.5734	0.022 06	0.9965
45.8	−3.6842	0.021 59	0.9972

$$\ln S = k_3 + k_4(\epsilon/k) \tag{9}$$

where S is the solution coefficient and k_3 and k_4 are fitting parameters which are polymer type dependent. The ϵ/k value used here is directly taken from Teplyakov.[24]

According to eq 9, in Figure 9 the natural logarithm of gas solubility for six gases at 30 °C is plotted as a function of its effective force constant in a series of PTMSP/TMSG composite membranes. From Figure 9 it is clear that the TMSG load reduces the solubility in PTMSP for six gases in a similar way. This behavior suggests that no special interaction is introduced by incorporation of TMSG in PTMSP. In Table 7 the intercept k_3 and the slope k_4 are presented. The slope k_4 is almost an invariable value (0.22), which is well in line with that of more than 50 homopolymers and copolymers fittings by Teplykov.[24] Theoretically, this factor k_4 is independent of the nature of the polymer, which can be derived by the regular solution approach. A systematic increase in the intercept k_3 is observed with the increased loading of TMSG. As a result of the decreased FFV in PTMSP, less volume is provided for gas absorption. The unchanged solubility selectivity proves that all of the increase in permeability selectivity in PTMSP/TMSG composites is based on an increase in gas diffusivity selectivity.

Activation Energies of Permeation. The temperature dependence of permeability coefficients in PTSMP/TMSG composite membranes for the gases He, H_2, CO_2, O_2, N_2, and CH_4 was measured by the pressure-increase apparatus, constructed by GKSS Research Center, Germany. Temperature was varied between 10 and 70 °C, and feed pressure was approximately 1

Table 8. Activation Energy of Permeation E_p and Front Factor P_0 for Six Light Gases in a Series of PTMSP/TMSG Composite Membranes

load of TMSG in PTMSP (vol %)	He		H_2		CO_2		O_2		N_2		CH_4	
	E_p	P_0	E_p	P_0	E_p	P_0	E_p	P_0	E_p	P_0	E_p	P_0
0.0	0.5	4922	−2.1	4227	−11.7	205	−5.5	627	−3.5	819	−5.3	980
6.6	1.5	3532	−1.4	2489	−10.3	112	−4.8	338	−3.1	349	−6.3	229
14.4	5.1	3022	2.5	1869	−8.7	36	0.8	322	4.0	420	0.9	236
17.7	10.4	15311	9.3	16306	1.1	922	8.7	3860	13.4	8330	12.1	9958
21.2	11.8	20263	11.9	30487	6.8	4678	10.8	5664	14.9	9125	15.0	16801
28.5	13.7	29476	13.5	37090	8.7	5708	14.8	14760	17.5	15771	19.0	43412
37.8	17.7	99551	18.7	184759	16.5	76519	22.3	183237	28.7	625308	29.5	1716040

bar. The temperature dependence of gas permeability can be expressed by the Arrhenius equation

$$P(T) = P_0 \exp\left(-\frac{E_P}{RT}\right) \tag{10}$$

where E_P (kJ/mol) is the activation energy of permeation, the preexponential factor P_0 has the same unit as the permeability, R is the gas constant (8.314 J/(mol K)), and T is absolute temperature (K).

The activation energy of permeation E_P and the front factor P_0 derived from the slope of Arrhenius plots are presented in Table 8. With an increased content of TMSG in PTMSP, the activation energy of permeation E_P for each gas increases systemically. The same trend is observed in the front factor P_0 as well, which will be further discussed later. PTMSP exhibits negative activation energy for most penetrants (excluding He) primarily due to the "microporous" structure.[3−5] This microporous structure leads to a considerably smaller activation energy for diffusion (E_D) since the heat of sorption (H_S) is always negative. The sum of activation energy of diffusion (E_D) and the heat of sorption (H_S) is the activation energy of permeation (E_P). Therefore, E_P in PTMSP is negative for most gases. The TMSG loading in PTMSP causes blocking of micropores in PTMSP. Hence, more diffusion jump energy for gas transport is required. For example, when the TMSG content in PTMSP is more than 28.5 vol %, the E_P for each gas is comparable to that of a typical glassy polymer like polycarbonate. On the other hand, the opposite relationship between E_P and gas molecular size is observed in PTMSP and PTMSP/TMSG composites. In PTMSP, the larger gas has a relatively smaller E_P, on the order of E_P (CO_2 < CH_4 < O_2 < N_2 < H_2 < He). In contrast, in PTMSP containing 37.8 vol % TMSG, the small gas requires a lower activation energy to permeate than the large one. The E_P in this composite is in the reverse order compared to that of PTMSP: CO_2 < He < H_2 < O_2 < N_2 < CH_4. The more polar gas CO_2 has always the lowest activation energy of permeation due to its high sorption interaction with polymer matrix.[31]

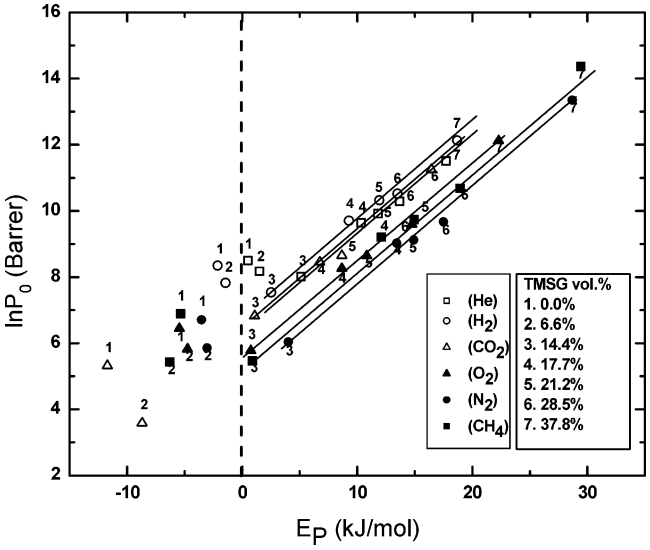

Figure 10. Correlation of activation energy of permeation E_P and the front factor ln P_0 in PTMSP/TMSG composites for six gases [(He (□), H_2 (○), CO_2 (△), O_2 (▲), N_2 (●), CH_4 (■)] at various amount of TMSG in PTMSP. The Arabic numbers represent the load volume content of TMSG in PTMSP [1 (0.0%), 2 (6.6%), 3 (14.4%), 4 (17.7%), 5 (21.2%), 6 (28.5%), 7 (37.8%)].

Table 9. "Compensation Effect" Linear Regression Parameters in PTMSP/TMSG Membranes

	a	b	R
He	6.6785	0.2721	0.9971
H_2	6.9168	0.2792	0.9965
CO_2	6.2930	0.3004	0.9979
O_2	5.5663	0.2892	0.9976
N_2	4.8414	0.2927	0.9968
CH_4	5.2091	0.3062	0.9974

In eq 11, van Krevelen[28] observed that the "compensation effect" could be used to relate the activation energy of permeation to the front factor:

$$\ln P_0 = a + bE_P \tag{11}$$

where a and b are fitting parameters. The validity of this equation has been tested with the data given in Table 8, and the results are illustrated in Figure 10. In the PTMSP composite membranes with relatively high TMSG loadings (TMSG loadings are 14.4, 17.7, 21.2, 28.5, and 37.8 vol %), the E_P and ln P_0 correlation fits well with the "compensation effect". The linear regression parameters are summarized in Table 9. Regarding the values of a and b in Table 9, b seems to vary relatively little for all six gases and is very close to the value 0.2770 observed by van Krevelen. [28] For the parameter a, an interesting observation is that it shows a clear trend with the gas permeability, namely, the gas with high permeability has large a value. In the PTMSP/TMSG composite with considerable TMSG loading, the gas permeability as well as the fitting parameter a follows the same order: CO_2 > H_2> He > O_2 > CH_4 > N_2. This also explained why van Krevelen observed an uncertain value of a in his work (the author thought the fitting parameter a was also gas type independent).

Furthermore, it can be seen from Figure 10 that the points (given by E_P and ln P_0) of pure PTMSP and PTMSP with low TMSG content (6.6 vol %) are apart from the E_P−ln P_0 line determined by the high TMSG loading composite membranes. Since a compensation effect means that the transport mechanism is similar among a series of polymers when eq 11 is obeyed,[32] the results shown in Figure 10 suggest that the gas transport in PTMSP and highly loaded PTMSP/TMSG composite membranes might follow different mechanisms. In PTMSP, the free volume elements appear to be connected and form the equivalent of a finely "microporous" material. In this regard, the gas permeation in PTMSP may fall in a transition region between the pore flow and solution−diffusion mechanisms.[33] When TMSG

is incorporated into the PTMSP host, it might occupy the "fine micropores". The PTMSP/TMSG composite membranes could be treated as a conventional glassy polymer, where the transport mechanism should be based on the solution−diffusion model.

Conclusions

We describe the blending of the high free-volume polymer poly(1-trimethylsilyl-1-propyne) (PTMSP) with the small organic filler trimethylsilylglucose (TMSG). Gas permeability coefficients for helium, hydrogen, carbon dioxide, oxygen, nitrogen, and methane decreased drastically with the incorporation of TMSG. Simultaneously, the permselectivity increased. The permeability and selectivity change could be well correlated with the gas molecular size. The largest gas methane experienced the highest loss in permeability. Theoretically, the diffusion and solubility coefficients can be correlated to the penetrants effective diameter and their force constant, respectively. It could be shown that the gas transport behavior in the PTMSP/TMSG composites is predominantly governed by the decrease of the diffusion coefficients. From the gas transport properties in the PTMSP/TMSG composites we conclude that the filler TMSG can enter the large free volume elements (FVE) in PTMSP and blocks effectively the transport through the microvoids, improving the size selectivity. In addition, we found an increase in the activation energy of permeation E_P with increasing TMSG content. This supports further the "pore-filling" assumption. The controlled addition of TMSG to PTMSP is a simple way of tailoring the permeability/selectivity behavior of high free volume polyacetylenes.

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