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Pure gas and vapor permeation properties of poly[1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene] (PTMSDPA) and its desilylated analog, poly[diphenylacetylene] (PDPA)

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Abstract

The permeabilities of He, H_2, N_2, O_2, CO_2, CH_4, C_2H_6, C_3H_8, and n-C_4H_{10} in poly[1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene] (PTMSDPA) and poly[diphenylacetylene] (PDPA) are presented and compared to those of poly(1-trimethylsilyl-1-propyne) (PTMSP), poly(1-phenyl-1-propyne) (PPP), and polysulfone. Like PTMSP, PTMSDPA, a disubstituted glassy acetylene-based polymer, exhibits higher permeabilities to organic vapors than to permanent gases due to its rigid polyacetylene backbone and bulky side groups, which provide a relatively high fractional free volume (FFV) value of 0.26. Desilylation was performed on PTMSDPA. The resulting material, PDPA, is totally insoluble in common organic solvents, so it has much higher chemical resistance than PTMSDPA. Additionally, due to its insolubility in polymerization solvents, desilylation provides the only known route to high molar mass PDPA. The FFV of the resulting membrane (PDPA) is reduced by approximately 12% relative to that of PTMSDPA. This leads to a decrease in gas permeability values and selectivity of organic vapors relative to nitrogen. For example, the oxygen permeability is reduced from 1200 to 500 Barrers upon desilylation. The pure gas selectivities decrease from 9 to 3 for n-C_4H_{10}/N_2 and from 26 to 9 for C_3H_8/N_2.

Keywords: Poly[1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene]; Poly[diphenylacetylene]; Permeability

1. Introduction

Glassy, disubstituted acetylene-based polymers are known for their unique gas transport properties [1–4]. They exhibit extremely high gas permeabilities and high vapor/gas selectivities, which is quite unusual for conventional glassy polymers such as polysulfone. The rigid double bond in the polyacetylene backbone, coupled with their bulky side groups, hinders chain segmental motion and restrains polymer chains from packing efficiently, creating large and possibly interconnected free volume elements in the polymer matrix that provide very efficient permeation pathway for penetrants. In addition, this very open structure attenuates the polymer's ability to discriminate between large and small penetrant molecules (i.e. it contributes to weak size-sieving ability). Thus, unlike conventional glassy polymers, these ultrahigh free volume polymers sieve penetrant molecules based strongly on their solubility coefficients and therefore, are more permeable to larger, more soluble, organic vapors than to smaller, less soluble, permanent gases.

Poly(1-trimethylsilyl-1-propyne) (PTMSP) is the first substituted acetylene-based polymer discovered to have these unique characteristics. PTMSP has extremely high fractional free volume (0.29) and the highest gas permeabilities of all known polymers [1,5]. For example, its oxygen permeability is 9000 Barrers [5]. The mixed-gas selectivities of organic vapors over permanent gases are as high as 27 for n-C_4H_{10}/CH_4 and 39 for n-C_4H_{10}/H_2 [6]. Such high vapor/gas selectivities might find application in organic vapor separation processes. For example, in the natural gas processing industry, higher hydrocarbon (C_{3+})

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removal from natural gas (CH_4) is necessary to decrease the dewpoint and heating value of natural gas to pipeline specification and to recover valuable higher hydrocarbons [7]. Another potential application is the removal of higher hydrocarbons from hydrogen in off-gas streams (e.g. from fluidized catalytic crackers) produced in refineries [8]. In both cases, PTMSP is more permeable to the more condensable higher hydrocarbons and maintains the methane or hydrogen product at high pressure. This characteristic eliminates high recompression costs of the methane and hydrogen streams, thereby potentially making membrane-based separation more competitive with conventional separation methods (e.g. condensation). However, PTMSP has not been reduced to commercial practice for such applications. One major issue is PTMSP's lack of chemical resistance. PTMSP is very soluble in many organic solvents [9], such as toluene and hexane, which might be present in process streams of interest. Another issue is physical aging, wherein the gas permeability of PTMSP decreases over time due to volumetric relaxation of the non-equilibrium, glassy state [10]. These challenges have motivated research to explore the gas transport properties of other disubstituted acetylene polymers in an attempt to identify materials with improved physical aging and chemical resistance characteristics.

Poly[1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene], PTMSDPA, is also a highly permeable, vapor selective, disubstituted acetylene-based polymer [4]. Like PTMSP, this glassy polymer is more permeable to larger, more condensable hydrocarbons than to smaller, less condensable, permanent gases. With a fractional free volume of 0.26, PTMSDPA exhibits permeabilities of 560 Barrers for N_2, 1200 Barrers for O_2, and 20,000 Barrers for n-C_4H_{10}, as reported earlier by Toy et al. [4]. The selectivities of hydrocarbons over nitrogen are 2.9 for CH_4/N_2, 4.8 for C_2H_6/N_2, 7.9 for C_3H_8/N_2, and 36 for n-C_4H_{10}/N_2 [4]. Unfortunately, PTMSDPA exhibits poor chemical resistance. PTMSDPA, like PTMSP, is soluble in common organic solvents. Recently, Teraguchi et al. presented a straightforward method to remove trimethylsilyl [TMS] groups from PTMSDPA (desilylation) by reacting the polymer with trifluoroacetic acid as shown in Fig. 1 [11, 12]. The resulting poly(diphenylacetylene) [PDPA] membrane is thermally very stable (no weight loss is observed up to about 500 °C in TGA) and completely insoluble in any organic solvent [11].

It is of great interest to study the gas permeation and separation properties of this chemically stable substituted acetylene polymer. Since PDPA is insoluble in solvents commonly used for synthesis of such polymers [9], desilylation of soluble precursors, such as PTMSDPA, is the only known synthetic route to such interesting membrane materials based on symmetrically substituted acetylene polymers. The effect of desilylation of PTMSDPA on its pure gas and vapor permeation properties is discussed in this paper. The permeabilities of various light gases and hydrocarbons in PTMSDPA and PDPA at 35 °C are presented and compared to those of PTMSP, PPP, and polysulfone.

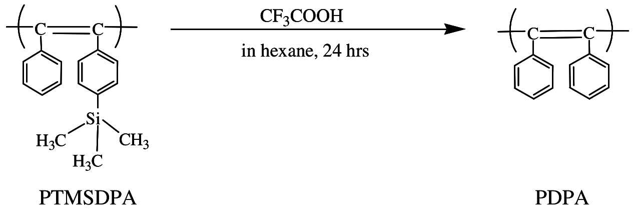


Fig. 1. Desilylation reaction.

2. Background

The steady state gas permeability coefficient of a polymer membrane is defined as follows: [13]

$$P = \frac{Nl}{p_2 - p_1} \tag{1}$$

where P is the gas permeability coefficient [cm^3(STP) cm/(cm^2 s cm Hg)], N is the steady state penetrant flux through the membrane [cm^3(STP)/cm^2 s], l is the membrane thickness (cm), p_2 is the upstream pressure (cm Hg), and p_1 is the downstream pressure (cm Hg).

When Fick's law is obeyed and the downstream pressure is much less than the upstream pressure, the permeability coefficient defined in Eq. (1) can be expressed as [13]

$$P = D \cdot S \tag{2}$$

where D is the average effective diffusion coefficient (cm^2/s), and S is the solubility coefficient [cm^3(STP)/(cm^3 cm Hg)].

The selectivity of a polymer for penetrant A relative to penetrant B is defined as the ratio of the permeability coefficients of the two penetrants: [13]

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{3}$$

Combining Eqs. (2) and (3) then gives [13]

$$\alpha_{A/B} = \left(\frac{S_A}{S_B}\right) \times \left(\frac{D_A}{D_B}\right) \tag{4}$$

where S_A/S_B is the ratio of solubility coefficients of penetrants A and B, which is called the solubility selectivity. D_A/D_B is the ratio of the average diffusion coefficient of penetrant A and B, and it is referred to as the diffusivity selectivity. Diffusion coefficients increase as penetrant molecular size decreases. Therefore, the diffusivity selectivity for organic vapors over permanent gases is always less than unity, since the diffusion coefficient of the larger organic vapor is always less than that of smaller permanent gases. The solubility coefficient is a function of penetrant condensability and polymer-penetrant interactions [13].

Solubility coefficients of more condensable organic vapors (e.g. n-C_4H_{10}) are always greater than those of less condensable permanent gases (e.g. H_2 or N_2), so solubility selectivity for organic vapor/permanent gas separations is always greater than unity. The design of vapor-selective polymers often involves structural modifications to alter solubility and diffusivity selectivity in ways that will increase permeability and selectivity [14].

3. Experimental section

3.1. Materials

Poly(1-phenyl-2-[*p*-(trimethyl-silyl)phenyl]acetylene) was synthesized as indicated previously [4]. Films of PTMSDPA were prepared from a 1 wt% solution of the polymer in toluene. The solution was filtered through filter paper using a syringe and then cast into a petri dish. After drying at ambient conditions for 3–5 days, the samples were stored in liquid methanol until the day before use to prevent physical aging. Prior to permeation experiments, samples were removed from methanol and dried at ambient conditions for approximately 15 h. The film thickness of these samples was approximately 73 μm.

Poly(diphenylacetylene) (PDPA) membranes were prepared from PTMSDPA samples following the desilylation procedure described earlier [11]. A PTMSDPA film (0.118 g) was placed in a 50 ml mixture of trifluoroacetic acid and *n*-hexane (50/50 by volume) at ambient conditions for approximately 24 h. Trifluoroacetic acid cleaves the trimethylsilyl groups from PTMSDPA (Fig. 1), while *n*-hexane serves as a diluent. The sample was then washed with *n*-hexane and immersed in a mixture of triethylamine and *n*-hexane (50/50 by volume) for 24 h to neutralize any remaining trifluoroacetic acid. The films were rinsed with *n*-hexane and stored in methanol for at least 24 h before being used.

FT-IR ATR spectra of the samples before and after desilylation were acquired using a Nexus 470 FT-IR spectrometer from Thermo Nicolet (Madison, WI). After desilylation, the spectrum showed essentially no absorption at 1250 ($\delta_{\mathrm{sSiC–H}}$), 1119, 855 ($\upsilon_{\mathrm{asSi–CH3}}$), and 812 ($\upsilon_{\mathrm{sSi–CH3}}$) cm^{-1}, indicating that the desilylation was complete [11] (Fig. 2).

Due to a significant decrease in the film diameter after desilylation, PDPA films prepared from PTMSDPA films that were previously used in permeation experiments could not be used for another permeability measurement. Therefore, larger PTMSDPA films were prepared for desilylation. Several samples were prepared exclusively to investigate the effect of desilylation on sample dimensions. The result of the study is shown in Table 1. As expected, the loss in sample mass after the desilylation corresponds to the chemical change implied by Fig. 1. The final thickness of PDPA films for permeability measurements was approximately 62 μm.

Table 1
Change in sample dimensions and density due to desilylation

	Before desilylation (PTMSDPA)	After desilylation (PDPA)
Thickness (μm)	120 ± 7	90 ± 6
Weight (g)	0.0761 ± 0.0001	0.0556 ± 0.0003
Diameter (cm)	3.07	2.78
Density (g/cm^3)	0.89	0.98

Polymer density was measured using a density determination kit for an AG204 balance from Mettler Toledo. The density of each film sample was obtained by measuring the weight of the film in distilled water and in air at 20 °C.

3.2. Permeation measurement

The permeability of PTMSDPA and PDPA films to various permanent gases and hydrocarbons at 35 °C was determined using the constant-pressure/variable volume method [15]. The permeate gas flow rate was measured with a soap film flowmeter. The gases were studied in the following order: N_2, H_2, He, O_2, CH_4, CO_2, C_2H_6, C_3H_8, and n-C_4H_{10}. Nitrogen permeability was measured after each of the gas permeation measurements to check for hysteresis or aging effects. The upstream pressure was set at 4.46 bar for the permanent gases (N_2, H_2, He, and O_2) as well as for methane, ethane and propane, and it was set to 1.56 bar for *n*-butane. The downstream pressure was atmospheric. To minimize any impact of physical aging on the permeation results, a complete cycle of permeation measurements for all gases was completed in a continuous 8 h period for each sample.

The gas permeability coefficient [$\mathrm{cm^3(STP)\ cm/(cm^2\ s\ cm\ Hg)}$] was calculated using the following expression:

$$P = \frac{l}{\Delta p}\frac{273}{TA}\frac{p_{\mathrm{atm}}}{76}\left(\frac{\mathrm{d}V}{\mathrm{d}t}\right) \tag{5}$$

where Δp is the difference between the upstream and downstream pressures (cm Hg), p_{atm} is the atmospheric pressure (cm Hg), A is the membrane area (cm^2), T is temperature (K), l is the membrane thickness (cm), and $\mathrm{d}V/\mathrm{d}t$ is the volumetric displacement rate of the soap film in the bubble flowmeter at steady state (cm^3/s).

4. Results and discussion

4.1. Density and fractional free volume of PTMSDPA and PDPA

Table 2 shows the chemical structure, density, and fractional free volume (FFV) of PTMSDPA, PDPA, and two

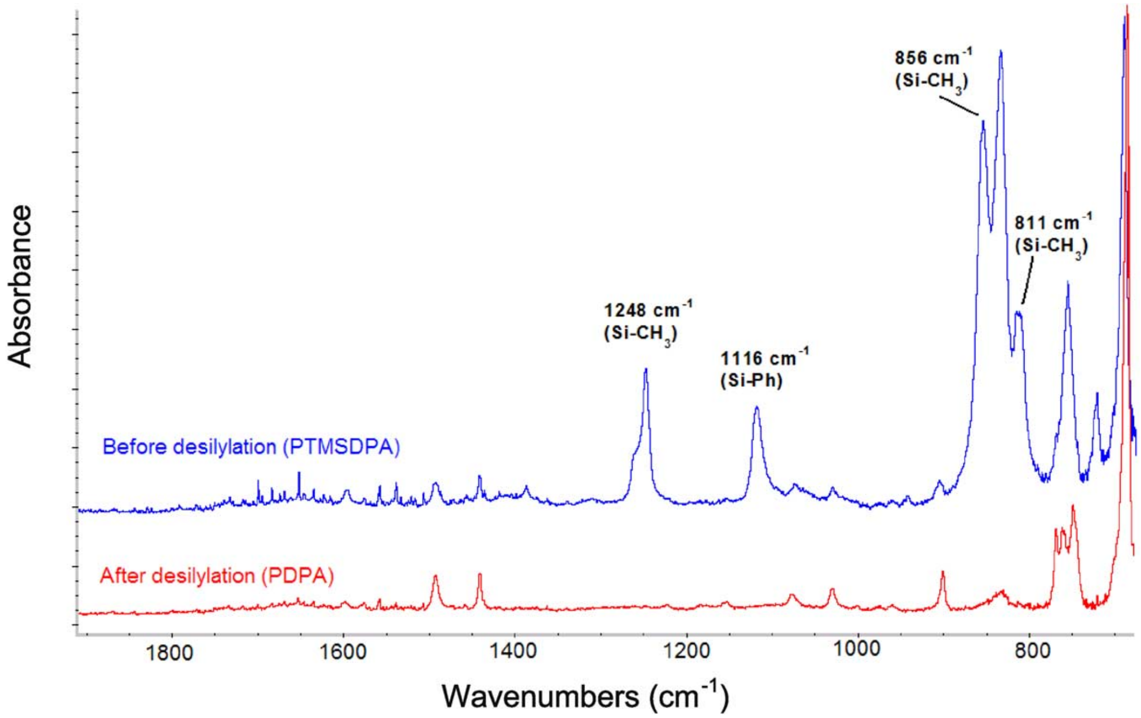


Fig. 2. FT–IR spectrum of PTMSDPA and PDPA.

other structurally-related glassy substituted acetylene polymers, PTMSP and PPP. The stiff nature of the polyacetylene backbone and the bulkiness of the large substituents contribute to inefficient chain packing in these polymers which, in turn, manifests itself in low polymer density values and rather high free volume values. Fractional free volume (FFV) [cm^3 of free volume/cm^3 of polymer] is commonly used to characterize the efficiency of chain packing and the amount of free space available for gas permeation in a polymer matrix: [16–18]

$$\mathrm{FFV} = \frac{v_{\mathrm{sp}} - v_0}{v_{\mathrm{sp}}} \approx \frac{v_{\mathrm{sp}} - 1.3v_{\mathrm{W}}}{v_{\mathrm{sp}}} \qquad (6)$$

where v_{sp} is the polymer specific volume, and v_0 is the occupied volume of the polymer. The occupied volume is typically estimated as 1.3 times the van der Waals volume (v_{W}), which is calculated using group contribution methods [16–19].

PTMSP has the highest FFV value (~0.29) among the four substituted acetylene polymers in Table 2. PPP has the lowest values of 0.22. PTMSDPA has an FFV value of 0.26, which is in excellent agreement with the value previously reported by Toy et al. [4]. PDPA, has a lower FFV value (~0.23) than PTMSDPA. This value is close to the fractional free volume of PPP and near the upper end of the FFV range for conventional glassy polymers.

4.2. Gas permeation properties of PTMSDPA and PDPA

Gas permeability coefficients in PTMSDPA are presented as a function of penetrant critical temperature in Fig. 3. The hydrocarbon permeability in PTMSDPA increases as penetrant critical temperature (i.e. condensability) increases. Due to its high FFV value and its limited segmental mobility, this polymer exhibits a very weak size-sieving ability, so that the diffusion coefficients of larger

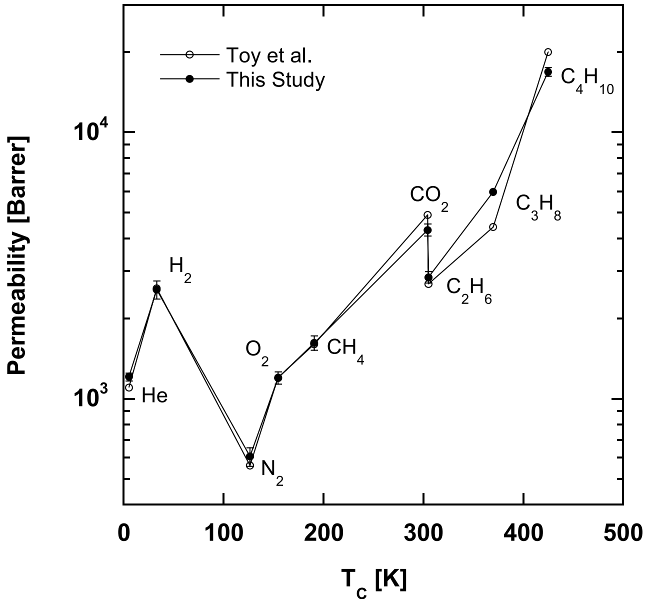
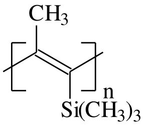
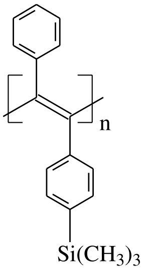
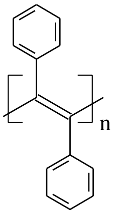
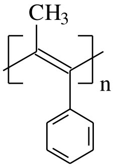


Fig. 3. Gas permeabilities in PTMSDPA at 35 °C as a function of penetrant critical temperature [28]. These permeability values are averages from independent measurements of two separate samples. The error bars represent the standard deviation of permeability in the two samples. For a comparison, data previously reported by Toy et al. [4] are also included.

Table 2
Physical properties of selected disubstituted polyacetylenes

Polymer	Chemical structure	Density (g/cm^3)	Fractional free volume (FFV)[a]
PTMSP		0.75[b]	0.29
PTMSDPA		0.89	0.26
PDPA		0.98	0.23
PPP		1.00[c]	0.22[d]

[a] Calculated using Eq. (6), where occupied volume, $\upsilon_0 \approx 1.3\upsilon_w$,was estimated from the Bondi group contribution method [18].
[b] Ref. [25].
[c] Refs. [26,27]
[d] Ref. [26].

penetrants are similar to those of smaller ones. Solubility, on the other hand, increases with increasing penetrant condensability and, in many cases, size. Thus, unlike conventional glassy polymers (e.g. polysulfone), PTMSDPA is more permeable to larger, more condensable vapor molecules than to smaller permanent gases. These results agree well with those reported by Toy et al. [4].

The selectivity of gases over nitrogen in PTMSDPA is presented in Fig. 4 as a function of penetrant critical temperature. The hydrocarbon/nitrogen selectivity increases with increasing critical temperature and penetrant size. PTMSDPA has selectivities of 2.6 for CH_4/N_2, 4.6 for C_2H_6/N_2, 9.2 for C_3H_8/N_2, and 26 for n-C_4H_{10}/N_2. In a weak size-sieving polymer, such as PTMSDPA, the diffusion coefficient is not a strong function of penetrant molecular size. The overall hydrocarbon/nitrogen selectivity in PTMSDPA is, therefore, controlled more by its solubility selectivity than by its diffusivity selectivity, and, consequently hydrocarbon/nitrogen selectivity increases with increasing hydrocarbon size.

To insure that the sample does not undergo physical changes such as aging or plasticization after exposure to a certain gas, nitrogen permeability was monitored after each gas permeability measurement. Fig. 5 shows no measurable change in nitrogen permeability in two PTMSDPA samples during the permeation experiment, indicating that the films did not experience any aging or hysteresis effects during the course of the permeability measurements.

Fig. 6 presents gas permeability coefficients in desilylated PTMSDPA (i.e. PDPA) as a function of penetrant critical temperature. Like PTMSDPA, PDPA is more permeable to larger, more condensable hydrocarbons than to smaller, permanent gases. However, the 12% decrease in FFV as a result of desilylation has significantly reduced the gas permeabilities in PDPA relative to PTMSDPA. The permeabilities of the C_{2+} hydrocarbons are similar to or higher than that of H_2 in PTMSDPA, but they are similar to or lower than that of H_2 in PDPA. Therefore, the size-sieving nature of PDPA appears to be stronger than that of PTMSDPA, which would also be a natural consequence of a decrease in FFV. The permanent gas permeabilities (He, H_2, N_2, and O_2) are reduced to 50–75% of their values before desilylation. The hydrocarbon vapor permeabilities decrease even more than the permanent gas permeabilities. The largest reduction is experienced by C_3H_8 and n-C_4H_{10}; their permeabilities are almost 10 times lower in the

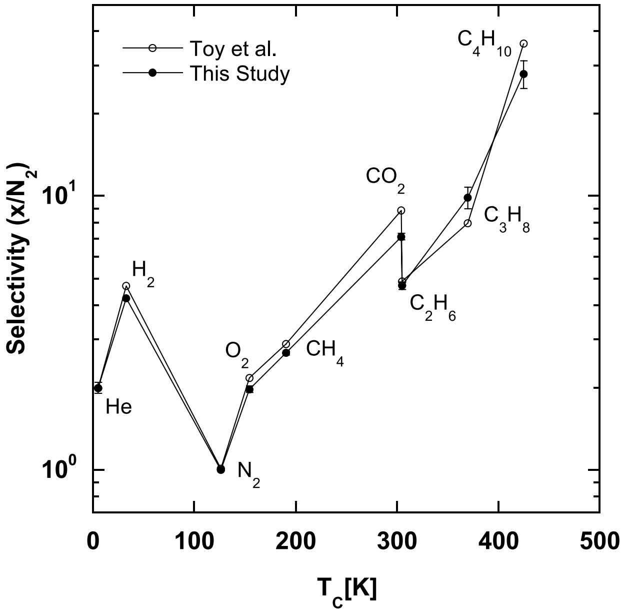


Fig. 4. Selectivity of various gases over nitrogen in PTMSDPA as a function of penetrant critical temperature [28]. These values were calculated from the average permeability of two independent samples. The error bars represent the standard deviation of each averaged value. These results are in good agreement with data previously reported by Toy et al. [4].

desilylated sample than in PTMSDPA. The present permeability values in PDPA are relatively close to those recently reported by Sakaguchi et al. [12], while they are considerably lower than those published earlier by Teraguchi and Masuda [11]. The earlier values are irreproducible and suggest that there might be some issue with the permeability measurement, such as pinhole defects in the desilylated sample, which could lead to higher permeability values and lower selectivities.

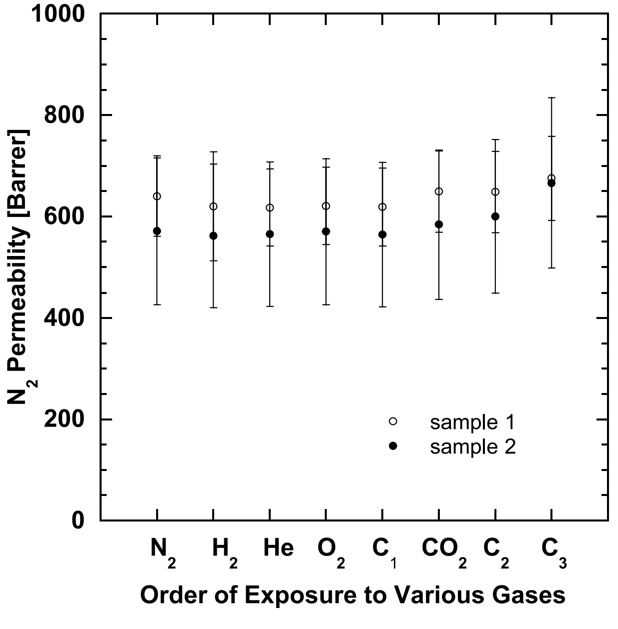


Fig. 5. N_2 permeability in two samples of PTMSDPA after each gas permeation experiment. The error bars were estimated using the propagation of errors method [29]. The uncertainties in measured film thickness and measured permeate flux contributes to the error in gas permeability. C_1=CH_4; C_2=C_2H_6; C_3=C_3H_8.

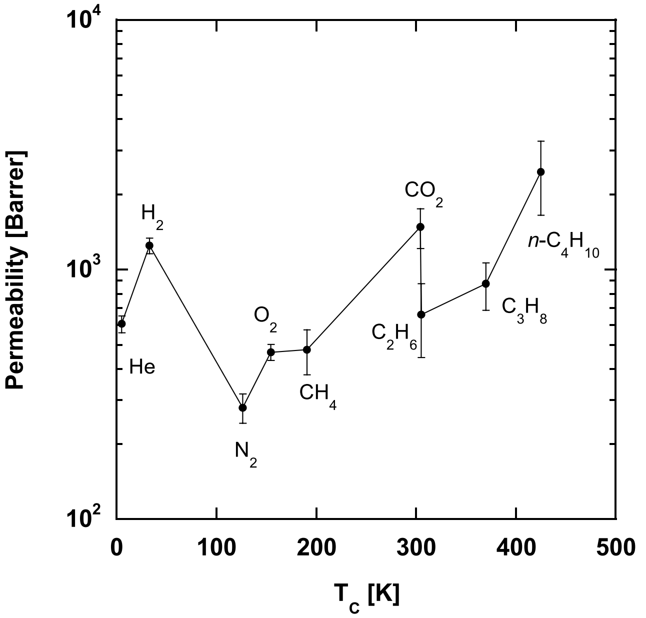


Fig. 6. Gas permeability coefficients in PDPA as a function of penetrant critical temperature [28]. These permeability values are an average from independent measurements of three separate samples. The error bars represent the standard deviation of the permeability coefficient in the three samples.

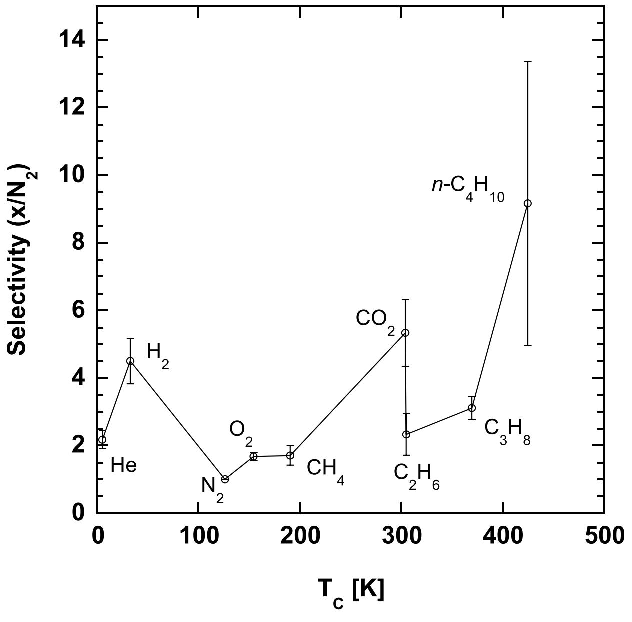


Fig. 7. Selectivity of various gases over nitrogen in PDPA presented as a function of penetrant critical temperature [28]. These values were calculated from the average permeability of three independent samples. The error bars represent the standard deviation in each average value.

The selectivity of gases over nitrogen in PDPA is presented in Fig. 7. Compared to PTMSDPA, the hydrocarbon/nitrogen selectivities in PDPA are 2–3 times lower. For example, PDPA has selectivities of 1.6 for CH_4/N_2, 2.0 for C_2H_6/N_2, 3.0 for C_3H_8/N_2, and 9.4 for n-C_4H_{10}/N_2. The decrease in hydrocarbon/nitrogen selectivity is attributed to the decrease in FFV upon desilylation. More in-depth discussion regarding this issue is presented later in this section.

As shown in Fig. 8, the nitrogen permeability in PDPA was constant, within the experimental uncertainty, during the gas permeation experiments up to and including C_3H_8. However, after exposing the film to *n*-butane, the nitrogen permeability decreased to almost half of its original value. This behavior can be related to penetrant-induced hysteresis, which has been observed in various glassy polymers [20–23]. The presence of high activity penetrant in the polymer could swell the polymer matrix [22–24]. Upon depressurization, the polymer often retains significant amounts of excess free volume that resulted from swelling, which increases gas permeability [9,23]. This trend, however, is not always the case. When the rate of volume relaxation of the polymer is greater than the rate of penetrant removal, the polymer chains can attain a more stable equilibrium state than that of the original polymer, which results in a FFV lower than that of the original sample [20]. This phenomenon was observed by Pope et al. [20] during a CO_2-induced dilation study in another disubstituted acetylene polymer, PTMSP. The data showed a decrease in the volume of the original sample after exposure to CO_2. Pope et al. attributed this behavior to the relatively fast volume relaxation of PTMSP upon depressurization. A similar explanation can rationalize the decrease in N_2 permeability in PDPA after exposing the film to *n*-butane. As *n*-butane molecules desorb from the polymer matrix following an *n*-butane permeability experiment, the polymer chains may rearrange themselves more efficiently, resulting in a partial collapse of free volume elements in the matrix (i.e. FFV lower than that of the original sample) which, consequently, decreases gas permeability.

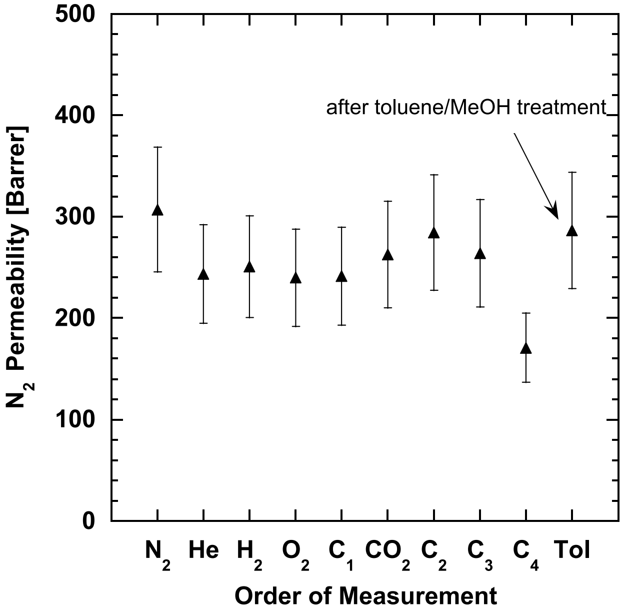


Fig. 8. N_2 permeability in PDPA after each gas permeability measurement. The error bars were determined using the propagation of errors method [29]. C_4=n-C_4H_{10}, Tol, toluene. For toluene exposure, no permeation experiments were performed; the film was only soaked in liquid toluene for 24 h and then in liquid methanol for 24 h at ambient conditions.

Various treatments were explored to return the nitrogen permeability to the original value obtained when the sample was freshly cast. Soaking a sample in *n*-hexane, the solvent for the desilylation process, and methanol (for 24 h at ambient temperature) did not significantly effect the permeability; nitrogen permeability was unchanged at 130 Barrers. This observation is interesting because methanol soaking is often used to restore gas permeability values in PTMSP films that have undergone physical aging [9]. The sample was later soaked in toluene for 24 h and then placed in methanol for another 24 h. The methanol immersion served two purposes: (1) to limit the effect of physical aging of the polymer to a minimum because methanol desorbs faster than toluene (i.e. shorter drying time), and (2) to be consistent with other permeability measurement where the films were soaked in methanol for 24 h and dried at ambient temperature for 15 h before every measurement. The toluene/methanol treatment resulted in nitrogen permeability returning to its original value of approximately 290 Barrer (Fig. 9). A slight increase in nitrogen permeability, relative to that of a fresh sample, was observed when the sample was treated for a second time with toluene and then methanol.

The permeability reduction due to desilylation differs from one gas to another. This phenomenon illustrated in

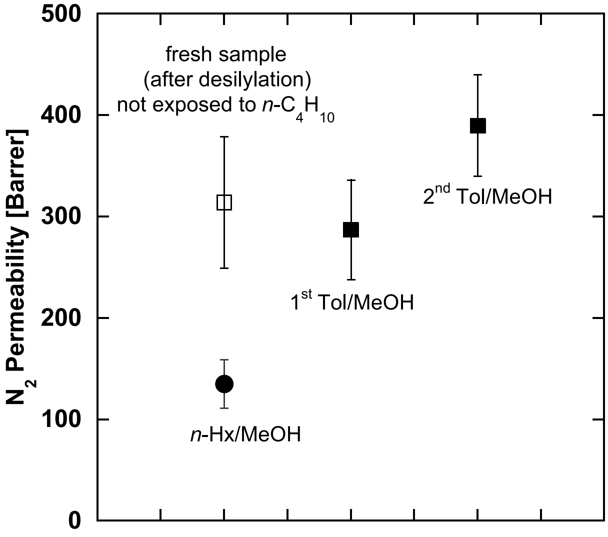


Fig. 9. N_2 permeability in PDPA films before (☐) and after (filled symbols) exposure to *n*-butane and then exposure to organic liquids. *n*-Hx/MeOH: after exposure to n-C_4H_{10}, the sample was immersed in *n*-hexane for 24 h and placed in methanol afterwards for another 24 h. Tol/MeOH: after exposure to n-C_4H_{10}, the sample was first soaked in toluene for 24 h and then placed in methanol for another 24 h.

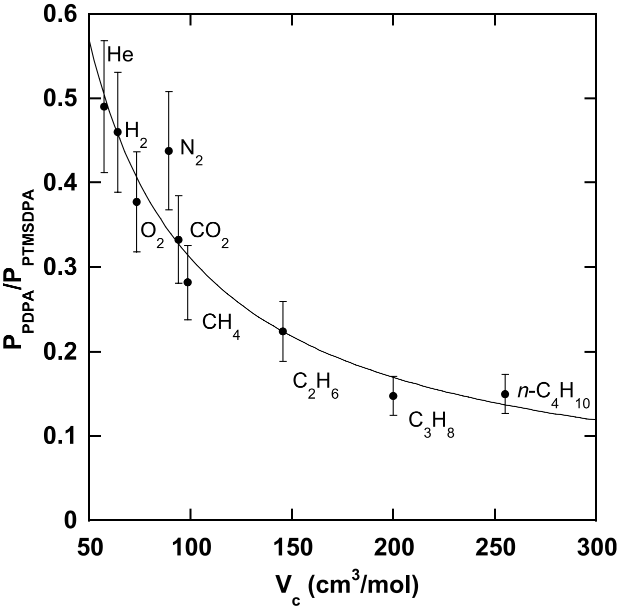


Fig. 10. Ratio of gas permeability in PDPA to gas permeability in PTMSDPA as a function of penetrant critical volume [28]. These values were calculated from the average permeability values of several samples. The error bars were determined using the propagation of errors method [29].

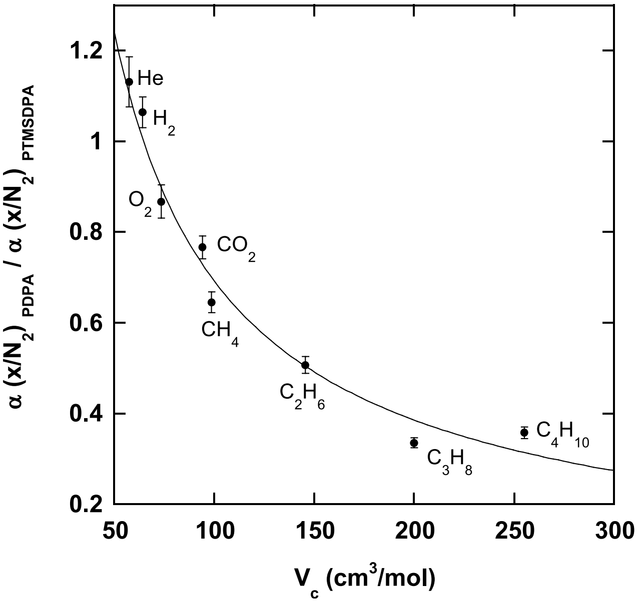


Fig. 11. Ratio of gas/N_2 selectivity in PDPA to that in PTMSDPA as a function of penetrant critical volume [28]. These values were calculated from the average permeability values of several samples. The error bars were determined using the propagation of errors method [29].

Fig. 10, where the permeability ratio of PDPA to PTMSDPA is presented as a function of penetrant critical volume. This figure shows a strong decrease in the permeability ratio as the penetrant size increases. In other words, the permeability coefficients of larger penetrants decrease more than those of smaller ones due to desilylation. For example, the C_2–C_4 alkane permeability values are reduced by almost 90%, relative to their values before desilylation, while the smaller, permanent gases experience only a 50–75% decrease in permeability.

Similar trends are observed when the ratio of gas/N_2 selectivity in PDPA to that in PTMSDPA is presented as a function of penetrant critical volume, as shown in Fig. 11. The selectivity over N_2 for light gases (i.e. He and H_2) increases after desilylation. For penetrant molecules larger than N_2, selectivities decrease after desilylation. Large hydrocarbon molecules, such as C_3H_8 and n-C_4H_{10}, experience a decrease in their selectivities over nitrogen by almost a factor of 3 after desilylation.

The loss in gas permeability and selectivity after desilylation is most likely caused by the decrease in FFV as a result of the desilylation process. The FFV value of PTMSDPA decreases about 12%, from 0.26 to approximately 0.23, after desilylation (PDPA). The reduction in gas permeability after desilylation is probably caused by a decrease in the diffusion coefficient, which is typically a much stronger function of FFV than solubility [13]. Decreasing FFV usually causes a polymer to become more size selective, or in other words, it increases the sensitivity of diffusion coefficient to penetrant size. Diffusion coefficients of larger penetrants decrease more than those of smaller penetrants, so the gas permeability ratio shown in Fig. 10 decreases as penetrant critical volume increases.

Fig. 12 presents gas permeabilities in PDPA compared to permeabilities in various substituted polyacetylenes (PTMSP, PTMSDPA, and PPP), and in a conventional

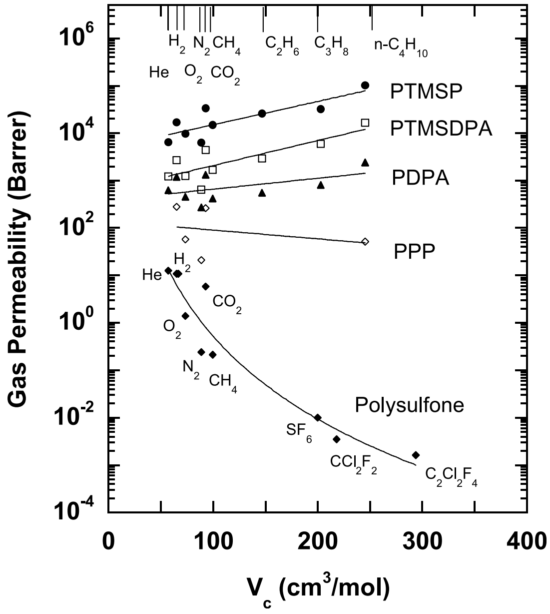


Fig. 12. Comparison of gas permeabilities in PTMSDPA and PDPA to permeabilities reported in PTMSP [5], PPP [27], and low free volume, glassy polysulfone as a function of penetrant critical volume [28]. T= 35 °C, except for PPP and polysulfone (25 °C). The gas permeabilities in PTMSDPA and PDPA shown in the plot are averages from several samples.

glassy gas separation polymer, polysulfone. Among the polyacetylenes, PTMSP, which has the highest FFV value (0.29), has the highest gas permeabilities. It is followed by PTMSDPA, PDPA, and PPP, which is in the order of decreasing FFV value. PTMSP, PTMSDPA, and PDPA, with their high FFV values, are all more permeable to larger, more condensable hydrocarbons than to light gases such as N_2. As the FFV decreases due to desilylation, the polymer becomes more and more size selective, and the permeability increase with increasing hydrocarbon penetrant size is attenuated.

5. Conclusions

Unlike conventional glassy polymers, poly[1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene] (PTMSDPA) is vapor-selective and sieves penetrant molecules based, to a significant extent, on their solubility. Desilylation improves the polymer chemical resistance by rendering it completely insoluble in organic solvents. The gas permeability decrease observed after desilylation is attributed mainly to the 12% reduction in FFV following desilylation. This FFV loss increases the size-sieving ability of the polymer, thus decreasing the permeability of larger penetrants more than that of smaller penetrants. As a result, the organic vapor (i.e. C_3H_8, n-C_4H_{10}) selectivities over nitrogen in PDPA are lower than those in PTMSDPA.

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