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# Investigation of Enhanced Free Volume in Nanosilica-Filled Poly(1-trimethylsilyl-1-propyne) by $^{129}$Xe NMR Spectroscopy

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ABSTRACT: The gas permeability of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) containing nanoparticulate fumed silica increases with increasing filler content. This unusual phenomenon is explored using $^{129}$Xe NMR spectroscopy to examine the effect of filler on the free volume of the PTMSP host matrix. The $^{129}$Xe NMR chemical shift decreases regularly with increasing fumed silica concentration, consistent with an increase in the average size of free volume elements or cavities through which molecular transport can occur. A relationship between the chemical shift and gas permeability in the filled polymer is reported.

## Introduction

$^{129}$Xe NMR spectroscopy has been widely used as a tool for investigating the structure of microporous materials including zeolites,[1] silicas,[2] and carbon nanotubes.[3] This technique has also been applied successfully to the study of microstructure in amorphous and semicrystalline polymer systems.[4] Numerous researchers have utilized $^{129}$Xe NMR to examine heterogeneity in polymer matrices due to crystallinity,[5] physical blending,[6] or phases in block copolymers.[7,8] Because of its high polarizability, the xenon atom is particularly sensitive to the density of its microenvironment. This attribute, combined with its small molecular size (4.4 Å atomic diameter), spherical symmetry, and chemical inertness, makes xenon an ideal probe of microstructure. In general, the chemical shift of $^{129}$Xe gas sorbed in a solid is proportional to its collision rate within the free volume environment in the material.[9,10] Referenced to a chemical shift of 0 ppm for gaseous xenon extrapolated to zero pressure, dissolved or adsorbed xenon exhibits a downfield shift, typically on the order of 190−220 ppm for common polymers.[11] Qualitatively larger local free volume or cavity size results in smaller shifts relative to the free-gas resonance line and vice versa.[4,12]

Several reports highlight the ability of $^{129}$Xe NMR to probe changes or differences in polymer free volume. For example, the sensitivity of xenon probe molecules to fractional free volume in a polymer has been demonstrated by the discontinuity in plots of chemical shift vs temperature in the vicinity of the glass transition temperature.[9,12] Kennedy[13] has shown changes in the $^{129}$Xe spectrum before and after cross-linking in EPDM rubber, while Morgan et al.[14] have reported changes that occur during the cross-linking process itself for polyurethane elastomer systems. In both instances, the spectrum changes were consistent with the free volume decrease (polymer densification) expected upon cross-linking. Recently, Suzuki et al.[6] have described the effect of polymer blending on the mean size of polymer free volume elements as calculated from the $^{129}$Xe chemical shift, while Wang and co-workers[15] have found that, compared to conventional glassy polymers, high-free-volume glasses exhibit significantly smaller $^{129}$Xe NMR chemical shifts.

Gas transport in polymers is known to be strongly dependent on the amount of free volume in the polymer matrix.[16,17] Relative to the densified domains occupied by polymer chains, free volume regions in a polymer provide efficient, low-resistance pathways for the permeation of gas molecules. Numerous studies have demonstrated a good correlation between gas permeability and polymer free volume as determined by group contribution methods or probe techniques such as positron annihilation lifetime spectroscopy (PALS).[16,17] To date, however, correlations of $^{129}$Xe NMR data with gas permeability of polymer membranes have not been reported in the literature. The ability of $^{129}$Xe NMR to probe local polymer microstructure and the success of free volume theories describing gas transport in polymers provide a compelling reason to seek such relationships.

In conventional filled polymer systems, the presence of nonporous particles typically reduces the permeability of a polymer by reducing the volume of polymer available for transport and increasing the tortuosity of the diffusion path available to gas molecules.[18,19] However, it was recently discovered that the addition of nanometer-sized fumed silica particles to certain high-free-volume, glassy polymers can systematically increase gas permeability.[20−22] This highly unusual and counterintuitive result suggests that the volume filling and tortuosity effects are offset by the ability of these tiny particles to disrupt packing of rigid polymer chains, thereby subtly increasing the amount of free volume in

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the polymer.[21,22] The free volume manipulation engineered by the fumed silica nanoparticles is sufficiently fine in nature (average increase in free volume element radius is <1 Å) such that useful transport property modifications result.[21,22] For example, in addition to increasing gas permeability, incorporation of silica into these polymers can also increase organic-vapor/permanent-gas selectivity.[20]

Thus far, enhanced-flux, fumed-silica-filled systems have been successfully prepared from high-free-volume, glassy, disubstituted polyacetylenes. These polymers have gas permeabilities that are significantly higher than those of conventional glassy polymers such as polysulfone and polycarbonate.[23,24] For example, poly[1-(trimethylsilyl)-1-propyne] (PTMSP), the most well-known member of this family of polymers, has an oxygen permeability coefficient that is approximately 10 000 times greater than that of polycarbonate.

The high permeability of PTMSP and other structurally similar polyacetylenes is attributed, in part, to their extremely high free volume.[25] For instance, the fractional free volume (FFV) of PTMSP is 0.29, compared to only 0.16 for polycarbonate.[23] The high free volume of these polyacetylenes results from the alternating double bonds in the polymer backbone that hinder chain segmental motion and the bulky pendant groups that frustrate efficient polymer chain packing. Free volume in PTMSP is so high that this polymer is generally envisioned as a transitional material in which molecular transport can occur not only by the solution/hindered-diffusion mechanism typical of conventional polymers but also by pore-flow mechanisms (e.g., surface diffusion) that are commonly observed in microporous solids.[25,26] This nanoporous structure endows PTMSP and some other high-free-volume polyacetylenes with gas/vapor transport properties that are very different from conventional glasses.[25,26] For example, PTMSP preferentially permeates large vapor molecules over smaller light-gas molecules, in contrast to conventional glassy polymers (e.g., polysulfone) that are size-sieving and, thus, selectively permeate the smaller gases. In fact, for hydrocarbon vapor separations, PTMSP exhibits the highest mixture $C_{3+}/CH_4$ and $C_{3+}/H_2$ selectivities and the highest mixture $C_{3+}$ permeabilities of all known polymers.[26] Hence, substituted polyacetylenes like PTMSP are sometimes referred to as “superglassy polymers”.

In light of the recent interest in filled superglassy polymers and because of the systematic manner in which their gas permeability can be varied through filler addition, these materials should be interesting systems to probe by $^{129}$Xe NMR. In this work, PTMSP was chosen as the polymeric matrix material because of its extremely high free volume, which allows the preparation of mechanically strong, defect-free films over a relatively large range of filler concentrations (up to 40 wt % fumed silica). The effects of fumed silica filler concentration on both gas permeability and $^{129}$Xe NMR chemical shift are investigated in the present study. Our objective is to establish whether the average free volume estimates yielded by $^{129}$Xe NMR measurements on the bulk polymer containing nanoscale silica fillers provide information on the gas permeability of these materials. Apart from the fundamental interest in a free volume interpretation of gas transport in filled systems, this study has practical merit as well. If at least a semiquantitative relationship does exist between $^{129}$Xe chemical shift and gas permeability, $^{129}$Xe NMR may provide a rapid, facile means of screening materials for their utility as gas separation or barrier membranes.

## Experimental Section

**Film Preparation.** Dense polymer/filler nanocomposite films were prepared by solution-casting physically blended mixtures of PTMSP and fumed silica in a procedure similar to that described elsewhere.[22] The PTMSP was synthesized using $TaCl_5$ catalyst and was kindly provided by Permea, Inc. (St. Louis, MO). The fumed silica filler used was nonporous Cab-O-Sil TS-530 (Cabot Corp., Tuscola, IL), which has a density of 2.1 g/cm$^3$, a primary particle diameter of 13 nm, and a nonpolar, trimethylsilylated surface as a result of treatment with hexamethyldisilazane.[27] All films were prepared from relatively viscous solutions of 1.5 wt % PTMSP in toluene. For filled films, polymer solutions containing the desired amount of fumed silica were stirred vigorously for 10 min to uniformly disperse the silica particles. Films were cast from solution into glass dishes and dried slowly at ambient conditions for 5 days to completely remove solvent. Dried films were approximately 100 $\mu$m in thickness and contained up to 40 wt % (20 vol %)[28] fumed silica. For filler loadings higher than 40 wt %, the films obtained were usually too brittle to be handled. Properties (e.g., density and gas permeability) of high-free-volume polyacetylenes such as PTMSP are known to be very sensitive to polymer processing history, film preparation methods, and aging conditions.[29−31] To minimize the effect of these factors in this study, the unfilled and filled PTMSP films were cast under identical conditions from the same batch of polymer, characterized in gas permeation experiments performed on the same day, and examined by $^{129}$Xe NMR spectroscopy immediately after completion of the permeation tests.

**Permeation Measurements.** The pure-gas permeation properties of PTMSP and fumed-silica-filled nanocomposites were determined at 22 °C with a constant-pressure/variable-volume apparatus.[32] The effective permeation area of the films was 13.8 cm$^2$, and gas flow rates were measured with a soap-film bubble flowmeter. Nitrogen and oxygen permeability coefficients in the films were measured at an upstream pressure of 50 psig and a downstream pressure of 0 psig (atmospheric).

**Xe NMR Measurements.** $^{129}$Xe NMR experiments were performed on a Bruker AVANCE 500 MHz spectrometer with Oxford narrow bore magnet, SGI INDY host workstation, and XWINNMR software. The instrument is equipped with three frequency channels with waveform memory and amplitude shaping unit, a three-channel gradient control unit (GRASP III), and a variable-temperature unit with precooling and temperature stabilization. For all NMR measurements, a 10-mm-i.d. 1H/BB probe (BB500-10EB, Nalorac Corp., Martinez, CA) tuned to the $^{129}$Xe frequency of 138.365 MHz in the 500 MHz spectrometer (1H frequency = 500.128 MHz) was used.

All NMR spectra were acquired at 25 °C. The resonance line from free xenon gas was used as the internal standard. The instrument parameters for acquisition of the one-dimensional, single-resonance $^{129}$Xe NMR spectra were as follows: spectrometer frequency = 138.365 MHz; spectral width = 83 333 Hz (equivalent to 602 ppm); number of data points = 16K; relaxation delay = 2 s; acquisition time = 0.098 s; pulse width = 16 $\mu$s (tip angle = 60°); number of transients > 10K; number of dummy scans = 0.

The silhouette of the sample container duplicated that of the ordinary 10-mm NMR glass tube installed in the sample spinner. In place of the glass tube, an Ultem tube (o.d. = 10 mm, i.d. = 6.35 mm) was used. A specially designed valve was housed in the spinner so that the sample could be charged with xenon gas. For the present study, a xenon gas pressure of 120 psig was used, and equilibration of the gas with the samples was almost instantaneous. As estimated from simple weighings, a typical PTMSP sample sorbed roughly 44% of its own weight in xenon at this pressure. Because of this significant xenon uptake and because xenon gas at natural abundance

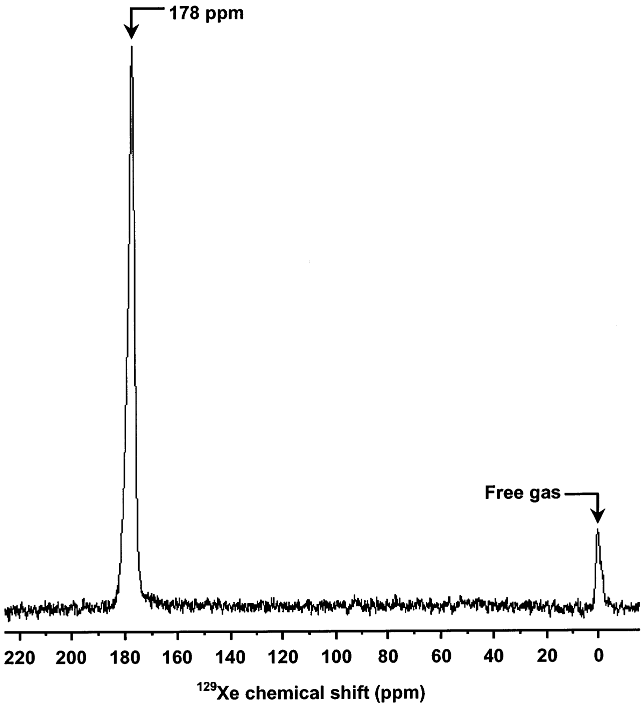

**Figure 1.** $^{129}$Xe NMR spectrum obtained for pure (unfilled) PTMSP at 25 °C and a xenon gas pressure of 120 psig.

contains 26.44% $^{129}$Xe, the strong NMR signal obtained for the PTMSP and PTMSP/fumed silica samples was not surprising.

## Results and Discussion

**$^{129}$Xe NMR Analysis.** As shown in Figure 1, the $^{129}$Xe NMR spectrum obtained for the unfilled (pure) PTMSP film exhibits two strong, distinct resonance signals: one associated with free xenon in the gas phase and the other associated with xenon gas sorbed (dissolved) in the polymer. Relative to the sorbed xenon peak, the free-gas peak assigned to a chemical shift of 0 ppm is small due to the rather high solubility of xenon in PTMSP at 120 psig. This result is consistent with the fact that PTMSP has been reported to exhibit the highest light-gas solubility of all known polymers.[33] The larger sorbed-xenon peak is observed further downfield at a chemical shift of 178 ppm. This value is considerably less than the chemical shift of 190–220 ppm typically obtained under similar test conditions for most hydrocarbon polymers.[11] This result suggests that PTMSP possesses relatively large free volume elements, consistent with gas permeability[23,25] and PALS data reported for this polymer.[34] The NMR spectrum in Figure 1 can therefore be considered to be characteristic of an exceptionally high-free-volume polymeric material. Unfortunately, though, it does not yield direct, quantitative information about the absolute average dimension of free volume elements in the polymer or their distribution.

In general, the chemical shift of sorbed xenon may be written as the sum of terms corresponding to the different types of interactions that the xenon molecule may be subject to:[35]

$$\delta = \delta_{\mathrm{s}} + \delta_{\mathrm{Xe}} + \delta_{\mathrm{SAS}} + \delta_{\mathrm{E}} + \delta_{\mathrm{M}} \tag{1}$$

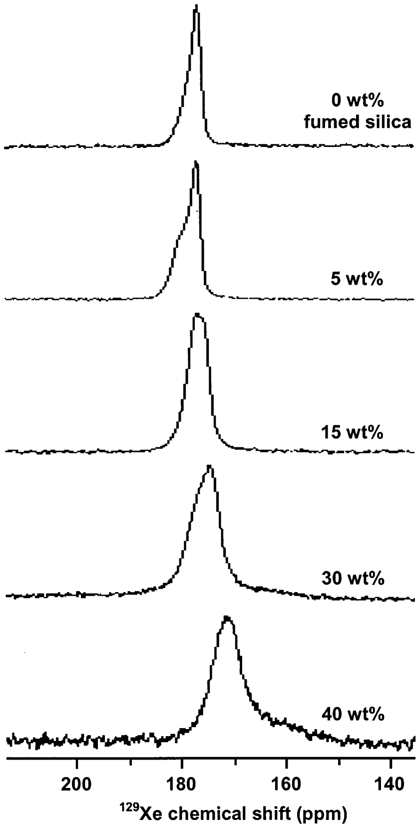

**Figure 2.** Gradual upfield shift (toward 0 ppm) of the $^{129}$Xe resonance signal with increasing fumed silica content in PTMSP. $^{129}$Xe NMR spectra were acquired at 25 °C and a xenon gas pressure of 120 psig.

where $\delta_{\mathrm{s}}$ is the shift due to interactions with the sorbing medium and is related to the shape and dimensions of the cavities containing the xenon molecules, $\delta_{\mathrm{Xe}}$ is the shift due to xenon–xenon interactions, $\delta_{\mathrm{SAS}}$ is the shift related to specific interactions with strong adsorption sites, and $\delta_{\mathrm{E}}$ and $\delta_{\mathrm{M}}$ are the shifts due to interactions with electric and magnetic fields, respectively, generated by ionic species. For our nonpolar, nanocomposite system of PTMSP and TS-530 fumed silica, the last three chemical shift terms on the right side of eq 1 are negligible. The $\delta_{\mathrm{Xe}}$ contribution is an increasing function of the experimental xenon pressure and, thus correspondingly, of the concentration of sorbed xenon. It may also be neglected because, at the fixed xenon experimental pressure, pure PTMSP and the fumed-silica-filled PTMSP samples would be expected to sorb approximately equivalent amounts of xenon, given that a recent study[22] has established that fumed silica filler has little impact on gas solubility in high-free-volume polymers. Therefore, any observed chemical shift differences between PTMSP samples containing varying amounts of fumed silica can be attributed primarily to $\delta_{\mathrm{s}}$ differences resulting from subtle changes in free volume dimensions.

To demonstrate the impact of adding fumed silica nanoparticles to PTMSP, the $^{129}$Xe NMR resonance signals presented in Figure 2 were collected for PTMSP films containing different silica concentrations. As fumed silica content in the polymer increases, the resonance signal for sorbed xenon gas gradually shifts upfield toward the free gas peak at 0 ppm. The $^{129}$Xe chemical shift decreases from 178 ppm for unfilled PTMSP to 172 ppm for PTMSP filled with 40 wt % fumed silica. To illustrate this trend more clearly, Figure 3 plots the observed chemical shift as a function of filler content in the polymer. A significantly negative

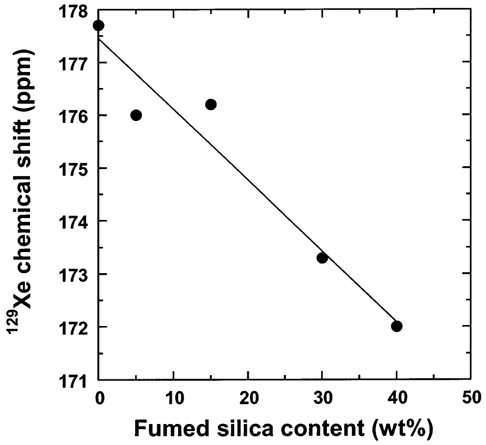

**Figure 3.** $^{129}$Xe NMR chemical shift for PTMSP nanocomposite films as a function of fumed silica content. NMR measurements were conducted at 25 °C and 120 psig xenon.

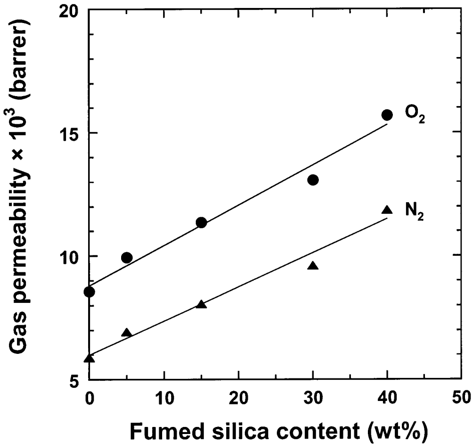

**Figure 4.** Pure nitrogen and oxygen permeability coefficients in PTMSP nanocomposite films as a function of fumed silica content at 22 °C. Pure-gas measurements were conducted at an upstream gas pressure of 50 psig and a downstream gas pressure of 0 psig. From a propagation-of-error analysis,[39] the uncertainty in measured permeability values is ±7%. 1 barrer $= 10^{-10}$ (cm$^3$ (STP) cm)/(cm$^2$ s cmHg).

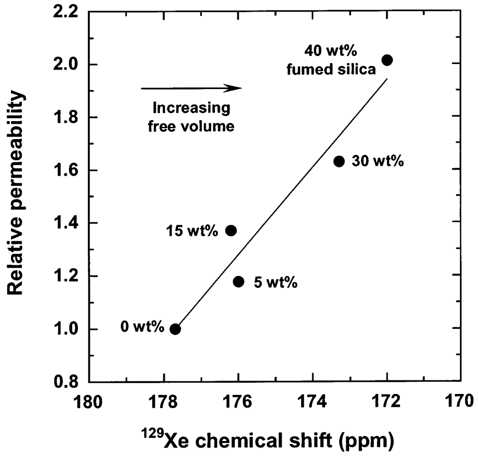

**Figure 5.** Relative nitrogen permeability in PTMSP nanocomposite films filled with fumed silica as a function of the observed $^{129}$Xe NMR chemical shift. The relative permeability is defined to be the permeability of the filled sample normalized by the permeability of pure PTMSP.

correlation is observed to exist between these two variables over the fumed silica concentration range of 0−40 wt %, indicating that free volume in the PTMSP nanocomposites increases as more and more silica is added. This result is unusual in the traditional sense because the added silica would generally be expected either to have little impact on free volume or to occupy part of the free volume such that a net decrease occurs in the free volume of the composite system. However, on the basis of previous results for filled superglassy polymers where free volume is enhanced upon filler addition,[21,22] the $^{129}$Xe NMR data are quite reasonable and, as will be shown, are consistent with gas transport data.

Free volume changes in the unfilled and filled PTMSP samples due to physical aging can also be detected by the $^{129}$Xe NMR technique. Over an aging period of 13 days at ambient temperature, the $^{129}$Xe chemical shift for PTMSP films having 0 and 30 wt % fumed silica increased (i.e., moved downfield) by 1.4 and 3.5 ppm, respectively, relative to the unaged chemical shifts. This result indicates that free volume in the aged samples has decreased and is consistent with the well-known phenomenon in which PTMSP densifies (ages) over time, leading to a reduction in its gas permeability.[29] Thus, $^{129}$Xe NMR spectroscopy, previously shown capable of detecting changes in polymer free volume resulting from cross-linking, polymer blending, and temperature changes, may also be used to measure polymer free volume changes induced by filler addition and those resulting from physical aging.

**Permeability.** Figure 4 presents the effect of fumed silica content on gas permeability coefficients in PTMSP. Consistent with previous results obtained for a similar filled superglassy polymer,[21,22] the permeability of PTMSP increases systematically as fumed silica concentration in the polymer increases. For example, at 40 wt % filler, the nitrogen permeability coefficient is twice that in unfilled PTMSP. Such increased permeability in a filled polymer is particularly unusual. Generally, in conventional filled polymers, filler particles obstruct gas transport, leading to a reduction in permeability.[19,36] This decreased permeability primarily results from an increase in the tortuosity of the gas diffusion path and a decrease in the effective cross-sectional area available for gas transport as filler content increases. While these effects must operate in the nanosilica-filled PTMSP samples as well, clearly there is an additional overriding effect causing permeability to increase. Previously, this enhanced permeability in filled superglassy polymers has been attributed to small increases in system free volume following incorporation of filler into the polymer.[22] Our NMR results for filled PTMSP provide further evidence that free volume is enhanced by silica addition, and the permeability data in Figure 4 behave accordingly. In fact, the regular manner in which both permeability and $^{129}$Xe chemical shift depend on fumed silica content in PTMSP (cf. Figures 3 and 4) suggests the existence of a correlation between these two parameters. This permeability−chemical shift relationship for the PTMSP/fumed silica nanocomposite system is presented in Figure 5. As chemical shift decreases (and free volume increases), gas permeability increases. One implication of this result is that perhaps a more general correlation can be obtained for a variety of polymers that would allow the prediction of gas permeability in new materials from $^{129}$Xe NMR measurements. Of course, given the various contributions to the chemical shift (cf. eq 1), such a correlation would most likely work best for polymers of similar chemistry and would require NMR measurements to be conducted under similar experimental conditions.

Although a best-fit line has been drawn in Figure 5 to show that permeability increases with decreasing chemical shift (and increasing polymer free volume), there is no reason to necessarily expect a linear relationship between these quantities. A number of theories for gas diffusion in polymers are based on the free-volume concept. That is, the mobility of gas molecules in a polymer (as well as that of polymer chain segments) is primarily determined by the amount of free volume available in the material. A classic statistical mechanics model of this scenario offers the following expression for the diffusion coefficient $D$ of a penetrant molecule in a polymer:[37]

$$D = A \exp\left(-\frac{\gamma v_0}{\langle v_f \rangle}\right) \tag{2}$$

where $\langle v_f \rangle$ is the fractional free volume (in the strictest sense, the average free volume) of the polymer matrix, $v_0$ is the minimum free volume element size that can accommodate the penetrant molecule, $A$ is a preexponential factor, and $\gamma$ is an overlap parameter that accounts for possible sharing of free volume elements by several penetrant molecules. According to eq 2, which is applicable to penetrant diffusion coefficients in glassy polymers at infinite dilution, gas diffusion coefficients should increase with increasing polymer free volume.[37] For a dense polymer film, its permeability is a function of both the diffusivity and the solubility of the penetrant molecule in the polymer matrix. Because polymer free volume has a weak effect on penetrant solubility,[38] permeability coefficients often mirror the behavior of gas diffusion coefficients. Consequently, the permeability $P$ of dense polymer films typically follows the functional form $P \propto \exp(-1/\langle v_f \rangle)$.

For polymers, $\langle v_f \rangle$ is commonly estimated from group contribution methods or from data obtained by a probe technique such as PALS. Estimates of free volume cavity size from $^{129}$Xe NMR measurements have been reported in the zeolite literature.[10] These studies have shown that the $^{129}$Xe chemical shift is related to the mean free path of the sorbed-xenon probe molecule, which depends on the dimensions of the cavity containing the molecule. The following correlation between chemical shift and cavity size has been proposed:[10]

$$\partial = 243\left(\frac{2.054}{2.054 + r_s - r_{Xe}}\right) \tag{3}$$

where $r_s$ is the radius (Å) of a spherical free volume element within which the xenon probe is localized and $r_{Xe}$ is the radius of the xenon atom, which is estimated to be 4.4 Å.[10] Applying eq 3 to our NMR data for filled PTMSP yields free volume elements that increase in diameter from 5.9 to 6.1 Å as filler content increases from 0 to 40 wt %. While these calculations are somewhat crude given that the actual free volume elements in a polymer are not likely to be spherical and that the xenon probe cannot access volume cavities smaller than itself, they nevertheless provide an average free volume element size (~6 Å) that is consistent with the current understanding of PTMSP microstructure. Furthermore, the relatively small increase in free volume element size upon filler addition (<1 Å) also agrees with previous PALS studies of a similar superglassy polymer filled with fumed silica.[21]

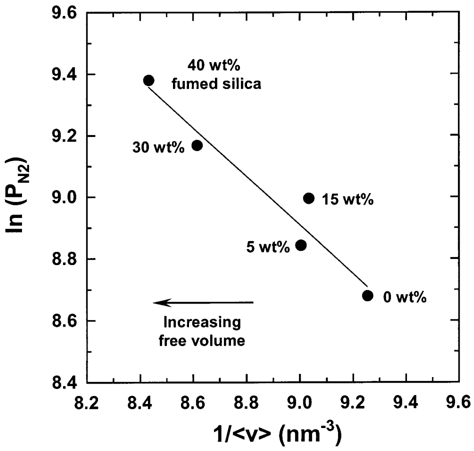

**Figure 6.** Natural logarithm of nitrogen permeability in PTMSP nanocomposite films filled with fumed silica as a function of the inverse average free volume cavity size estimated from $^{129}$Xe chemical shift data for these films. Spherical free volume elements were assumed for the free volume cavity size calculations.

By using the estimated cavity dimensions calculated from the observed $^{129}$Xe chemical shifts, Figure 6 illustrates the relationship between nitrogen permeability coefficients and average free volume element size $\langle v \rangle$ for filled PTMSP. These data show that the logarithm of permeability essentially decreases linearly with the inverse of free volume size. Thus, the functional dependence of filled PTMSP permeability on free volume, as approximated from $^{129}$Xe NMR data, appears to be consistent with the relationship given in eq 2. Previously, PALS results on conventional glassy polymers[38] and another superglassy polyacetylene[21] have shown a good fit of permeability to the mean free volume size, similar to the results shown here. Because the concentration of free volume elements is not included in any of these correlations, it implies that permeability changes in these materials (including the silica-filled PTMSP system studied in this paper) are largely due to changes in mean free volume element size rather than to changes in the concentration of free volume elements.

## Conclusions

Up to the maximum filler level at which an integral membrane could be fabricated, gas permeability in PTMSP/fumed silica nanocomposites increases with increasing filler content. As measured by $^{129}$Xe NMR spectroscopy, the free volume of PTMSP also increases correspondingly with silica filler concentration. The $^{129}$Xe NMR chemical shift, which decreases with increasing polymer free volume, is shown to correlate well with the enhancement of gas permeability in filled PTMSP. At this time, however, the general applicability of this correlation, particularly its potential usefulness for screening and designing membrane materials having a target or predetermined permeability, cannot be assessed without more data on a wider set of polymers.

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