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Gas Transport in Poly(silylpropynes): The Chemical Structure Point of View

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ABSTRACT: Poly[1-(trimethylsilyl)propyne] (PTMSP) has the highest gas permeability of any known polymer.[1] Understanding the structural origins of the exceedingly high gas permeability of PTMSP should facilitate the design of other highly gas permeable glassy polymers. Results of a systematic investigation of a homologous series of closely related polymers prompt us to offer a structure/property rationale to explain the high gas permeability of PTMSP. The following polymers were synthesized: poly[1-(*n*-alkyldimethylsilyl)-propyne]; **A–E**), poly[1-(isopropyldimethylsilyl)propyne]; **F**), poly[1-(phenyldimethylsilyl)propyne]; **G**), and poly[1-[*p*-(trimethylsilyl)phenyl]propyne]; **H**). Polymer conformation is herein discussed in relation to the steric requirement for main-chain conjugation, dynamic mechanical spectra, and a proposed mechanism of polymerization. The critical surface tension of pendant groups was used to qualitatively rationalize the intermolecular interactions for poly(silylpropynes). Gas permeability (*P*) was measured. For polymers **A–E**, as the chain length of the *n*-alkyl group decreases, the gas permeability increases. The large differences in the oxygen permeability coefficient, $P(O_2)$, for poly[1-(isopropyldimethylsilyl)propyne] (**F**) and poly[1-(*n*-propyldimethylsilyl)propyne] (**C**) as well as those between polymer **G** and polymer **H** can be explained on the basis of the subtle but important London forces of side-chain association. Our conclusion is that the extraordinarily high gas permeability of PTMSP is a consequence of large excess free volume within the polymer matrix which is itself ascribed to (1) the rigid and irregular main-chain conformation and (2) the low interchain attraction force of the side chains which shield the main chain.

Introduction

Glassy polymers have found broad application in the area of gas separation membranes.[2-4] The transport of gas molecules through a polymer matrix can be described well by the sorption–diffusion mechanism.[5] However, at present, the selection of a suitable membrane polymer for a specific gas pair separation is somewhat empirical and relies on available materials instead of tailor design. This may be a consequence of both cost consideration and limited information on chemical structure/permeation relationships for polymeric systems. Establishing chemical structure/permeation relationships has to date been limited by the lack of a polymer system in which gas permeability is very sensitive to minor structural changes.

Higashimura, Masuda, and co-workers[1] reported a glassy polymer with exceptional properties: poly[1-(trimethylsilyl)propyne] (PTMSP). PTMSP has unique properties when compared to its parent, polyacetylene. For instance, the main-chain double bonds are nonconjugated; furthermore, PTMSP is colorless, soluble in many organic solvents, and amorphous. Most surprisingly, however, is that PTMSP has the highest gas permeability reported for any known polymer. Because of its very high gas permeability and its unusual physical properties by comparison with polyacetylene, an intensive effort[6-19] has been directed toward understanding the nature of these novel properties of PTMSP. From the sorption and diffusion analysis, it has been suggested that the existence of a very large Langmuir capacity is the major contributor to PTMSP's very high permeability.[6] However, a clear correlation of the formation of this large Langmuir capacity to PTMSP's chemical composition has not yet appeared in the literature.

We have completed a systematic study of a family of poly(silylpropyne) polymers where minor changes in chemical structure result in major differences in gas permeability. Permeability and other intrinsic properties of a polymer are affected significantly by conformation and chain–chain interaction. This report explores the role of main-chain conformation and intermolecular chain–chain interaction in the extraordinarily high gas permeability of PTMSP. We believe this insight will provide potential guidance for the design of other glassy polymers with high gas permeability.

Experimental Section

1. **Materials. (a) Monomers.** The (trimethylsilyl)propyne was obtained from Petrarch. The synthesis of 1-[*p*-(trimethylsilyl)phenyl]propyne was reported earlier.[19] Most of the monomers were prepared by following the reported procedure[20] involving the direct silylation of propynyllithium with the appropriate alkylchlorosilane. Propynyllithium was prepared by the metalation of propyne with *n*-butyllithium (Scheme I). The general synthetic procedure is illustrated below for the preparation of (octyldimethylsilyl)propyne.

A 1-L, three-necked, round-bottom flask was equipped with a mechanical stirrer, a nitrogen inlet tube, and a dry-ice trap. A total of 70 g of *n*-butyllithium and 600 mL of diethyl ether were charged into the flask at 0 °C. The mixture was cooled to −30 °C, and 100 g of propyne was added. This mixture was stirred for ~1 h and warmed to 0 °C, and 150 g of octyldimethylchlorosilane was added. The resulting mixture was stirred for another 1 h and allowed to warm to room temperature overnight. The reaction mixture was washed with water, and the aqueous phase was extracted with ether. The combined ether extracts were dried over anhydrous $MgSO_4$. After ether was removed, the monomer was distilled several times from CaH_2 before polymerization. Yield: 134 g (87%). Bp: 43–45 °C (~0.05 mmHg). All the monomers were purified by repetitive fractional distillation until high purity was achieved (>99.5% by GC).

(b) Polymerization. The polymerization was carried out in a drybox according to the general procedure given by Higashimura, Masuda, and co-workers.[7] In all cases, film-forming polymers were obtained. Specific polymerization conditions and polymer molecular weights are given in Table I. The following polymerization of TMSP is representative: $TaCl_5$ (0.5 g, 1.4 mol) was dissolved in 10 mL of toluene. The mixture was stirred for 30 min at room temperature. To this catalyst solution was added

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Scheme I. Synthesis of [Alkyl(or Aryl)dimethylsilyl]propynes

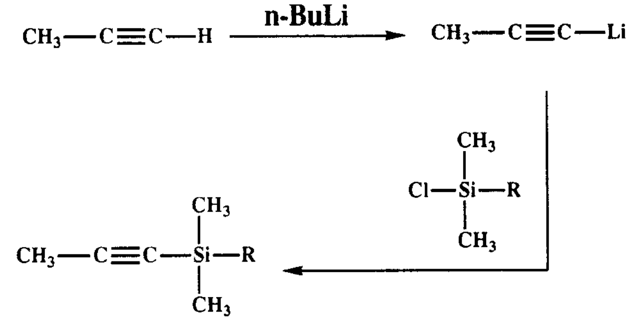
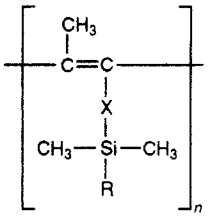


Table I. Preparation and Molecular Weight of Si-Containing Polypropynes



polymer[a]	R	X	catalyst[b]	$10^{-3} M_w$[c]	M_w/M_n
A	CH_3		I	1650	3.2
B	C_2H_5		II	538	2.4
C	n-C_3H_7		II	430	2.7
D	n-C_4H_9		II	617	2.4
E	n-C_8H_{17}		II	3251	3.0
F	i-C_3H_7		II	85	3.7
G	C_6H_5		II	655	3.2
H	CH_3	C_6H_5	III	156	2.1

[a] Polymers A and H were prepared at room temperature. The rest were prepared at 80 °C. [b] I, $TaCl_5$; II, $TaCl_5/Ph_3Bi$ (1:1); III, $TaCl_5/Ph_4Sn$ (1:1). [c] Molecular weights were estimated by GPC in THF as polystyrene equivalents.

TMSP (12 g, 100 mmol). The mixture immediately turned dark brown, and the solution solidified within 30 min. After 24 h the polymerization mixture was worked up by precipitation of the polymer in rapidly stirred excess hot methanol. This procedure was repeated three times. The polymer was filtered and dried at 60 °C overnight under vacuum. A yield of >95% was typically achieved by this process.

(c) Film Casting. Poly(silylpropyne) films were cast from a 2% toluene solution onto clean glass plates. After the solvent vaporized, the films were then floated off the plates. The dense films were dried under a nitrogen purge for several days.

(d) Gas Permeability Measurements. The gas transport properties of these films were measured in a Model CS-135 permeability cell (Custom Scientific Instruments, Inc., Whippany, NJ), using ASTM procedure D-1434. All permeability values are reported in units of barrers, where a barrer is defined as 1 × 10^{-10} cm^3 of gas at STP moving through a 1-cm-thick film (surface area of 1 cm^2) per 1 s (1 barrer = 10^{-10} cm^3 (STP)·cm/cm^2·s·cmHg).

Results and Discussion

1. Conformation. 1.1. Adjacent Segmental Double Bonds: Parallel vs Orthogonal.

Extensive conjugation among adjacent double bonds lowers the total energy of a system and is favored by most polyenes.[21-23] The existence of extensive conjugation in polyenes is usually characterized by the appearance of color which ranges from light yellow to deep red depending upon the chain length of the conjugated system. This is because (1) the energy gap between the HOMO and LUMO orbitals is narrowed and (2) as the number of double bonds involved in conjugation increases, the energy gap narrows further, and the color deepens. While the total energy of a conjugated polyene is lowered by conjugation, the energy of the HOMO is raised and the molecule becomes more vulnerable to chemical reagents. Electronically, conjugation requires the overlap of π-orbitals. The most favorable conformation for conjugation between adjacent double bonds is that in which the double bonds are parallel, providing for maximum π-orbital overlap. When the two double bonds are orthogonal, the overlap between adjacent π-orbitals cannot occur and conjugation is almost nonexistent. Deep color, electrical conductivity, chain stiffness, and air instability are typical characteristics of the extensive conjugation in polyacetylene.[24] Although structurally related to polyacetylene with main-chain alternating double bonds, poly(silylpropynes) are colorless, nonconductive, relatively air and UV stable at room temperature, and essentially nonconjugated.[25,26]

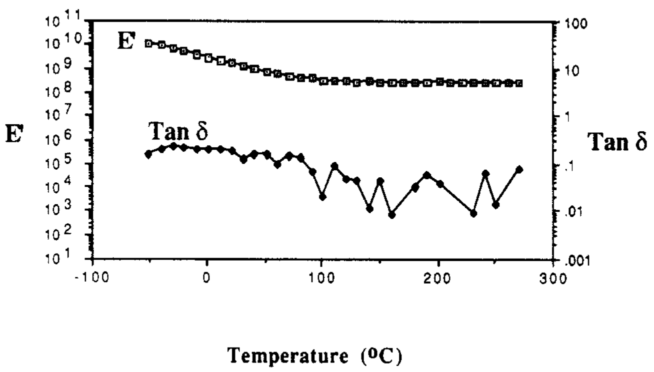


Figure 1. Temperature dependence of E' and tan δ for poly[(octyldimethylsilyl)propyne] (A) and poly[[p-(trimethylsilyl)phenyl]propyne] (B).

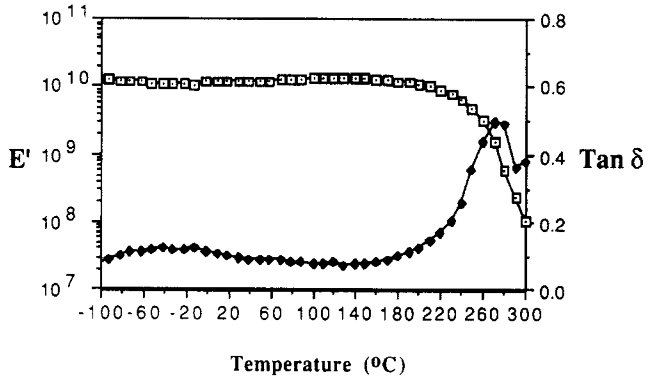


Figure 2. Temperature dependence of E' and tan δ for poly[1-[p-(trimethylsilyl)phenyl]propyne].

The temperature dependence of dynamic viscoelasticity for poly[(trimethylsilyl)propyne] and several derivatives was reported earlier by Masuda and co-workers.[12] They found variations of storage modulus (E'), loss modulus (E''), and loss tangent (E'/E'') with temperature to be quite small for all of the poly(silylpropynes) studied. However, small changes in E' are observed as the side-chain alkyl groups become larger. This phenomenon is exemplified in the case of poly[1-(n-octyldimethylsilyl)propyne] (Figure 1) where small but significant changes in E' and tan δ are noted over the temperature range from −50 to +100 °C. These changes might be caused by energy dissipation due to the local motion of the alkyl groups. A sharp drop in E', which corresponds to the T_g, is observed only for poly[1-[p-(trimethylsilyl)phenyl]propyne] (Figure 2).

A molecular model was employed to illustrate the stereochemical requirement for major conformational change in PTMSP. Conformational change in the polymer's main-chain, with the exception of vibration and

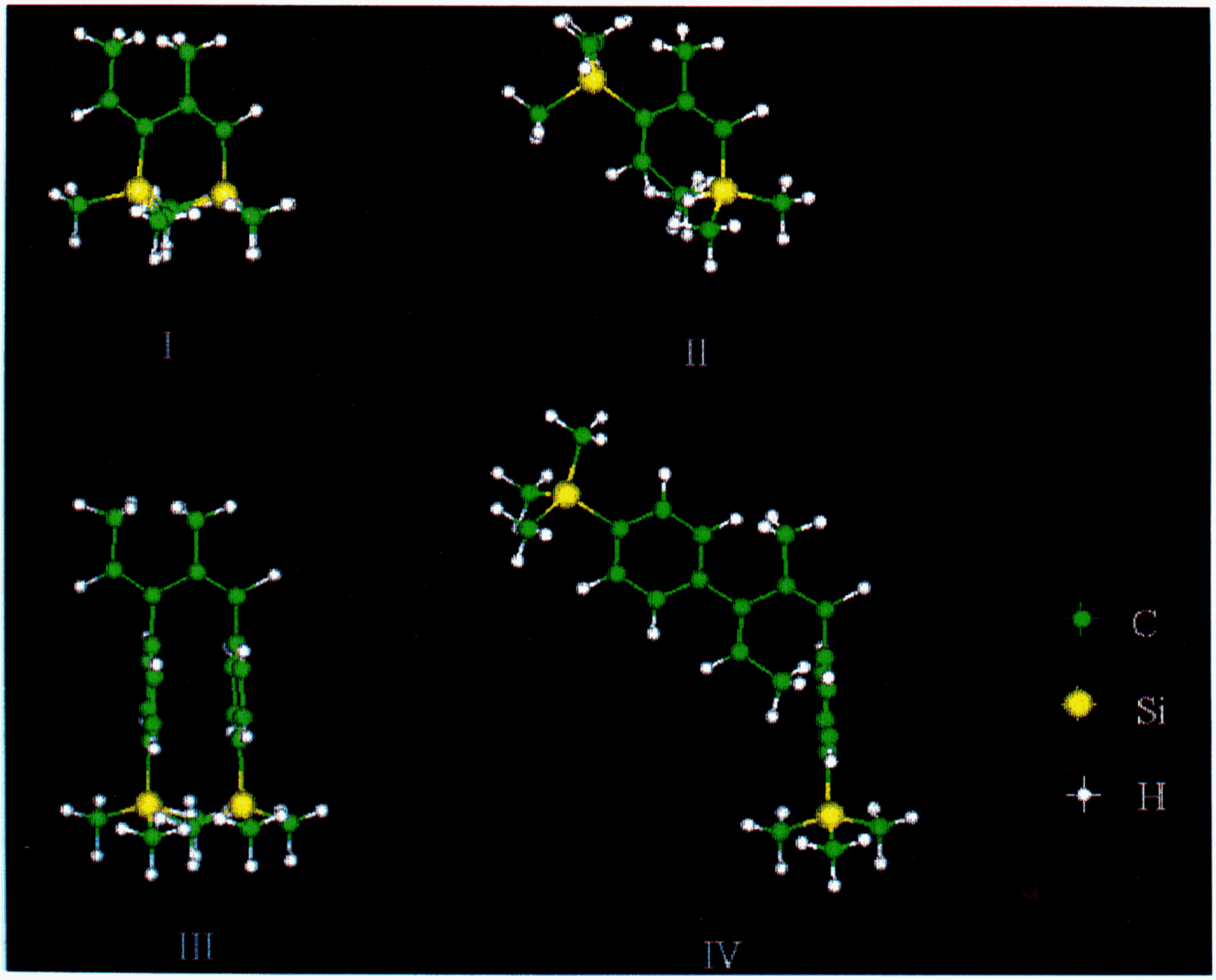


Figure 3. Planar conformations for adjacent segments in PTMSP (**I** and **II**) and poly[1-[*p*-(trimethylsilyl)phenyl]propyne] (**III** and **IV**).

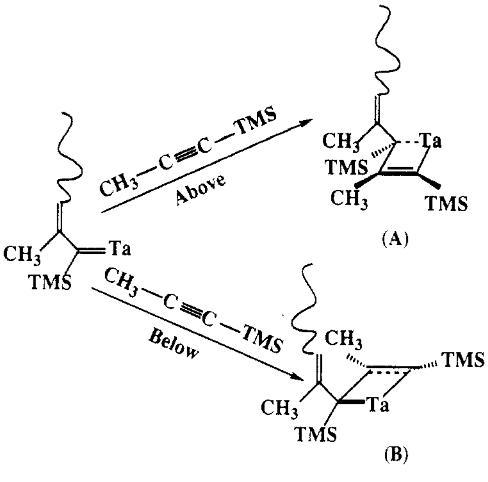
rocking, requires rotation of at least one of the main-chain single bonds. In the case of PTMSP, a 180° rotation of a main-chain single bond requires passage through one of two planar conformations for the two adjacent segments which are linked together by that single bond (Figure 3: transoid, I; cisoid, II).

A common feature of these two conformations is the coplanarity of the four main-chain carbon atoms, the two carbon atoms of the pendant methyl groups, and the two silicon atoms of the pendant trimethylsilyl groups. Very severe steric interaction results in each case. Either two trimethylsilyl groups must overlap (conformation **I**) or a methyl group must overlap a trimethylsilyl group (conformation **II**). Rotation through either conformation is severely restricted. These extremely crowded and high-energy conformations force the adjacent segmental units of PTMSP to be orthogonal, minimize conjugation of main-chain double bonds, restrict rotation around the main-chain single bonds, and are responsible for PTMSP's very rigid main-chain conformation.

With methyl being the smallest possible alkyl substituent, it stands to reason that poly(silylpropynes) with larger alkyl group substitution on silicon should experience an even greater barrier of rotation around main-chain single bonds. This is supported by the high T_g (above the decomposition temperature of these polymers; >300 °C) for the poly(silylpropynes) presented herein. It suggests that members of this polymer family are restricted to a rigid, nonrotatable, and nonconjugated conformation and the side groups shield the double bonds from hostile agents. To summarize, severe steric crowding in the parallel conformation for any two adjacent segments in poly(silylpropynes) accounts for the major physical property differences between these polymers and polyacetylene.

For poly[1-[*p*-(trimethylsilyl)phenyl]propyne], a phenyl ring separates the trimethylsilyl group from the main chain for each segmental unit. Shown in Figure 3 are the two planar conformations (transoid III and cisoid IV) for two adjacent segmental π-orbitals in poly[1-[*p*-(trimethylsilyl)phenyl]propyne]. It can be seen that pendant groups do not overlap to a significant extent in conformation IV. There is little steric barrier to rotation around main-chain single bonds. This may be one of the reasons that poly[1-[*p*-(trimethylsilyl)phenyl]propyne] has a lower T_g (~270 °C) than poly(silylpropynes).

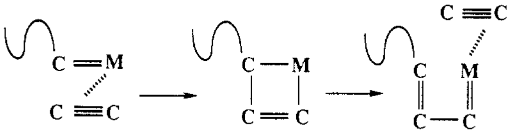
1.2. Secondary Structure. Having concluded that nonconjugation and rigidity between adjacent segmental units for poly(silylpropynes) are due to steric interactions between the pendant groups, we became interested in the secondary structure of these polymers. Since PTMSP has the highest gas permeability of any known polymer, the secondary structure for this material is of special interest. The central issue is whether PTMSP adopts a *helical, rigid-rod-like structure* or a *rigid irregular structure*. It



TMS = (CH3)3Si

Figure 4. Representative configurations of metallocyclobutene.

Scheme II. Proposed Mechanism for the Polymerization of Silylpropynes



was calculated that a helical conformation is thermodynamically most stable for PTMSP.[27,28]

It has been observed, however, that PTMSP fails to show lyotropic characteristics in solution, forms a transparent film, and fails to crystallize under stretching. These are typical characteristics for structureless, amorphous polymers and atypical for helical, rigid-rod-like materials.

Recently, from X-ray diffraction measurement and the Mark-Houwink relationship, Masuda, Higashimura, and co-workers proposed that disubstituted polyacetylenes (including PTMSP) are amorphous in the solid state and adopt a more expanded irregular conformation than do vinyl polymers in solution.[8] That PTMSP adopts an irregular conformation in lieu of the more stable helical conformation suggests that the secondary structure of PTMSP is of kinetic rather than thermodynamic origin.[28] We propose that the irregular conformation of PTMSP is established during polymerization.

It has been proposed that polymerization of (trimethylsilyl)propyne by tantalum pentachloride is metal carbene mediated[9] (Scheme II): If the propagating species is a tantalum carbene of the general structure given in Figure 4, then formation of two enantiomeric metallocyclobutenes (**A** and **B**) is possible upon reaction of the tantalum carbene with (trimethylsilyl)propyne. Kinetic formation of the α-helix requires approach of the monomer above the C_1/C_2/Ta plane whereas the alternative formation of a β-helix should result if the monomer approaches from below the C_1/C_2/Ta plane. Since the two intermediates **A** and **B** are pseudo mirror images, then transition states leading to their formation should be of essentially equivalent energy.

Consequently, formation of either intermediate is equally likely. This type of polymerization is a Bernoullian process and should afford a polymer chain of an irregular conformation. Since conformational change is disfavored once PTMSP has formed, this highly rigid polymer remains is an irregular conformation. It is likely that the same mechanism is operative for the formation of any poly(silylpropyne) according to the standard procedure. Thus, we believe that all poly(silylpropynes) adopt a kinetically controlled, rigid, irregular conformation, and it should not be unexpected that increasing the length of the side chain does not lower the T_g for poly(silylpropynes).

2. Chain-Chain Interaction. The poly(silylpropyne) polymers are distinguished from each other by the nature of the pendant groups attached to the silicon. For our study, this group ranged from a linear alkyl group with varying chain length to a branched alkyl group to an aryl group. Although these groups are all hydrocarbon in nature, they do contribute differently to the intermolecular forces. The lowest of the London dispersion forces are the weakest intermolecular interactions between molecules and, for pendant groups in polymers, are those associated with aliphatic hydrocarbon and fluorocarbon groups. The weak intermolecular interactions between these groups are reflected in Zisman's critical surface tension of wetting.[29] The origin of surface tension is due to the unbalancing of intermolecular forces at a surface.[30] This same unbalance of forces is also responsible for the internal pressure and cohesive pressure as shown by the qualitative correlation for certain homopolymers where homopolymers with low critical surface tensions usually also have low cohesive energy densities.[29] For the family of poly(silylpropyne) polymers with identical main chains and very rigid and similar conformations, intermolecular interactions should depend upon the nature of the silyl substituents which stick out of and shield the extremely rigid main chain. It is reasonable to presume that poly(silylpropynes) carrying pendant groups with low critical surface tension should exhibit low intermolecular interactions. Zisman reported the following trend in critical surface tension: C_6H_5 (phenyl edge; 35 dyn/cm) > C_2H_5 (25 dyn/cm) > CH_3 (22–24 dyn/cm) > CF_3 (6 dyn/cm).[29] PTMSP then should exhibit the lowest intermolecular interactions of any known poly(silylpropyne).

3. Chemical Structure/Permeation Relationship. For most polymers, at temperatures lower than the glass transition temperature (T_g), large segmental mobility is highly restricted, free volume is smaller, and interpolymer packing is tighter. Thus, the gas permeability of polymers is usually, but not always, low at temperatures below T_g.

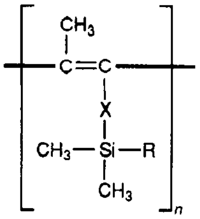
PTMSP is an amorphous polymer. It has a very high glass transition temperature ($T_g > 300$ °C), very low density ($\sim$0.8 g/cm^3), and the highest gas permeability of any known polymer. This unusual combination of properties poses a very interesting question. This is, *what is the unique structural feature responsible for PTMSP's extraordinarily high gas permeability*?

For gas transport in glassy polymers, it is generally agreed that the mechanism involves sorption and diffusion.[5] However, the intent of this report is to focus on chemical structure/gas permeation relationships instead of sorption and diffusion of individual gases. To elucidate the structural features which are responsible for PTMSP's unusually high gas permeability, a systematic study of the gas transport through a family of poly(silylpropynes) was conducted. This study made possible the correlation of gas permeation and polymer structure. Table II lists the gas permeation data for this family of poly(silylpropyne) polymers.

Table II clearly shows the same trend for permeation of gas through different polymer samples. For the sake of simplicity, this discussion will be centered on oxygen. The structure/permeation relationship established by oxygen transport properties of poly(silylpropyne) polymers can be used to rationalize the permeation of other gas through these materials.

3.1. Side-Chain *n*-Alkyl Group Effect. It is commonly observed that, for glassy polymers with identical

Table II. Gas Permeability of Poly(silylpropynes)[a]



polymer	R	X	$P(H_2)$	$P(He)$	$P(O_2)$	$P(N_2)$	$P(CH_4)$	$P(CO)$	$P(CO_2)$
A	CH_3		16200	6500	10000	6700	16000	7700	33100
B	C_2H_5		1930	830	970	490	1200	630	4600
C	n-C_3H_7		250	150	70	21	44	29	230
D	n-C_4H_9		65	62	29	8	17	11	100
E	n-C_8H_{17}		47	37	23	19	13	10	100
F	i-C_3H_7		1650	680	460	170	360	230	2200
G	C_6H_5		14	8.3	4.4	1.2	1.7	2.8	37.6
H	CH_3	C_6H_5	510	270	240	100	200	110	950

[a] The permeability coefficients (barrer) are units of 10^{-10} cm^3 (STP)·cm/cm^2·s·cmHg.

Table III. Thermal Effect on PTMSP's Oxygen Permeability Coefficient[a]

	RT	160 °C, 16 h	200 °C, 4 h	250 °C, 4 h	(1) 250 °C 4 h^+, (2) RT[b]
$P(O_2)$	10 000	7500	4000	2900	9200

[a] $CHCl_3$ was the casting solvent, and all the films were heated under full vacuum. [b] After heating under vacuum at 250 °C for 4 h, the film was redissolved and recast from $CHCl_3$.

backbones and varying sizes of n-alkyl side groups, the longer side-chain-containing polymer has a lower glass transition temperature due to the effect of n-alkyl side groups which can improve the side-chain flexibility and increase free volume. However, for poly(silylpropynes), n-alkyl group substitution on silicon relative to methyl substitution has no effect on lowering the T_g and actually decreases gas permeability (compared polymers A–E in Table II). PTMSP (R = CH_3) is 1 order of magnitude more permeable than poly[(isopropyldimethylsilyl)propyne] (R = C_2H_5) and 2 orders of magnitude more permeable than poly[(n-propyldimethylsilyl)propyne] (R = n-C_3H_7). The data are rationalized in the Summary section.

3.2. Side-Chain Isomeric Effect. Isomeric small molecules generally have different physical properties (such as melting point, boiling point, etc.) and different chemical reactivities. For the poly(silylpropyne) polymers, a branched alkyl side chain, as in poly[(isopropyldimethylsilyl)propyne] (R = i-C_3H_7, $P(O_2)$ = 460 barrers), affords a much higher gas permeability than the isomeric linear alkyl side chain, as in poly[(n-propyldimethylsilyl)propyne] (R = n-C_3H_7, $P(O_2)$ = 70 barrers). The branched alkyl group is more sterically hindered than the linear alkyl group and may impede interpolymer packing and increase interchain distance. Also, branched alkyl groups contain more methyl groups. It was reported that methyl groups provide a much lower critical surface tension at the air–solid interface than methylene groups. It is reasonable that the interpolymer (and penetrant–polymer) interaction is smaller when the polymer has more methyl groups per side chain. These effects may contribute to the higher gas permeability of poly[(isopropyldimethylsilyl)propyne] compared to that of poly[(n-propyldimethylsilyl)propyne].

3.3. Interpolymer Packing. The high gas permeability of PTMSP may be due to the presence of a large excess free volume in the glassy state which results in its low density (0.79–0.81 g/cm^3). The very low interpolymer interaction of PTMSP might be one of the factors creating such a large excess free volume within the polymer. The proposed very low interpolymer interaction of PTMSP originates from the trimethylsilyl group and methyl group in each segment. It is well-known that the trimethylsilyl group and methyl group have low critical surface tensions.[12] If one of the silicon substituents is phenyl rather than methyl, low permeability is to be expected since phenyl has a much higher critical surface tension than methyl. This is indeed the case for poly[(phenyldimethylsilyl)propyne] (R = C_6H_5, $P(O_2)$ = 4.4 barrers), for which a drop in the oxygen permeability by a factor of nearly 2300 is observed. This change in gas permeability is due to the strong chain–chain interaction caused by phenyl substitution. The strong interchain interaction combines with the planar structure of the phenyl ring which allows intimate packing, thus reducing the excess free volume and drastically lowering gas permeability.

To support this hypothesis further, the following comparison between poly[(phenyldimethylsilyl)propyne] and poly[1-[p-(trimethylsilyl)phenyl]propyne] was done. The two polymers have similar structural compositions. However, the presence of the trimethylsilyl group at the para position of the phenyl ring in the poly[[p-(trimethylsilyl)phenyl]propyne] should reduce interchain interaction and render the intimate packing between phenyl rings impossible. These two factors should increase the excess free volume and consequently increase the gas permeability. The oxygen permeability of poly[1-[p-(trimethylsilyl)phenyl]propyne] is indeed about 55 times higher than that of poly[(phenyldimethylsilyl)propyne].

3.4. Thermal Effect. After thermal treatment, the oxygen permeability of the PTMSP decreases. The data are listed in Table III.

After heating, the film became more brittle and slightly brownish. However, upon dissolving and recasting, the film returned to its original oxygen permeability and flexibility. Apparently, the thermal treatment changed the PTMSP's internal packing without seriously degrading the polymer itself.

3.5. Summary. It is generally believed that the overall gas transport process in a polymer depends on two major factors: *polymer segmental mobility* (free volume) and *excess free volume in the nonequilibrium glassy state* (microvoid, frozen hole, microcrack, etc.).[31]

When an amorphous polymer is above its glass transition temperature, the polymer is in a rubbery state and is characterized by liquidlike motion which involves large segments of the molecule. This motion in the rubbery state requires much more volume than that for the same polymer in its glassy state where only motion of atoms and small groups of atoms against the local restraints of secondary bond forces is possible. Thus, the free volume is generally small and the gas permeability is usually low for most glassy polymers. However, when an amorphous polymer is cooled from the melt through its glass transition temperature, an accelerated increase in the viscosity and elastic modulus occurs as the temperature approaches T_g. The rate of a polymer equilibration into its thermodynamically most stable packing is much slower than the rate of cooling. The glassy polymer is, thus, in a metastable and unrelaxed state and has excess free volume which is frozen into the polymer matrix. A similar phenomenon occurs during film casting. In solution, the polymer–polymer interaction is largely replaced by the polymer–solvent interaction. Due to the increase in interpolymer distance in solution, the polymer is able to adopt one of several interconvertible and thermodynamically stable conformations, if rotation around the main chain is possible. During the film formation, the solvent molecules vaporize and the polymer–polymer interaction again replaces the polymer–solvent interaction. At this stage, the polymer will try to adjust into the proper conformation for thermodynamically favorable packing. One of the major parameters responsible for tight packing is chain–chain interaction force. However, during the last stage of film formation, the solution becomes extremely viscous and the rate of solvent vaporation is much faster than the rate of conformation readjustment for the polymer. As a consequence, an excess free volume is frozen into the polymer matrix. The existence of this excess free volume constitutes another sorption process for the polymer in the glassy state. This phenomenon is mathematically represented very successfully by the "dual-sorption mode" model and distinguishes the sorption process between polymers in glassy and rubbery states. In most cases, the contribution of excess free volume to the overall gas transport within a glassy polymer is minor. However, under certain circumstances, this might be the primary gas transport path for a specific polymer. We believe this is exactly the case for PTMSP. PTMSP has a rigid, irregular, and noninterconvertible conformation which renders tight packing more difficult. Additionally, the pendent methyl and trimethylsilyl groups combine to provide a very low London dispersion force. These parameters result in PTMSP coming out of solution as a very loosely packed film with a large excess free volume. This is exemplified in its low density (0.79–0.81 g/cm^3) and very high gas permeability. Since this is basically a metastable state for PTMSP, thermal treatment can be visualized as improving the vibrational amplitude which densifies packing, reduces excess free volume, and decreases the gas permeability. Alternatively, replacing the methyl group adjacent to silicon by other alkyl or aryl groups improves the interaction force, fills up the void space, and decreases the gas permeability.

4. Conclusion. This study prompts us to suggest that the extraordinarily high gas permeability and unusual physical properties of PTMSP are due to two major factors. They are (1) a *rigid, nonlinear, and irregular main-chain conformation* and (2) a *low interpolymer chain–chain interaction.* Combination of these two factors creates a large excess free volume within PTMSP. This large excess free volume contributes to the extremely high gas permeability of PTMSP. The generally accepted process of gas transport through the glassy polymers can be used to completely rationalize the abnormally high gas permeability of PTMSP. However, this investigation shows that it is possible to improve a glassy polymer's gas permeability by increasing the contribution from the excess free volume, and this can be done by *manipulating the polymer's intramolecular conformation and interpolymer interaction.* Other highly gas permeable polymer systems can be similarly rationalized. We will be reporting on extensions of this work in the near future.

References and Notes

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