

Gas Permeability of Polyacetylenes Carrying Substituents

KOICHI TAKADA* and HIDEHIKO MATSUYA, *Technological Research Department, Sanyo Chemical Industry, Ltd., Kyoto 605, Japan*, and
TOSHIO MASUDA* and TOSHINOBU HIGASHIMURA, *Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan*

Synopsis

The gas permeabilities of three polyacetylene films, prepared from poly[1-(trimethylsilyl)-1-propyne], poly(*tert*-butylacetylene), and poly(1-chloro-2-phenylacetylene), were studied. Although depending on conditions of polymerization and membrane preparation, typical permeability coefficients P of the polymers to oxygen and nitrogen at 25°C were as follows: poly[1-(trimethylsilyl)-1-propyne], $P_{O_2} = 40 \times 10^{-8}$, $P_{N_2} = 20 \times 10^{-8}$; poly(*tert*-butylacetylene), $P_{O_2} = 3.0 \times 10^{-8}$, $P_{N_2} = 1.0 \times 10^{-8}$; poly(1-chloro-2-phenylacetylene), $P_{O_2} = 9.4 \times 10^{-10}$, $P_{N_2} = 2.0 \times 10^{-10}$ cm³(STP) · cm/(cm² · s · cm Hg). Thus P_{O_2} of a poly[1-(trimethylsilyl)-1-propyne] film is the largest among those ever known, and the values of poly(*tert*-butylacetylene) and poly(1-chloro-2-phenylacetylene) films are also fairly large. Influences of polymer structure, measuring temperature, and so forth on the P_{O_2} and P_{N_2} of these polyacetylene films were studied. The possibility of applying these films to oxygen enrichment of air are being discussed.

INTRODUCTION

Membranes for gas separation have recently received much attention since membrane processes have the potential for energy efficient operation.¹ Essential requirements to such membranes are high permeability and high permselectivity for a particular gas. Polydimethylsiloxane has been known to show the highest permeability coefficient P to oxygen among the existing polymers: $P_{O_2} = 6.0 \times 10^{-8}$ cm³(STP) · cm/(cm² · s · cm Hg). This polymer, however, is a rubbery material, and difficult to cast into thin films. [P is usually given in the units of cm³(STP) · cm/(cm² · s · cm Hg), which will be often omitted for simplicity in the following text.]

We have found that catalysts based on group 5 and 6 transition metals (Nb, Ta, Mo, and W) are capable of polymerizing many substituted acetylenes.² One important feature of these catalysts is that they are especially effective to sterically fairly hindered acetylenes such as 1-(trimethylsilyl)-1-propyne, *tert*-butylacetylene, and 1-chloro-2-phenylacetylene; no other kind of catalysts can polymerize these monomers. Unlike polyacetylene, these polymers, obtained from sterically hindered acetylenes, are stable in air at room temperature over a long period of time. Polyacetylenes have alternating double bonds along the main chain and may show unique properties that are not expected from vinyl polymers. As an example we have

* To whom correspondence should be addressed.

preliminarily reported that poly[1-(trimethylsilyl)-1-propyne] films show an oxygen permeability even higher than that of polydimethylsiloxane films.³ Other polyacetylene films are also fairly permeable to oxygen.⁴

The present paper reports on the gas permeability of three polyacetylene films stable in air at room temperature, that is, films of poly[1-(trimethylsilyl)-1-propyne], poly(*tert*-butylacetylene), and poly(1-chloro-2-phenylacetylene): The permeabilities of various gases through these films have been revealed. Further, oxygen permeability (P_{O_2}) and permselectivity of oxygen to nitrogen (P_{O_2}/P_{N_2}) have been studied in detail. The possibility of applying these polymers as membranes for oxygen enrichment is discussed.

EXPERIMENTAL

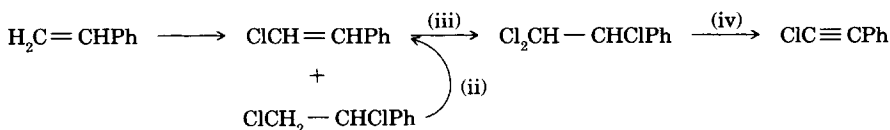
Monomer Syntheses

1-(Trimethylsilyl)-1-propyne. This synthesis was carried out under dry nitrogen. Hexane solution of butyllithium (1.6*M*, 700 mL) was concentrated by evaporation of hexane (450 mL), and then diluted by addition of ether (600 mL). Propyne (1.0 mol, 40 g) was bubbled into this solution cooled at -30°C . The resulting white creamy solution was stirred at room temperature for 1 h. Subsequently, chlorotrimethylsilane (0.90 mol, 98 g) was added dropwise at 0°C , and the solution was refluxed for 3 h. After confirmation of the complete conversion of chlorotrimethylsilane by gas chromatography, water (500 mL) was added. The solution was vigorously shaken, the upper layer was separated off, and the aqueous layer was extracted with ether. The solution was dried with anhydrous sodium sulfate overnight, it was fractionally distilled, and the fraction boiling around 100°C was collected: bp $99\text{--}100^\circ\text{C}$, yield 65%, purity 98% (lit. bp $99\text{--}100^\circ\text{C}/760$ mm Hg).⁵

1-(Alkyldimethylsilyl)-1-propyne. The procedure for 1-(dimethyl-*n*-hexylsilyl)-1-propyne is stated as an example: To a mixture of 1-hexene (1.0 mol, 84 g), chloroplatinic acid (0.50 mmol, 205 mg), and hexane (300 mL), chlorodimethylsilane (1.0 mol, 95 g) was added dropwise at ca. 60°C under nitrogen. The solution was refluxed over a period of 1 h to complete the reaction. Hexane was then removed by evaporation, and the residue was distilled, giving chlorodimethyl-*n*-hexylsilane: bp $102\text{--}103^\circ\text{C}/50$ mm Hg, yield 74%, purity 96%. The second step (the reaction of this silane with 1-propynyllithium) is essentially the same as the above-stated synthesis of 1-(trimethylsilyl)-1-propyne: bp $94\text{--}96^\circ\text{C}/8$ mm Hg, yield 79%, purity 97%.

***tert*-Butylacetylene.** This monomer was prepared by the literature method⁶ from pinacolone by chlorination and subsequent dehydrochlorination.

1-Chloro-2-phenylacetylene. Though other synthetic methods for this monomer⁷ (e.g., reaction of lithium phenylacetylide with chlorine^{7a}) had been known, we prepared it as follows:



(i) A mixed gas of chlorine and nitrogen (vol ratio 3:1) was bubbled into styrene (5.0 mol, 520 g) with stirring and keeping the temperature below 50°C. On bubbling chlorine at 1200 mL/min, styrene reacted completely in 90 min, and the system turned pale yellow. Then bubbling of nitrogen was continued for a while to remove the evolved hydrogen chloride completely. The chlorination product weighed ca. 800 g and consisted of β -chlorostyrene (30 wt %), α , β -dichloroethylbenzene (60 wt %), and others.

(ii) A mixture of the above chlorination product (200 g) and nickel(II) chloride (5.0 g) was heated to 160–170°C. Hydrogen chloride ceased to evolve in ca. 3 h, and then the complete conversion of α , β -dichloroethylbenzene was confirmed by gas chromatography. Distillation of the reaction mixture gave 145 g of β -chlorostyrene: bp 90–95°C/20 mm Hg, yield 0%.

(iii) Chlorination of β -chlorostyrene was carried out just as that of styrene, (i). Hydrogen chloride hardly evolved.

(iv) To a mixture of potassium hydroxide (180 g), water (180 g), and benzyltrimethylammonium chloride (4.0 g), α , β , β -trichloroethylbenzene (168 g) was added dropwise over a period of 1 h at 70°C under stirring. The reaction was completed by stirring at that temperature for 1 h, and then 300 g of water were added. The organic layer was separated off, and distilled at reduced pressure: bp 52–53°C/3 mm Hg (lit. bp 66°C/17 mm Hg^{7a}), yield 87 g.

Polymerization and Polymer Characterization

According to the methods described elsewhere, 1-(trimethylsilyl)-1-propyne was polymerized with group 5 transition metal chlorides^{3,8} (TaCl_5 , NbCl_5) as catalysts, *tert*-butylacetylene with group 6 transition metal-based catalysts MoCl_5 , WCl_6 ,⁹ $\text{Mo}(\text{CO})_6\text{-CCl}_4\text{-}h\nu$, $\text{W}(\text{CO})_6\text{-CCl}_4\text{-}h\nu$,¹⁰ and 1-chloro-2-phenylacetylene with Mo-based catalysts $\text{Mo}(\text{CO})_6\text{-CCl}_4\text{-}h\nu$,¹¹ and $\text{MoCl}_5\text{-Et}_3\text{SiH}$.¹² The following are the standard polymerization conditions to obtain polymer samples for the preparation of membranes. 1-(Trimethylsilyl)-1-propyne³: $[\text{TaCl}_5] = 20 \text{ mM}$, $[\text{M}]_0 = 1.0\text{M}$, in toluene, 80°C, 24 h (polymer yield 100%, $\bar{M}_w 8.5 \times 10^5$). *tert*-Butylacetylene⁹: $[\text{MoCl}_5] = 20 \text{ mM}$, $[\text{M}]_0 = 1.0\text{M}$, in toluene, 30°C, 24 h (polymer yield 100%, $\bar{M}_n 3.0 \times 10^5$, cis content 76%). 1-Chloro-2-phenylacetylene¹¹: $[\text{Mo}(\text{CO})_6] = 10 \text{ mM}$, $[\text{M}]_0 = 1.0\text{M}$, in CCl_4 , 30°C, 24 h; the catalyst was UV irradiated at 30°C for 1 h before use (polymer yield 80%, $\bar{M}_w 2.0 \times 10^6$). The polymers formed were isolated by precipitation in large amounts of methanol, filtered off, and dried.

Molecular weights of polymers were calculated from their viscosities by using viscosity–molecular weight relationships obtained earlier. Equations: 1-(trimethylsilyl)-1-propyne,⁸ *tert*-butylacetylene,⁹ and 1-chloro-2-phenylacetylene.¹¹ The intrinsic viscosities of polymers were measured in toluene at 30°C. The geometric structure of poly(*tert*-butylacetylene) was determined by ¹³C NMR.¹⁰

Preparation of Membranes

Toluene for membrane preparation was distilled from calcium hydride to remove small amounts of water. A solution of the polymer in toluene (1–5 wt/vol %) was cast on a glass plate with a doctor's knife (200–1000 μm), and then dried at room temperature for several days to evaporate

most of the solvent slowly. The residual solvent was completely removed *in vacuo*. This procedure provided a homogeneous membrane with a uniform thickness of 10–50 μm .

To study effects of heat treatment, membranes were kept in air at given temperatures for given times before use.

Measurement of Gas Permeability

The permeability coefficients were determined on a K-315-N gas permeability apparatus (Rikaseiki Co., Japan) equipped with a MKS Baratron detector. The principle of measurement is to evacuate the downstream side of the membrane (7.0 cm^2 disc) to about 0.1 mm Hg, provide the upstream side with a permeate at about 1 atm, and monitor the increase in pressure in a fixed downstream receiving volume. Permeation coefficients P were calculated from slopes in the steady-state (where Fick's law holds) time–pressure relationship.

RESULTS AND DISCUSSION

Permeability of Various Gases

Table I lists permeability coefficients of three polyacetylene films to various gases. Very interestingly, poly[1-(trimethylsilyl)-1-propyne] films show permeability coefficients as high as 10^{-7} – 10^{-6} to every gas. However, permselectivities of these films for two different gases are relatively poor. When compared with poly(dimethylsiloxane) films, the P_{O_2} of poly[1-(trimethylsilyl)-1-propyne] films is about 10 times larger, and the ratio $P_{\text{O}_2}/P_{\text{N}_2}$ is ca. 2, virtually the same as that of polydimethylsiloxane films.

Poly(*tert*-butylacetylene) films possess gas permeabilities of 10^{-8} – 10^{-7} , which are similar to those of polydimethylsiloxane films. When inspected in more detail, however, the permselectivity of poly(*tert*-butylacetylene) films for two kinds of gases differ appreciably from those of polydimethylsiloxane. For example, poly(*tert*-butylacetylene) is superior in $P_{\text{O}_2}/P_{\text{N}_2}$ to polydimethylsiloxane.

TABLE I
Permeability of Various Gases through Polyacetylenes^a

Polymer	-(C=C)_n	-(CH=C)_n	-(C=C)_n
	$\begin{array}{c} \quad \\ \text{CH}_3 \text{ SiCH}_3 \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \\ t\text{Bu} \end{array}$	$\begin{array}{c} \quad \\ \text{Cl} \quad \text{Ph} \end{array}$
O_2	40×10^{-8}	3.0×10^{-8}	8.0×10^{-10}
N_2	20×10^{-8}	1.0×10^{-8}	1.7×10^{-10}
CO_2	180×10^{-8}	13.6×10^{-8}	61.0×10^{-10}
CH_4	42×10^{-8}	1.6×10^{-8}	2.6×10^{-10}
He	41×10^{-8}	8.1×10^{-8}	34.8×10^{-10}
H_2	69×10^{-8}	11.5×10^{-8}	44.8×10^{-10}
$P_{\text{O}_2}/P_{\text{N}_2}$	2.0	3.0	4.7
$P_{\text{CO}_2}/P_{\text{CH}_4}$	4.3	8.5	23.5

^a At 25°C, in unit of $\text{cm}^3(\text{STP})/(\text{cm}^2\text{cm Hg})$.

Permeability coefficients of poly(1-chloro-2-phenylacetylene) range from 10^{-10} to 10^{-9} , not very large compared with many other polymers. It should, however, be noted that its P_{O_2}/P_{N_2} is one of the highest values among those of various polymers. Further, the P_{CO_2}/P_{CH_4} of poly(1-chloro-2-phenylacetylene) is even larger than that of MEM-079 ($P_{CO_2}/P_{CH_4} = 20$)¹³ which has been used for the separation of CO_2 from CH_4 . Therefore, this polyacetylene will be useful for removal of CO_2 both from souer (CO_2 -containing) natural gas and from biogas obtained by the CH_4 -evolving fermentation.

It can be concluded that, in general, these polyacetylene films are highly permeable to gases, when they are compared with vinyl polymer films having similar substituents: poly[1-trimethylsilyl]-1-propyne] vs. poly(vinyltrimethylsilane)¹⁴ ($P_{O_2} = 3.6 \times 10^{-9}$, $P_{N_2} = 0.8 \times 10^{-9}$); poly(*tert*-butylacetylene) vs. poly(4-methyl-1-pentene)¹⁵ ($P_{O_2} = 32 \times 10^{-10}$, $P_{N_2} = 7.8 \times 10^{-10}$); poly(1-chloro-2-phenylacetylene) vs. poly(vinyl chloride)¹⁵ ($P_{O_2} = 4.5 \times 10^{-12}$, $P_{N_2} = 1.2 \times 10^{-12}$) and polystyrene¹⁵ ($P_{O_2} = 26 \times 10^{-11}$, $P_{N_2} = 7.9 \times 10^{-11}$).

Polydimethylsiloxane and *cis*-polyisoprene are rubbery polymers, and their very high gas permeabilities have been attributed mainly to their flexible backbones and resultant high free volumes. On the other hand, poly[1-(trimethylsilyl)-1-propyne], poly(*tert*-butylacetylene), and poly(1-chloro-2-phenylacetylene) are amorphous according to the X-ray diffraction,^{3,9,11} and their glass transition temperatures (T_g) are all above 200°C.¹⁶ Therefore, it is very interesting and important that these polyacetylenes show high gas permeability irrespective of being glassy polymers around room temperature.

The main chain of polyacetylenes possesses the following characteristics associated with gas permeation: (i) Since it comprises alternating double bonds, it is stiffer than that of vinyl polymers, which is endorsed by large values of exponent a in the viscosity-molecular weight relationship.^{3,9,11} This stiffness enables the formation of tough films. (ii) The double bonds along the main chain may have an affinity for oxygen, which will contribute to the P_{O_2} of polyacetylene films.

The following arguments might apply to the interpretation of effects of the substituents on the gas permeabilities of the corresponding membranes: (i) The trimethylsilyl and *tert*-butyl groups possess large three-dimensional bulks, bringing about the increase of free volumes; (ii) the trimethylsilyl group might weaken the interpolymeric interaction due to the nature of silicon in poly[1-(trimethylsilyl)-1-propyne], which will endow a high flux; (iii) phenyl groups can stack one another, resulting in an aggregated membrane structure unfavorable to gas permeation; (iv) chlorine will also contribute to an aggregation of polymer molecules due to its polarity.

It is a future problem why these polyacetylene films, especially a poly[1-(trimethylsilyl)-1-propyne] film, show high gas permeabilities. The solution will be obtained when the permeation mechanism has been studied in detail. Here, we refer to two possible reasons for the high gas permeabilities: One is that, although the main chains are rather stiff, the substituents are mobile enough, which endows the polymers with sufficient free volumes. The other is that these glassy polymers have holes (diameter $< 5 \text{ \AA}$), gas permeation proceeding through Langmuir's sorption into them as well as

through Henry's law dissolution. The second speculation could be examined by the pressure dependence of gas permeability.^{17,18} Anyhow, it can be concluded that no pores (diameter > 10 Å) exist in these polyacetylene films because the gas permeability does not vary inversely as the square root of the molecular weight of permeates.

In the following sections, the oxygen permeability and permselectivity of the three polyacetylenes will be described in detail.

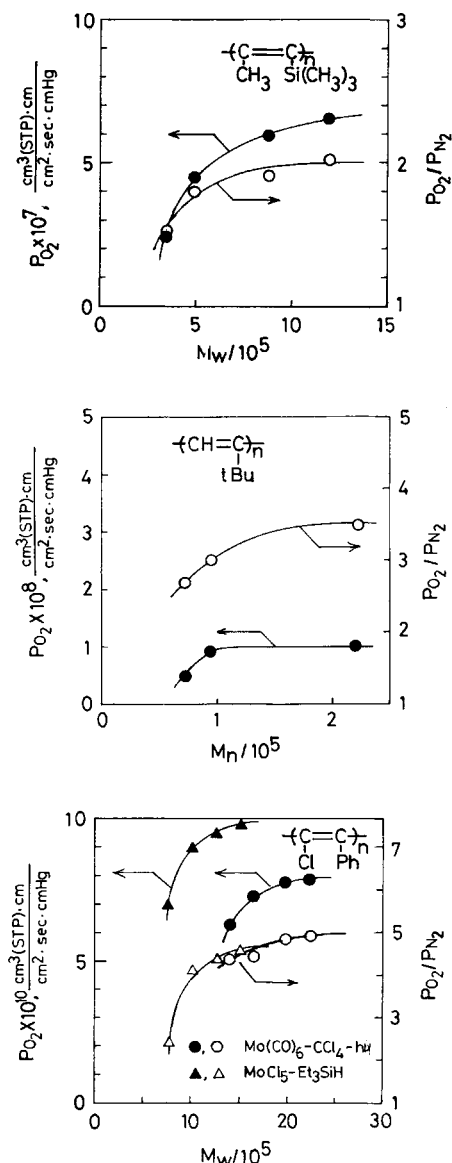


Fig. 1. Effect of polymer molecular weight on oxygen permeability and selectivity (25°C): (a) poly[1-(trimethylsilyl)-1-propyne]; (b) poly(*tert*-butylacetylene); (c) poly(1-chloro-2-phenylacetylene): (●,○) $\text{Mo(CO)}_6\text{-CCl}_4\text{-}h\nu$; (▲,△) $\text{MoCl}_5\text{-Et}_3\text{SiH}$.

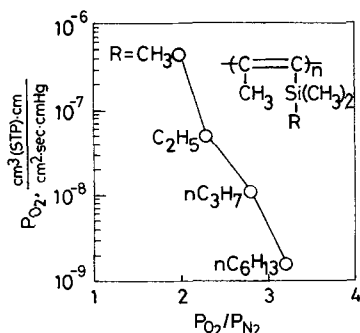


Fig. 2. Dependences of oxygen permeability and selectivity on the alkyl group of poly[1-(alkyldimethylsilyl)-1-propyne] (25°C).

Effects of Polymer Molecular Weight and Structure on P_{O_2} and P_{O_2}/P_{N_2}

Figure 1 shows the dependences of P_{O_2} and P_{O_2}/P_{N_2} on polymer molecular weight for the three polyacetylenes. The polymer samples with different molecular weights were prepared by varying only the monomer concentration without changing any other polymerization condition. For every polymer, not only P_{O_2} but also P_{O_2}/P_{N_2} increased and gradually leveled off with increasing molecular weight. Therefore, it is desirable for oxygen enrichment to use polymers having molecular weights as high as possible.

When one of the methyl groups on the silicon in poly[1-(trimethylsilyl)-1-propyne] was replaced by longer alkyl groups (plasticizing effect expected), then P_{O_2} decreased and P_{O_2}/P_{N_2} increased; the longer the alkyl group the more remarkable the tendency (Fig. 2). This might be due to the fact that the longer alkyl groups render the polymers less flexible and reduce their free volumes.

The geometric structure of poly(*tert*-butylacetylene) can be evaluated from its ¹³C NMR spectrum.¹⁰ By choosing polymerization conditions, especially the kind of catalyst, it is possible to control the *cis* content in a range of 50–100%. Figure 3 shows effects of the geometric isomerism of poly(*tert*-butylacetylene) on P_{O_2} and P_{O_2}/P_{N_2} . With increasing *cis* content,

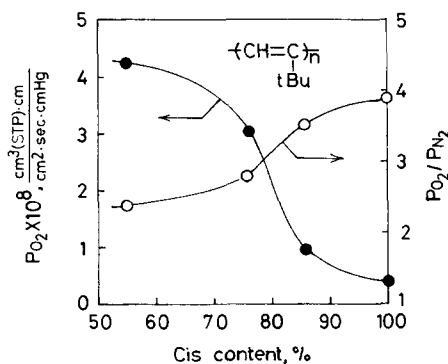


Fig. 3. Effect of the geometric structure of poly(*tert*-butylacetylene) on oxygen permeability and selectivity (25°C).

P_{O_2} decreased and P_{O_2}/P_{N_2} increased. This is explained as follows: As the *cis* content increases and approaches 100%, the polymer structure becomes more regular, resulting in a more aggregated membrane structure.

Thermal Effect and Activation Energy

A trend that P_{O_2} decreases and P_{O_2}/P_{N_2} increases was generally observed on heat treatment of polymers around 100°C or above (see Fig. 4). When poly[1-(trimethylsilyl)-1-propyne] films were heated at 100°C for 15 h, their P_{O_2} decreased to become 1/10 of the original value, while P_{O_2}/P_{N_2} increased

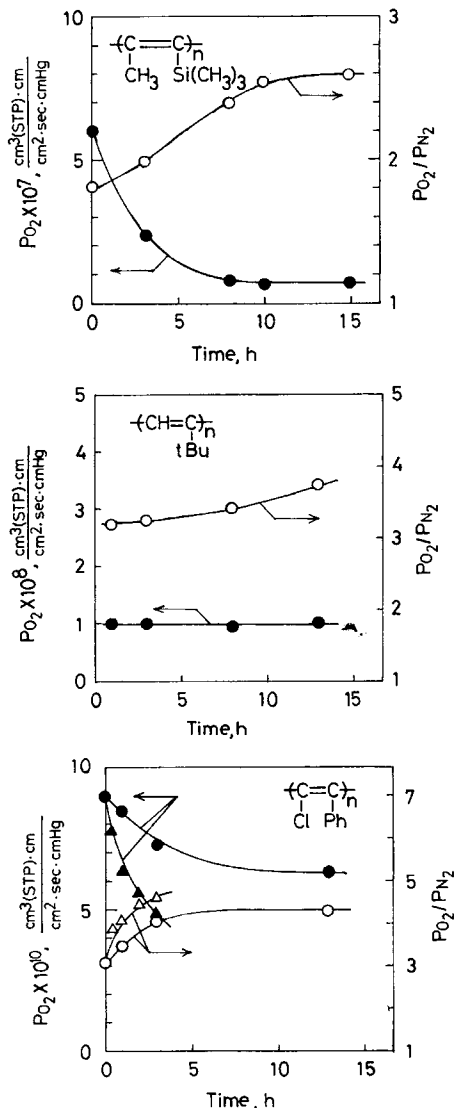


Fig. 4. Effect of heat treatment on oxygen permeability and selectivity (measured at 25°C): (a) 100°C, poly[1-(trimethylsilyl)-1-propyne]; (b) 70°C, poly[*tert*-butylacetylene]; (c) (●,○) 70°C, (▲,△) 140°C, poly(1-chloro-2-phenylacetylene).

from ~ 2.0 to ~ 2.6 . No such change was seen by heat treatment of this polymer at 50°C for 15 h. Poly(*tert*-butylacetylene) did not show large changes in P_{O_2} and $P_{\text{O}_2}/P_{\text{N}_2}$ with heat treatment at 70°C ; since poly(*tert*-butylacetylene) was somewhat unstable in air above 100°C , heat treatment at higher temperature was not examined. The P_{O_2} of poly(1-chloro-2-phenylacetylene) was reduced and its $P_{\text{O}_2}/P_{\text{N}_2}$ was enhanced by heat treatment above ca. 70°C ; the trend was more significant when the polymer was heated at a higher temperature and/or for a longer time. At temperatures at which the thermal effect was studied, no change in the molecular weights, IR spectra, and mechanical properties of the polymers occurred.¹⁸

Such effects of heat treatment can be interpreted as follows: When a membrane is kept at a high temperature, then it becomes more aggregated or, from another respect, it gets relaxed and holes which might take part in sorbing and transporting gases become smaller. This will make the membrane less permeable and more permselective.

Temperature dependences of the P_{O_2} and P_{N_2} of three polyacetylenes were studied, and their activation energies were evaluated by the Arrhenius plot. The measurements of P_{O_2} and P_{N_2} were carried out, starting from low temperature, in a range of 10 – 50°C in which the effect of heat treatment is negligible. The results are shown in Figure 5.

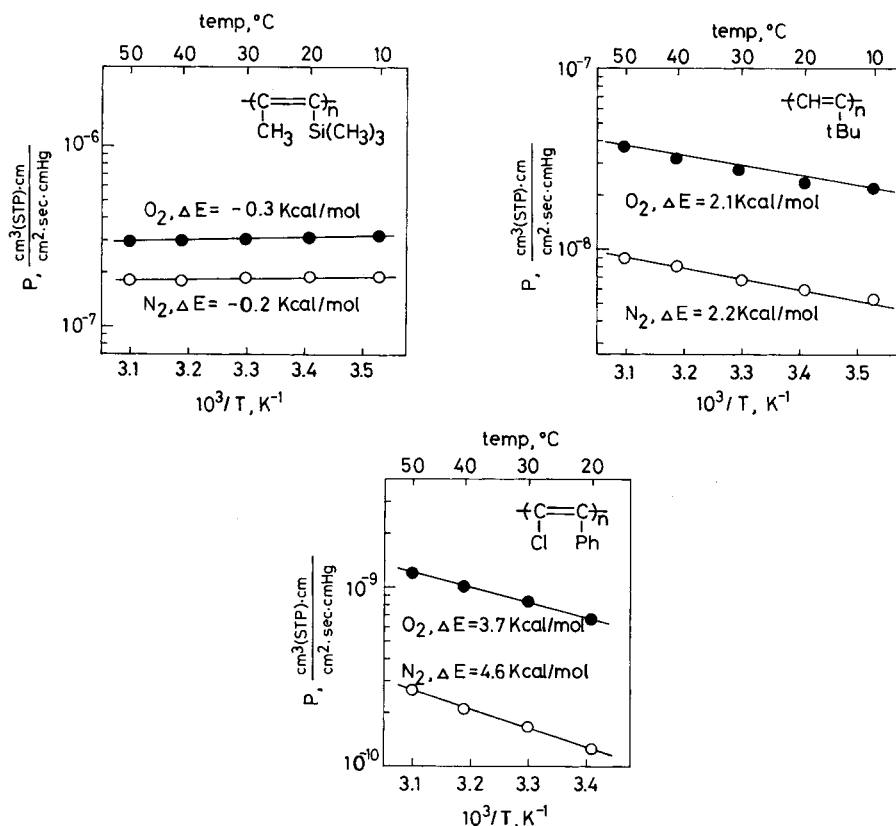


Fig. 5. Arrhenius plots of the permeabilities of oxygen and nitrogen: (a) poly[1-(trimethylsilyl)-1-propyne]; (b) poly(*tert*-butylacetylene); (c) poly(1-chloro-2-phenylacetylene).

It is of great interest that the activation energies for the P_{O_2} and P_{N_2} of poly[1-(trimethylsilyl)-1-propyne] films are very small negative values, which can be regarded as virtually zero. The permeability coefficient P at steady state is defined as the product of S and D ($P = S \times D$), which are the sorption and diffusion coefficients, respectively. Therefore, the activation energy for P is the sum of those for S and D . Determination of each activation energy for S and D will enable a more detailed discussion of the permeation mechanism. Further study on this subject is in progress.

With both poly(*tert*-butylacetylene) and poly(1-chloro-2-phenylacetylene) films, P_{O_2} increased and P_{O_2}/P_{N_2} slightly decreased with increasing temperature. This is a trend observed with most polymer membranes. Poly(1-chloro-2-phenylacetylene) films are less permeable than poly(*tert*-butylacetylene) films, and, as expected from this, the former polymer showed larger values of activation energy than the latter did.

On the Possibility of Applying to Oxygen Enrichment of Air

The oxygen concentration of air after permeation through a membrane, X_{O_2} , is given by the following equation:¹⁹

$$X_{O_2} = \frac{(\alpha - 1)(r + 0.21) + 1 - \sqrt{[(\alpha - 1)(r + 0.21) + 1]^2 - 4r(\alpha - 1) \cdot \alpha \cdot 0.21}}{2r(\alpha - 1)}$$

where α and r are defined as

$$\alpha \equiv \frac{P_{O_2}}{P_{N_2}}, \quad r \equiv \frac{\text{Pr}(L)}{\text{Pr}(H)}$$

[$\text{Pr}(H)$ and $\text{Pr}(L)$ are the respective upstream and downstream pressures (cm Hg)]

Poly[1-(trimethylsilyl)-1-propyne] films possess an extremely high value of P_{O_2} . Moreover, unlike rubbery polymers, this polymer can be fabricated into a membrane as thin as 0.1 μm , which favors the achievement of a very high flux. As its P_{O_2}/P_{N_2} is 2.0, the oxygen concentration of the oxygen-enriched air obtained will be 30–35%, not very high, at $\text{Pr}(H) = 76$ cm Hg and $\text{Pr}(L) = 15$ cm Hg. Therefore, this polymer could find application in the fields which do not require very high oxygen concentrations, such as for combustion furnaces and car engines.

On the other hand, the P_{O_2} of poly(1-chloro-2-phenylacetylene) is not very high ($\sim 10^{-9}$). However, it can afford at $\text{Pr}(H) = 76$ cm Hg and $\text{Pr}(L) = 15$ cm Hg an air whose oxygen concentration is as high as 45–50% since its P_{O_2}/P_{N_2} ranges from 4 to 5. Thus this polymer might be useful for breathing systems such as curers for respiratory diseases.

Poly(*tert*-butylacetylene) behaves in an intermediate way between poly[1-(trimethylsilyl)-1-propyne] and poly(1-chloro-2-phenylacetylene) with respect to both P_{O_2} and P_{O_2}/P_{N_2} . Consequently, it can be used for various purposes.

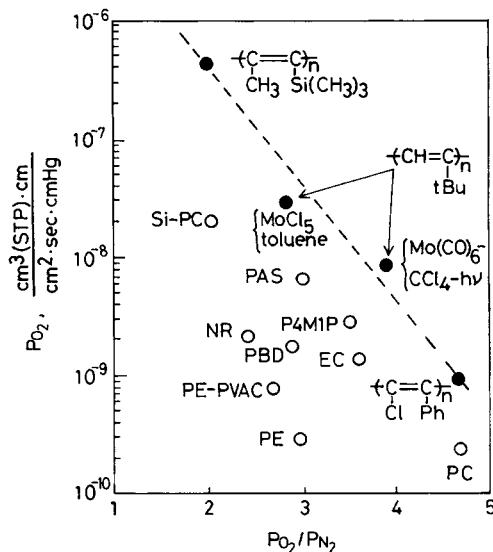


Fig. 6. Oxygen permeabilities and selectivities of polyacetylenes and other polymers (25°C): Si-PC, silicone/polycarbonate block copolymer; PAS, polyalkylsulfone (C_{16}); P4M1P, poly(4-methyl-1-pentene); NR, natural rubber; PBD, *cis*-1,4-polybutadiene; EC, ethyl cellulose; PE-PVAC, ethylene/vinyl acetate copolymer; PE, polyethylene, PC, polycarbonate (data for the polymers other than polyacetylenes are from Refs. 1, 15, and 17).

Figure 6 plots P_{O_2} vs. P_{O_2}/P_{N_2} for films (membranes) prepared from three polyacetylenes and various polymers for the sake of comparison. It is obvious from this figure that poly[1-(trimethylsilyl)-1-propyne], poly(*tert*-butylacetylene), and poly(1-chloro-2-phenylacetylene) films possess remarkably high values of P_{O_2} and/or P_{O_2}/P_{N_2} in comparison to permeabilities of films cast from other known film-forming polymers.

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