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# Gas Permeability of Polyacetylenes with Bulky Substituents

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## SUMMARY

In search of new materials for oxygen-enrichment membranes, high polymers of acetylenes with bulky substituents [2-octyne (1), 2-decyne (2), t-butylacetylene (3), 1-phenyl-1-propyne (4), and 1-chloro-2-phenylacetylene (5)] were synthesized with Mo- or Ta-based catalysts, and their permeability coefficients to oxygen ($P_{O_2}$), nitrogen ($P_{N_2}$), and carbon dioxide were determined at 25°C. Polymer membranes of the aliphatic acetylenes (1 - 3) were highly permeable to oxygen. In particular, poly(3) showed a large $P_{O_2}$ value in the order of $10^{-8}$ [$cm^3(STP)\cdot cm/cm^2\cdot sec\cdot mmHg$] together with a fairly high permselectivity for oxygen ($P_{O_2}/P_{N_2} \sim 3$). Polymers of the aromatic acetylenes (4 and 5) were less oxygen-permeable, giving $P_{O_2}$ in the order of $10^{-10}$, slightly larger than that for polystyrene.

## INTRODUCTION

Polymer membranes with both high permeability and permselectivity for gases have recently been under very active research and development for commercialization (1,2). Thanks to recent advance in membrane technology that has enabled preparation of ultrathin films, gas separation using polymer membranes is now almost ready for practical applications.

Membrane-based oxygen enrichment, in particular, is quite attractive in view of its potential versatility. Among existing polymeric materials, silicon polymers exhibit the highest permeability coefficient to oxygen ($P_{O_2}$), followed by diene polymers. Not only these rubbery materials but polymers with bulky substituents, e.g., poly(4-methylpentene-1) and ethyl cellulose, have relatively large $P_{O_2}$ values as well.

The good gas permeability of rubbery polymers is due to thermal movement of their flexible backbones, but this characteristic in turn renders them very difficult to fabricate into thin films. Combination of a rigid backbone and a flexible side-chain may, therefore, lead to highly gas-permeable polymers that are tractable into strong thin membranes. Synthesis of such polymers, however, is difficult in general; only one successful example to date is poly(alkyl sulfone) having a long substituent (3).

Using transition metal catalysts, we recently obtained high polymers from acetylenes with bulky substituents (4 - 8). Since these acetylenic polymers have a rigid backbone consisting of alternating double bonds, we then expected that, given a bulky substituent, they might be both highly gas-permeable and easy to fabricate into thin membranes. This communication concerns excellent gas permeability of polymer membranes of aliphatic acetylenes. For comparison's sake, poly(aromatic acetylene)s were also examined for gas permeability.

## EXPERIMENTAL

Materials. Commercial 2-octyne, 2-decyne, and 1-phenyl-1-propyne (all from Farchan Labs) were distilled over $CaH_2$ before use (purity >99 %). t-Butylacetylene was prepared from pinacolone (3,3-dimethyl-2-butanone) by the literature method (purity >99 %) (9, 10). 1-Chloro-2-phenylacetylene was used as donated by Sanyo Chemical Industries (purity >98 %).

$MoCl_5$, $Mo(CO)_5$, and $TaBr_5$ (all from Alfa Ventron) were used as commercially supplied. Tetraphenyl tin ($Ph_4Sn$) was recrystallized from $CCl_4$ several times. Polymerization solvents (toluene and $CCl_4$) were washed with aqueous acid and alkali solutions, dried over $CaCl_2$, and distilled over $CaH_2$ just before use.

Polymer Synthesis. The five monomers [2-octyne (4), 2-decyne (4), t-butylacetylene (5), 1-phenyl-1-propyne (6) and 1-chloro-2-phenylacetylene (7,8)] were polymerized in solution under dry nitrogen, as described proviously. Product polymers were precipitated from the reaction mixture into excess methanol, filtered off, washed with methanol, and dried in vacuo. Their molecular weights ($\bar{M}_W$) were measured by light scattering. Table 1 summarizes these data along with synthesis conditions.

Table 1

Polymerization of Acetylenes with Bulky Groups (Solvent; Toluene, 30°C, 24 hr)

| Monomer | Catalyst | $[M]_0$ (mol/l) | $[C]_0$ (mmol/l) | Yield (%) | $MW \times 10^{-4}$ |
|---|---|---|---|---|---|
| $CH_3C{\equiv}C(CH_2)_4CH_3$ | $MoCl_5 \cdot Ph_4Sn$ | 0.50 | 30 | 63 | 50 |
| $CH_3C{\equiv}C(CH_2)_6CH_3$ | $MoCl_5 \cdot Ph_4Sn$ | 0.50 | 30 | 50 | 50 |
| $HC{\equiv}CtBu$ | $MoCl_5$ | 1.0 | 20 | 100 | 60 |
| $CH_3C{\equiv}CPh$ a) | $TaBr_5$ | 1.0 | 20 | 57 | 90 |
| $ClC{\equiv}CPh$ b) | $Mo(CO)_6$-hν | 1.0 | 10 | 81 | 200 |

a) 80°C  b) In $CCl_4$.

Gas Permeability Measurement. Membrane samples for gas permeability measurement were prepared by solution-casting: A polymer solution in toluene was poured over a glass plate, and extended with a doctor knife, and the solvent was evaporated slowly to give a homogeneous membrane with a uniform thickness of 25 - 30 μ. The permeability coefficients of the membranes (50 $cm^2$ discs) to pure gases were determined at 25°C by the pressure method on a Seikaken-type gas permeability apparatus (Rikaseiki Co.) which detects the pressure increase in a receiver cell due to the transmission of penetrant.

## RESULTS AND DISCUSSION

Table 2 lists the gas permeability coefficients of the five polymers shown in Table 1 to nitrogen, oxygen, and carbon dioxide ($P_{N_2}$, $P_{O_2}$, and $P_{CO_2}$, respectively) along with the permeability ratios (permselectivity) relative to nitrogen.

Table 2

Gas Permeability of Poly(Acetylenes) (25°C)

| Polymer | cm$^3$(STP)·cm/cm$^2$·sec·cmHg $P_{N_2}$ | $P_{O_2}$ | $P_{CO_2}$ | $P_{O_2}/P_{N_2}$ | $P_{CO_2}/P_{N_2}$ |
|---|---|---|---|---|---|
| $-\!(CH_3C{=}CnC_5H_{11})\!-$ | $1.35\times10^{-9}$ | $3.40\times10^{-9}$ | $7.76\times10^{-9}$ | 2.5 | 5.8 |
| $-\!(CH_3C{=}CnC_7H_{15})\!-$ | $1.43\times10^{-9}$ | $3.84\times10^{-9}$ | $7.63\times10^{-9}$ | 2.7 | 5.7 |
| $-\!(HC{=}CtBu)\!-$ | $3.83\times10^{-9}$ | $1.18\times10^{-8}$ | $2.32\times10^{-8}$ | 3.1 | 6.1 |
| $-\!(CH_3C{=}CPh)\!-$ | $2.78\times10^{-10}$ | $7.46\times10^{-10}$ | $2.63\times10^{-9}$ | 2.7 | 9.5 |
| $-\!(ClC{=}CPh)\!-$ | $2.32\times10^{-10}$ | $5.92\times10^{-10}$ | $1.37\times10^{-9}$ | 2.6 | 5.9 |
| $-\!(Si(CH_3)_2O)\!-$ 11) | $2.81\times10^{-8}$ | $6.05\times10^{-8}$ | $3.24\times10^{-7}$ | 2.15 | 11.5 |
| Natural Rubber 11) | $9.43\times10^{-10}$ | $2.33\times10^{-9}$ | $1.53\times10^{-8}$ | 2.47 | 16.2 |

Permeability to Oxygen. Figure 1 illustrates a diagram of $P_{O_2}$ against $P_{O_2}/P_{N_2}$ ratios for the five acetylenic polymers (Table 2) and a few existing polymers (11). Poly(2-octyne) and poly(2-decyne) showed high gas permeabilities, as expected from their structures involving flexible, long, linear side-chains. The $P_{N_2}$ and $P_{O_2}$ values for these polymers were somewhat larger than for natural rubber, though not exceeding that for polydimethylsiloxane; their $P_{O_2}/P_{N_2}$ ratios were comparable with those for the latter two polymers. The poly(2-octyne) and poly(2-decyne) can readily form flexible, non-sticky, thin membranes.

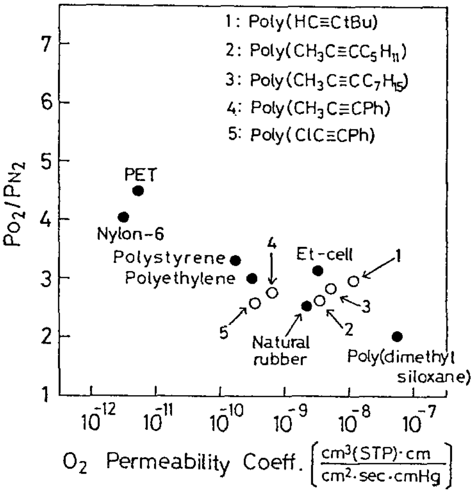

Figure 1. Gas permeability and selectivity of typical polymers and poly(acetylenes) with bulky groups at 25°C. (Et-cell; ethyl cellulose)

Interestingly, poly(t-butylacetylene) exhibited a good gas permeability with $P_{O_2}$ in the order of $10^{-8}$ and $P_{O_2}/P_{N_2}$ close to 3. The sample obtained under the conditions of Table 1 had a geometrically random backbone (cis/trans ∿3/1) (12) and gave a tough, hard film when cast from solution. Inspection of space-filling (CPK) molecular models indicates that, because of the alternating double bonds in the backbone and the bulkiness of the side-chain, the polymer chain is quite rigid, with free-rotation of the side-chains being hampered. It is therefore of particular interest that the membranes of such a rigid polymer showed good gas-permeation characteristics ($P_{O2}$ and $P_{O2}/P_{N2}$).

Gas permeability was also measured for poly(aromatic acetylene)s, i.e., poly(1-phenyl-1-propyne) and poly(1-chloro-2-phenylacetylene), as other examples of polymers with bulky substituents. The $P_{O2}$ values for these polymers of disubstituted acetylenes fell in the range of $10^{-10}$, greater than that of polystyrene, but much smaller than those of the poly(aliphatic acetylene)s. These facts show that poly(acetylene)s with bulky substituents, in general, have good gas permeabilities and that the aliphatic derivatives surpass the aromatic counterparts in permeation properties.

Permeability to $CO_2$. Inspection of Table 2 shows that the poly(acetylene)s which well permeate nitrogen and oxygen tend to permeate carbon dioxide as well. None of their $P_{CO2}$ values, however, exceeded those for existing polymers; the $P_{CO2}/P_{N2}$ ratios were as small as ca. 6. Thus, neither aliphatic nor aromatic acetylene polymers have particular permeabilities for carbon dioxide.

## CONCLUSIONS

Aliphatic 2-alkynes and t-butylacetylene yielded high polymers with group 5 or 6 transition metal compounds as catalysts, in spite of their sterically-hindered substituents. They readily formed flexible membranes that exhibited unexpectedly excellent permeability to oxygen; in particular, the $P_{O2}$ for poly(t-butylacetylene) reached the order of $10^{-8}$. These membranes are tough, non-sticky, and easy to prepare; and hence potentially useful as permselective membranes for oxygen enrichment.

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