4218 Macromolecules 1992, 25, 4218–4219

Gas Permeation in a Fluorine-Containing Polynorbornene

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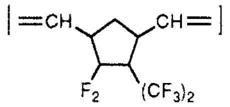
Received February 27, 1992
Revised Manuscript Received May 4, 1992

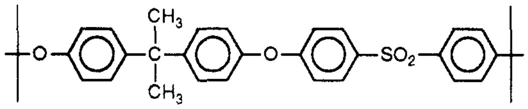
Introduction

There has been considerable interest recently in the relationship between the repeat unit molecular structure of polymers and the gas permeability characteristics of these materials[1–16] driven by the need for improved membranes for separation processes. Structures that lead to both high permeability and high selectivity for certain gas pairs like O_2/N_2, He/CH_4, and CO_2/CH_4 are sought. The most promising membrane candidates tend to have rigid backbones to suppress chain motion and substitutions that prohibit dense packing,[3,7,9,10] i.e., high fractional free volume (FFV). Polymers made by metathesis polymerization of norbornene and its derivatives have been described recently,[17–19] but investigations of their gas permeation behavior are quite limited.[14–16] The purpose here is to report the gas transport properties of poly[5,5-difluoro-6,6-bis(trifluoromethyl)norbornene] (DFHFPNB)



and compare them with other pertinent polymers. This polymer and other fluorine-containing norbornene derivatives were synthesized by metathesis polymerization at the A. V. Topchiev Institute of Petrochemical Synthesis using procedures and a catalyst developed there[19] that yield a mixture of cis/trans bonds in the repeat unit, typically in a ratio of about 2 to 1. A more detailed stereochemical characterization of this material is not available at this time.

Comparisons will be made with the polysulfone (PSF)



that has been used for more than a decade to form commercial hollow fiber gas separation membranes.[20] In addition, comparisons will be made with modifications to PSF[9,10] that have four methyl groups symmetrically placed on the Bisphenol A monomer [tetramethylpolysulfone (TMPSF)] to open up free volume, the isopropylidene unit replaced with a hexafluoroisopropylidene [hexafluoropolysulfone) (HFPSF)] to stiffen the chain among other things, and both of these substitutions combined [tetramethylhexafluoropolysulfone TMHFPSF)]. Finally, DFHFPNB will be compared to unsubstituted polynorbornene (PNB), which unlike all the other polymers considered here is in the rubbery state at the temperature where permeability measurements were made, 35 °C, and with some substituted polynorbornenes.

Experimental Section

The DFHFPNB sample investigated had $\bar{M}_w = 112\,600$ and $\bar{M}_w/\bar{M}_n \sim 1.24$ (data courtesy of O. Semenov of the Topchiev Institute). Films were cast from methyl ethyl ketone solution onto aluminum foil coated with Teflon. After casting, the films were placed in a vacuum oven for 1 month at 35 °C. Thermogravimetric analysis confirmed that all of the residual solvent was removed by this procedure. Differential scanning calorimetry to 400 °C revealed no crystallinity and produced the glass transition information shown in Table I.

Films of thicknesses l in the range of 50–60 μm were used for permeability measurements at 35 °C using techniques described previously.[21] All gases were of chromatographic grade having purities of 99.97% or higher. Upstream driving pressures were held within 1.5–1.7 atm. In addition to steady-state permeability coefficients, P, time lags, θ, were determined where possible and used to compute diffusion coefficients, D, from $l^2/6\theta$. Solubility coefficients, S, were calculated from $S = P/D$.

The densities of DFHFPNB films were measured in water–ethanol solutions of $ZnCl_2$. The occupied polymer chain volume, V_0, was estimated by the Bondi method[22] which combined with the specific volume, V, computed from the measured density allowed calculation of the fractional free volume

$$\text{FFV} = \frac{V - V_0}{V}$$

The results are shown in Table I and compared with those of the other polymers mentioned earlier.

Results and Discussion

Table II summarizes the transport properties measured for six gases in DFHFPNB films. Absolute permeabilities and selectivities for three gas pairs for this and the other polymers mentioned are compared in Table III. All of the modifications to PSF increase the glass transition temperature and the FFV. Largely as a consequence of the latter, the gas permeability coefficients are increased by these substitutions while the selectivities for the gas pairs shown generally remain constant with a few exceptions. Ordinarily a trade-off between permeability and selectivity is observed.[1] Substitution of the fluorine atoms and bulky trifluoromethyl groups onto the norbornene ring also raises T_g, FFV, and the permeability. The O_2 permeability is increased by 1 order of magnitude relative to that of PNB. It is quite clear that these substitutions onto the PNB ring decrease chain packing and increase gas permeability in a similar fashion as the modifications of PSF do. Interestingly, this modification of PNB considerably improves selectivity, relative to PNB, although it should be noted that this involves comparing rubbery and glassy polymers which must be done with care. Compared to the polysulfones in Table III, DFHFPNB is considerably less selective but more permeable.

These and other results[14–16] suggest metathesis polymerization of derivatives of norbornene and related monomers as a fruitful new area for investigation of structure–property relationships in the continuing search for interesting new membrane materials. Most of the work to date in this area has focused on the placement of organosilicon and/or nitrile substituents on the cyclopentane ring.[14–16] Direct comparisons with the present material at the same temperature are not possible at this time; however, it appears that only poly[5-(trimethylsilyl)-norbornene] approaches the high levels of permeability

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Table I
Physical Properties of Polymers Considered Here

polymer	T_g (°C)[a]	density (g/cm^3)[b]	fractional free volume, FFV
PSF	186	1.240	0.156
TMPSF	242	1.151	0.171
HFPSF	192	1.427	0.168
TMHFPSF	248	1.286	0.196
PNB	31	0.98	0.172
DFHFPNB	176	1.55	0.227

[a] By differential scanning calorimetry (midpoint) at 20 °C/min. [b] By density gradient column at 30 °C.

Table II
Experimental Results for DFHFPNB at 35 °C

gas	permeability (barrers)[a]	diffusivity (10^{-8} cm^2/s)	solubility (cm^3(STP)/cm^3·atm)
He	185		
H_2	122		
CH_4	9.5	13.5	0.53
CO_2	102	29.0	2.67
O_2	27.7	65.0	0.32
N_2	10.5	32.5	0.25

[a] 1 barrer = 10^{-10} cm^3(STP)·cm/cm^2·s·cmHg.

Table III
Comparison of Permselectivity Characteristics with Other Polymers

polymer	P_{He}	P_{He}/P_{CH_4}	P_{O_2}	P_{O_2}/P_{N_2}	P_{CO_2}	P_{CO_2}/P_{CH_4}
PSF[a]	13	49	1.4	5.6	5.6	22
TMPSF[a]	41	45	5.6	5.3	21	22
HFPSF[a]	33	63	3.4	5.1	12	22
TMHFPSF[b]	113	38	18	4.5	72	24
PNB[c]			2.8	1.9	15.4	6.2
DFHFPNB	185	19.5	27.7	2.6	102	10.7

[a] Data from ref 9 at 10 atm except for O_2/N_2 which is at 5 atm. [b] Data from ref 10 at 10 atm except for O_2/N_2 which is at 5 atm. [c] Data from ref 14 at <1 atm.

exhibited by DFHFPNB. Most of the organosilicon-substituted polynorbornenes are more selective for O_2/N_2 separation than DFHFPNB; however, the latter appears to be more selective for separations involving CO_2/CH_4 and H_2/CH_4. Organosilicon substituents can raise the T_g of polynorbornene materials[14-16] but generally not to the extent observed for this fluorine-containing example. To fully understand the properties of the current polymer, it would be useful to examine separately the effects of the fluoro and trifluoromethyl substituents with more detailed measurements. These two substitutions may have opposing effects on permeability deriving from issues of polarity and packing inhibition.

Acknowledgment. We thank the National Academy of Sciences (Washington, DC) for the award of a Visiting Fellowship to V. V. Teplyakov which enabled him to spend 3 months at the University of Texas at Austin to execute this research. Also, we thank S. A. Lermontov and A. V. Popov, who developed the method and synthesized the new fluorine-containing monomers.

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