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# Synthesis, Gas Permeability, and Gas Sorption Properties of Fluorine-Containing Norbornene Polymers

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ABSTRACT: Two fluorine-containing glassy polynorbornenes were synthesized, and their properties (permeability (*P*), diffusion (*D*), and solubility (*S*) coefficients, sorption isotherms, and lifetime positron annihilation spectra) were studied. Both polymers, poly[5,5-difluoro-6,6-bis(trifluoromethyl)norbornene] (PFMNB) and poly[5,5,6-trifluoro-6-(heptafluoropropoxy)norbornene] (POFPNB), were demonstrated to be highly permeable materials having *P* values much larger than the *P* value of nonsubstituted polynorbornene. Positron annihilation analysis and density measurements showed that these polymers have high free volumes. However, the reasons for the high permeabilities of these two materials were different. The permeability of PFMNB ($T_g$ = 169 °C) is related to its very high solubility coefficients while that of POFPNB ($T_g$ = 77 °C) appears to be caused by both its diffusion and solubility coefficients. Sorption isotherms have the form expected for materials behaving according to the dual-mode sorption model. The parameters for this model were determined by a least squares analysis of the isotherms. It was shown that the Henry's law solubility coefficient $k_D$ is enhanced in these fluorine-containing polymers compared to other polynorbornenes. On the other hand, the Langmuir capacity parameter $C'_H$, which characterizes the nonequilibrium state of a polymer, also correlates with the $T_g$ values of these norbornene polymers. Hence, both equilibrium and nonequilibrium factors appear to be responsible for the enhanced solubility and permeability seen for these fluorine-containing norbornene polymers.

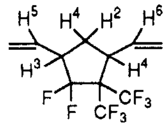
## Introduction

The advances and growth in the field of membrane gas separation that have taken place over the past decade or so have encouraged the search for even better polymers and membranes for gas separation. They also have encouraged studies of the relationship between the structure and transport properties of different classes of polymers. There are several reasons to carry out such studies and extensive screening programs.

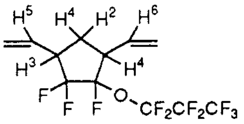
1. Finding consistent correlations between the structure of repeat units and permeability coefficients, separation factors, and other relevant physicochemical properties should result in a deeper insight into and a better understanding of the mechanism of polymer gas transport.
2. Such correlations could also permit the development and tailoring of improved structures and properties in materials for the next generation of gas-separating membranes.
3. Screening a large number of polymers having different chemical structures increases the chances of finding specific polymers with improved transport parameters even without a refined understanding of the intrinsic properties leading to such characteristics.

These studies can be particularly revealing when one looks at a series of polymers within the same class. By studying several polymers from a group, one can note the effects of different structural features. Once the data have been gathered, a comparison with other polymer classes can be made. In fact, the results recently reported on the transport properties of polycarbonates,[1] polysulfones,[2] polyimides,[3,4] silicon-containing polyacetylenes,[5] and vinylic polymers[6] confirm the value of this approach.

Interest has recently been demonstrated in the literature in norbornene polymers with different side groups.[7,8] These polymers can be easily prepared via ring-opening metathesis polymerization on bicycloolefins. The latter can be synthesized by [4 + 2] cycloaddition of olefins to cyclopentadiene or to its derivatives. The products of the polymerization of norbornene derivatives are known to have a cyclolinear backbone and substituents of desired structure located at specified positions along a main chain. Earlier, the transport[9] and sorption[10] properties of polynorbornenes with silicon-containing side chain groups were reported. In the present paper, the synthesis of two examples of another interesting group of norbornene polymers is reported. They are fluorine-containing polynorbornenes having the structures



poly[5,5-difluoro-6,6-bis(trifluromethylnorbornene] (PFMNB)



poly[5,5,6-trifluro-6-(heptafluropropoxy)norbornene] (POFNB)

Preliminary data on the synthesis and permeability of the first polymer have been previously published.[11,12] In the present paper, the results of the investigation of the

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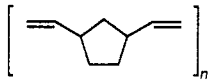
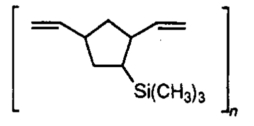
permeability and diffusion coefficients as well as gas sorption isotherms are presented. These fluorine-containing polynorbornenes were also studied by the positron annihilation method, and positron annihilation lifetimes are reported. To elucidate structure–property relationships for these polymers, comparisons are made with the nonsubstituted and silicon-substituted polynorbornenes studied earlier:



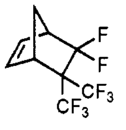
polynorbornene (PNB)



poly(trimethysilylnorbornene) (PTMSNB)

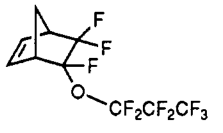
## Experimental Section

**Synthesis of Monomers.** The following fluorine-containing derivatives of norbornene as monomers were studied: 5,5-difluoro-6,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene, having the structure



I

and 5,5,6-trifluoro-6-(heptafluoropropoxy)bicyclo[2.2.1]hept-2-ene, having the structure



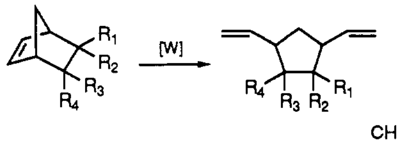
II

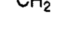
Monomers I and II were prepared by the Diels–Alder reaction of cyclopentaidene with perfluoroisobutene and perfluorovinyl perfluoropropyl ether, respectively. For the preparation of I, a 400-mL steel autoclave was charged with 55.6 g (0.8 mol) of cyclopentadiene, 208 g (1.0 mol) of perfluoroisobutene, and 2 g of hydroquinone. The mixture was heated to 155 °C for 48 h. The autoclave was cooled to ambient temperature and opened. The excess perfluoroisobutene was removed by distillation. Sulfuric acid (5 mL or 0.09 mol) was added to the mixture, and the mixture was stirred for 10 min. Distillation of the crude product under reduced pressure afforded 134.7 g of I (yield 61%); mp 81–83 °C, in agreement with the literature.[13] The absence of bicyclopentadiene was shown by GLC. I was sublimated 2–3 times prior to polymerization.

$^1$H NMR ($C_3D_6O$, $\delta$) 1.9 (m, 1H), 2.38 (m, 1H), 3.1 (m, 1H), 3.4 (s, 1H), 6.4 (m, 1H), 6.5 (m, 1H). Anal. Calcd for $C_9H_6F_8$ (mol wt 266): C, 40.60; H, 2.25; F, 57.14. Found: C, 40.43; H, 2.30; F, 56.90.

Monomer II, which has not been described before, was prepared under similar conditions by the reaction of cyclopentadiene and perfluorovinyl perfluoropropyl ether. The reaction time was 5 h at 170 °C. A yield of 44% (148 g of product) was obtained. The measured bp was 56–57 °C (10 mmHg). Mass spectrum (70 eV, *m/e* (I)): 66 (100), 115 (43), 169 (4), 263 (15), 313 (10), 332 (13). Anal. Calcd for $C_{10}H_6OF_{10}$ (mol wt 332): C, 36.14, H, 1.80; F, 57.22. Found: C, 36.06; H, 1.77; F, 57.00.

**Polymerization.** Ring-opening polymerization proceeds according to the equation



All manipulations with the catalysts  $WCl_5[Me_2Si(CH_2)_2SiMe_2]$ and $WCl_6$+$[Me_3SiCH_2]_4Sn$ were performed in an inert atmosphere using the Schlenk technique. The solvents (benzene, toluene) were distilled over Na or $CaH_2$ prior to use and stored under Ar. The catalyst $WCl_6$ was purified by vaccum sublimation and kept under Ar (solutions in benzene or toluene). Both cocatalysts were prepared according to refs 14 and 15.

For the preparation of PFMNB, 5 mL of a benzene solution containing 1.33 g (0.005 mol) of I under an Ar atmosphere was added to an ampule previously heated and degassed under vacuum. Solutions of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (0.2 mL, $2 \times 10^{-6}$ mol) and $WCl_6$ (0.1 mL, $101^{-6}$ mol) in benzene were added. The mixture was frozen at 77 K and pumped at 0.001 mmHg. The ampule was sealed and, after reaching ambient temperature, kept at 50 °C for 2.5 h. The obtained polymer was dissolved in methyl ethyl ketone and precipitated by dilution with ethanol. The yield of polymer was 55% or 0.73 g. It had the following molecular mass characteristics: $M_n$ = 90 650, $M_w$ = 112 580, $M_w/M_n$ = 1.24, $n$ = 340. Anal. Calcd for $C_9H_6F_8$ (repeat unit): C, 40.60; H, 2.25; F, 57.15. Found: C, 40.68; H, 2.30; F, 57.00. IR spectrum (film, $cm^{-1}$): 720 (m), 789 (m), 902 (m), 955 (s), 981 (m), 1013 (w), 1051 (w), 1116 (w), 1141 (m), 1205–1315 (m), 1462 (w), 1670 (w), 2888 (w), 2955 (w), 2982 (w), 3025 (w). 200-MHz $^1$H NMR ($C_3D_6O$/TMS, $\delta$): 5.9 (2H, $H^5$,$H^6$), 3.3–3.9 (2H, $H^3$,$H^4$), 2 (1H, $H^1$), 1.9 (1H, $H^2$).

POFPNB was prepared in a similar manner. Five milliliters of a benzene solution containing 1.66 g (0.005 mol) of II was added to an ampule. Benzene solutions of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (2 mL, $2 \times 10^{-5}$ mol) and $WCl_6$ (1 mL, $10^{-5}$ mol) were added (concentration 0.01 mol/L). The reaction was carried out at 50 °C for 2.5 h. The polymer was dissolved in methyl ethyl ketone and precipitated by adding ethanol. Yield of polymer: 63% or 1 g. Molecular mass characteristics: $M_n$ = 45 720, $M_w$ = 57 607, $M_w/M_n$ = 1.26, $n$ = 136. Anal. Calcd for $C_{10}H_6F_{10}O$ (repeat unit): C, 36.14; H, 1.80; F, 57.22; O, 4.82. Found: C, 36.08; H, 1.78; F, 56.80. Ir (film, $cm^{-1}$): 455 (m), 537 (m), 642 (m), 749 (w), 947 (m), 975–1001 (s), 1068 (s), 1100 (s), 1136–1273 (s), 1339 (s), 1416 (m), 1461 (s), 2890 (w), 2956 (w), 2986 (w), 3041 (w). 200-MHz $^1$H NMR ($C_3D_6O$/TMS, $\delta$): 5.7 (2H, $H^5$,$H^6$), 3.6 (1H, $H^3$), 3.3 (1H, $H^4$), 2.3 (1H, $H^1$), 1.7 (1H, $H^2$).

**Characterization.** IR spectra of the norbornene polymers were obtained using a Bruker IFS-113 instrument. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker MSL-300 spectrometer. A Kratos MS-80 instrument was used for mass spectrometric analysis of monomer II. The mechanical properties of the film were determined on an Instron 1122 instrument. A thermogravimetric study of the polymers was performed using an MOM Model OD-102 instrument. DSC measurements were made with a Mettler TA 3000 instrument (heating rate 10–20 K/min). Polymer density was determined by hydrostatic weighing using 2-propanol as the nonsolvent liquid phase.

Permeability (*P*) and diffusion (*D*) coefficients were measured by a mass spectrometric method as described in detail elsewhere.[16] An MI-1309 spectrometer was used. While measurements were being made, the pressure on the upstream side of the permeation cell was maintained in the range 10–500 Torr, and the pressure on the downstream side of the membrane was $\sim 10^{-3}$ Torr. Permeability coefficients at 22 ± 1 °C were calculated from the steady-state slopes of the appropriate ion currents versus time. Diffusion coefficients were obtained using the time-lag method. The standard deviation in parallel runs was 10% for *P* and 20% for *D*. No pressure dependence for the *P* and *D* values was observed in the upstream pressure range indicated. The films of fluorine-containing norbornene polymers for these and other tests were cast from dilute solutions (5–7%) in methyl ethyl ketone over cellophane surfaces on a horizontal table. Thickness was in the range 50–150 μm. The films were exhaustively dried in air at 25 °C for 200–500 h and then under vacuum.

Sorption measurements were made with a Sartorius electrobalance (Model 4436 MP6) at 25.0 ± 0.1 °C. Corrections for buoyancy and swelling of the films were introduced.

The positron annihilation lifetime spectra were measured on a standard instrument (Ortec). The $^{22}$Na isotope was used as a source of positrons. The source was sandwiched between two stacks of sample polymer films of diameter 10–15 mm and thickness ~100 μm. The overall thickness of the stack was in the range 1–2 mm.

**Table 1. Physical Properties of Fluorine-Containing Norbornene Polymers**

| characteristic | PFMNB | POFPNB |
|---|---|---|
| intrinsic vis in MEK, $\eta$ (dL/g) | 2.4 | 2.2 |
| $T_g$ (°C) | 169 | 77 |
| tensile strength, $\sigma$ (kg/mm$^2$) | 5.0 | 1.6 |
| elongation at break, $\epsilon$ (%) | 3 | 6 |
| temp of 5% wt loss (TGA in $N_2$) | 342 | 323 |
| density, $\rho$ (g/cm$^3$) | 1.586 | 1.626 |

**Table 2. Permeability of Norbornene Polymers $P_i$ (Ba)[a]**

| polymer | $H_2$ | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ | $C_2H_6$ |
|---|---|---|---|---|---|---|
| PNB | 21 | 2.8 | 1.5 | 15.4 | 2.5 | 1.4 |
| PFMNB | 166 | 50 | 17 | 200 | 13 | 6.6 |
| POFPNB | 130 | 55 | 17 | 200 | 18 | 14 |
| PVTMS | 150 | 30 | 8 | 130 | 13 | 7.5 |

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

## Results and Discussion

**Physical Properties.** The physical characteristics of the fluorine-containing polynorbornenes are listed in Table 1. The intrinsic viscosity indicates that both polymers are high molecular mass materials. In spite of some similarity in the structure of the side groups in these polymers, they have glass transition temperatures which differ significantly. It has been shown[9] that unsubstituted polynorbornene (PNB) has a $T_g$ of 31 °C. Hence, the introduction of fluorine-containing side groups appears to cause an increase in the rigidity of polymer chains. However, the magnitude of this effect strongly depends on the structure of the repeat units. The introduction of a branched site directly associated with the main chain, as in the case of PFMNB, leads to higher $T_g$ values than for the structure where a linear fluorine-containing group is separated from the main chain by a spacer (C–O–C linkage) as in the case of POFPNB. It should be noted that the same tendency has previously been observed bysilyl-substituted polynorbornenes.[9] The introduction of the $Si(CH_3)_3$ group in this latter case results in an increase in the glass transition temperature ($T_g$ = 110 °C for PTMSNB), whereas the introduction of the even bulkier side group $Si(CH_3)_2CH_2Si(CH_3)_2$ with a Si–C–Si flexible linkage does not increase $T_g$ but actually results in a decrease in $T_g$ to a value lower than the $T_g$ of PNB.

The mechanical properties observed for fluorine-containing polynorbornenes are in line with the observed $T_g$. PFMNB has a higher $T_g$ than POFPNB and is characterized by a greater tensile strength but a lower elongation at break. The thermal stabilities of the polymers are approximately the same. The volumetric properties of the polymers studied (specific volume, van der Waals volume, and free volume) are discussed below in relation to the observed transport parameters.

**Permeability.** In Table 2, gas permeability coefficients of the fluorine-containing polymers are reported together with the corresponding values of PNB and poly(vinyltrimethylsilane) (PVTMS). The latter polymer can be viewed as a standard highly permeable glassy polymer.[6] It can be observed that the introduction of fluorine-containing moieties into the five-membered ring of the PNB main chain results in a significant increase in permeability for all the gases. Interestingly, the high level of permeability obtained for the polymers studied here is typical for a range of polymers containing trimethylsilyl side groups (PVTMS,[6] PTMSNB,[9] silylated poly(phenylene oxide),[17] etc.). This indicates that the introduction of a silicon-containing side group is not the only approach for creating high-permeability polymer materials.

**Table 3. Separation Factors $P_i/P_j$ of Norbornene Polymers**

| polymer | $H_2/N_2$ | $H_2/CH_4$ | $O_2/N_2$ | $CO_2/CH_4$ | $CO_2/N_2$ |
|---|---|---|---|---|---|
| PNB | 14.4 | 8.6 | 1.9 | 6.3 | 10 |
| PFMNB | 9.8 | 12.7 | 2.9 | 15.4 | 12 |
| POFPNB | 7.6 | 6.5 | 3.2 | 11 | 12 |
| PVTMS | 18 | 12 | 4 | 10 | 16 |

Table 3 presents the separation factors $\alpha_{ij} = P_i/P_j$ for different gas pairs. It is well know that, in the vast majority of polymers, there is a trade-off between permeability ($P_i$) and selectivity ($\alpha_{ij}$); increasing $P_i$ generally leads to lower values of $\alpha_{ij}$ and vice versa. Therefore, cases in which this principle does not hold are of potential interest. Tables 2 and 3 show that the introduction of fluorine-containing groups results not only in an increase in permeability but, for some gas pairs, in an improvement in selectivity. This combination of properties is rather unusual and deserves further investigation.

The actual values of the separation factors $\alpha_{ij}$ are not sufficiently high, according to contemporary standards, to propose an immediate practical application. However, the tendency of a combined increase of permeability and permselectivity found in the present work owing to the introduction of branched fluorine-containing groups confirms some similar observations of this effect that have been made elsewhere.[3] Therefore a further search for similar behavior might be beneficial for preparing advanced materials for gas-separating membranes.

The separation factors for various gas pairs observed for fluorine-containing norbornene polymers studied in the present paper are somewhat lower than those found for other polymers containing $C(CF_3)_2$ groups.[18] There are two possible explanations of this difference.

1. In the vast majority of other polymers studied (polycarbonates, polyimides, etc.), this group serves as a bulky linkage restricting dense packing of aromatic type backbones. In our case, the $C(CF_3)_2$ groups appear as side chain moieties; hence, one might anticipate the different structural effects of their introduction and the resulting changes of size distribution of free volume elements.

2. If we compare nonsubstituted PNB with aromatic backbone type polymers such as polycarbonates and polysulfones, we can conclude that even PNB is a rather loosely packed material. This is confirmed, for example, by a decrease in the permeability coefficients induced by an introduction of hydrocarbon radicals into the cyclopentane ring of PNB.[19] For aromatic type polymers, alkylation of phenyl rings results, on the contrary, in the increase of fractional free volume as well as diffusion and permeability coefficients.[18] Introduction of the fluorine-containing moieties into the main chain of PNB leads to further growth of free volume. For such loosely packed materials, it is hard to expect highly permselective properties such as those that have been found for aromatic backbone polymers.

One of the advantages of fluorine-containing norbornene polymers as materials for membranes is that they are insoluble in hydrocarbons. PVTMS membranes are not practical for many gas separation applications because PVTMS is soluble in hydrocarbons and, hence, is very sensitive to even minor hydrocarbon impurities which are common in many industrial gas streams (e.g., $CH_4/H_2$ fractions of refinery or petrochemical plants). Therefore, hydrocarbon vapors can plasticize membranes made of PVTMS, decreasing their selectivity and, ultimately, destroying their separation properties. Ketones, which are, in general, good solvents for PFMNB and POFPNB, are not present as impurities in most industrial gas streams.

**Table 4. Diffusion Coefficients of Norbornene Polymers $D \times 10^7$ (cm$^2$/s)**

| polymer | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ | $C_2H_6$ |
|---|---|---|---|---|---|
| PNB | 1.5 | 0.44 | 1.6 | 0.36 | 0.16 |
| PFMNB | 1.4 | 0.84 | 0.84 | 0.33 | 0.056 |
| POFPNB | 5.7 | 4.4 | 4.0 | 2.3 | 0.42 |
| PTMSNB | 4.2 | 3.0 | 3.3 | 1.4 | 0.2 |

**Table 5. Solubility Coefficients of Norbornene Polymers $S \times 10^2$ (cm$^3$(STP)/(cm$^3$·cmHg)) as Determined by Permeation Measurements**

| polymer | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ | $C_2H_6$ |
|---|---|---|---|---|---|
| PNB | 0.19 | 0.33 | 0.96 | 0.68 | 0.87 |
| PFMNB | 3.7 | 2.0 | 24 | 3.9 | 12 |
| POFPNB | 0.96 | 0.39 | 5.0 | 0.78 | 3.3 |
| PTMSNB | 0.71 | 0.39 | 5.0 | 0.78 | 3.3 |

**Table 6. Solubility Coefficients $S \times 10^2$ (cm$^3$(STP)/(cm$^3$·cmHg)) Determined from Sorption Isotherms**

| polymer | $N_2$ | Ar | $CH_4$ | $CO_2$ | $C_2H_6$ |
|---|---|---|---|---|---|
| PNB | 0.07 | 0.13 | 0.26 | 1.6 | 2.1 |
| PFMNB | 0.76 | 1.07 | 1.9 | 10.9 | 12 |
| POFNB | 0.26 | 0.42 | 0.64 | 4.2 | 3.1 |

Hence, membranes based on these and similar polymers could have a wider range of applications.

**Diffusion and Solubility Coefficients.** The basic permeability equation, valid in the pressure range used in the present paper, is

$$P = DS \qquad (1)$$

where $D$ is the diffusion coefficient and $S$ is the solubility coefficient. Changes in $P$ values can result from alterations in mobility ($D$) and thermodynamic ($S$) contributions; hence, it is worthwhile to evaluate these quantities independently for norbornene polymers. The relevant data are presented in Tables 4 and 5. Diffusion coefficients were determined directly by the time-lag method, whereas the solubility coefficients were found using eq 1.

Interestingly, the high permeabilities of PFMNB and POFPNB are caused by factors which are somewhat different for the two polymers. It is seen from Table 4 that the diffusivities of PFMNB and PNB do not differ significantly. On the other hand, the diffusion coefficients of POFPNB are several times higher than those observed for PNB. The introduction of fluorine-containing moieties enhances the solubility coefficients of both polymers and particularly those of PFMNB (Table 5).

The solubility coefficients determined from the initial slopes of the sorption isotherms for all three polymers studied are shown in Table 6. As is frequently the case for other polymers (see, for example, ref 20), solubility coefficients determined directly and those estimated from $P$ and $D$ values do not coincide. Nevertheless, the trend in the changes of $S$ values for the series PNB, PFMNB, and POFPNB are similar and are independent of the method by which they were obtained. Possible reasons for the effects of fluorine-containing groups on the thermodynamic and transport properties of the polymers studied are given below.

**Positron Annihilation and Free Volume.** Previously, it has been shown that positron annihilation lifetime spectra provide information useful for interpreting the diffusivity and permeability behavior of polymers on the basis of free volume.[21-23] Accordingly, we investigated here the lifetime spectra of positrons in two fluorine-containing polynorbornenes and, additionally, in PNB and PTMSNB. Table 7 presents these spectra along with the previously reported spectrum for PVTMS. It has been shown[21] that valid correlations exist in rubbers between diffusion coefficients and parameters of the annihilation spectra such as the long-lifetime component $\tau_3$ of the product $\tau_3 I_3$ (where $I_3$ is the corresponding statistical weight). Recently, similar correlations were confirmed in the literature[24] for a number of glassy polymers. We felt it would be of interest to check this correlation for a group of polymers that are structurally closely related but which differ significantly in their diffusivities.

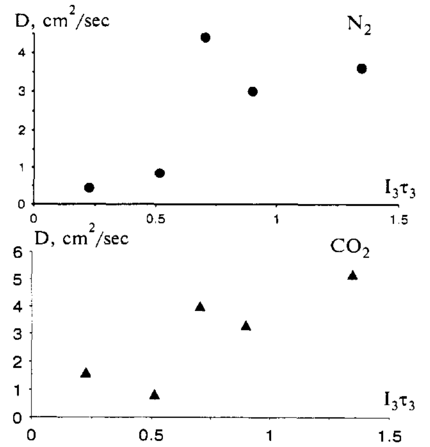


**Figure 1.** Diffusion coefficients versus the parameter $\tau_3 I_3$ (ns).

**Table 7. Positron Annihilation Spectra of Norbornene Polymers and PVTMS ($\tau_i$, ns; $I_i$, %)**

| polymer | $\tau_1$ | $I_1$ | $\tau_2$ | $I_2$ | $\tau_3$ | $I_3$ |
|---|---|---|---|---|---|---|
| PNB | 0.3106 | 69.8 | 0.5495 | 18.9 | 1.9969 | 11.3 |
| PFMNB | 0.3466 | 68.9 | 0.7401 | 17.3 | 3.75 | 13.7 |
| POFPNB | 0.2940 | 47.6 | 0.5913 | 33.6 | 3.74 | 18.8 |
| PTMSNB | 0.2123 | 27.9 | 0.4520 | 37.6 | 2.6021 | 34.5 |
| PVTMS[a] | 0.1950 | 31.1 | 0.5620 | 28.5 | 3.34 | 40.3 |

[a] Data from ref 21.

**Table 8. Volumetric Properties of Norbornene Polymers**

| polymer | $v_{sp}$ (cm$^3$/g) | $v_w$ (cm$^3$/g) | $v_f$ (cm$^3$/g) | FFV |
|---|---|---|---|---|
| PNB | 1.02 | 0.663 | 0.159 | 0.156 |
| PFMNB | 0.63 | 0.405 | 0.104 | 0.165 |
| POFPNB | 0.61 | 0.385 | 0.115 | 0.187 |
| PTMSNB | 1.09 | 0.669 | 0.218 | 0.200 |

Analysis of the data in Table 7 indicates that polymer structure in the polynorbornene series influences significantly the annihilation parameters observed. Thus, the value $\tau_3$ found for PNB is characteristic for amorphous, relatively low permeability polymers. The lifetimes $\tau_3$ observed for PFMNB and POFPNB are higher and close to those reported for high permeability, high free volume polymers such as PVTMS, poly(phenylene oxide), and poly(dimethylsiloxane).[21] According to accepted models of the behavior of positrons in polymers, $\tau_3$ values characterize so-called disordered regions within polymers, where relatively loosely packed chains and larger free volume elements can be found. Figure 1 shows the correlation between diffusion coefficients and $\tau_3 I_3$ for norbornene polymers and PVTMS. It is seen that, in spite of some scatter, the values $D$ and $\tau_3 I_3$ are sensitive to the same structural features of the polymers. It can be inferred that the introduction of bulky fluorine-containing groups into the PNB main chain seems to be accompanied by an increase in free volume.

A more traditional and conventional approach[25] for estimating free volume involves determining the specific volume of polymers, defined as $v_{sp} = 1/\rho$, and estimating the occupied volume according to Bondi.[26] This method usually gives good results for low-polarity polymers but

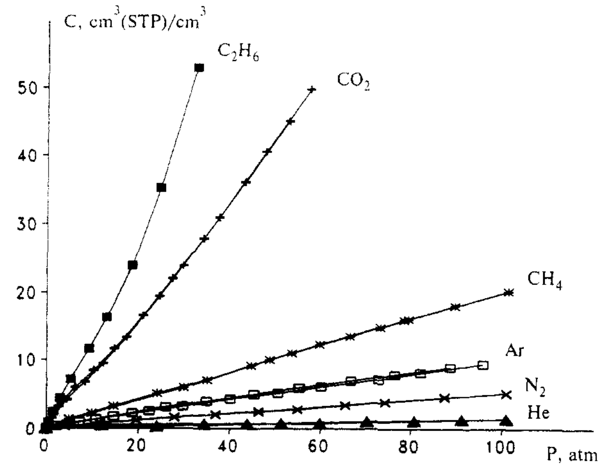


**Figure 2.** Sorption isotherms in PNB at 25 °C.

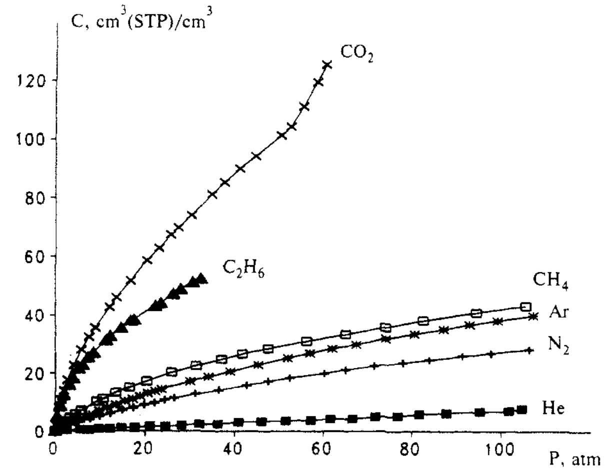


**Figure 3.** Sorption isotherms in PFMNB at 25 °C.

sometimes fails to correlate $D$ and $P$ values with reasonable accuracy for polymers containing polar groups.[27]

Table 8 gives volumetric data for the norbornene polymers. The van der Waals volume $v_w$ was calculated using group contributions while occupied volume is defined as $v_o = 1.3v_w$.[26] From these values the free volume $v_f = v_{sp} - v_o$ and fractional free volume FFV = $v_f/v_{sp}$ can be calculated. As is evident from Tables 8 and 4, there is a rough correlation between the diffusivity of norbornene polymers and their FFV. The latter value correlates with the product $\tau_3 I_3$ (Table 7), confirming once more that this parameter can serve as an approximate measure of free volume. However, a more careful inspection of the diffusion coefficients of norbornene polymers indicates that there must also be other factors in addition to free volume affecting $D$ values (differences of size distributions of free volume elements, variation in topology of different routes, etc.). For example, the free volumes found for PNB and PFMNB differ significantly even though the diffusion coefficients of these two polymers are very similar.

**Sorption Isotherms.** Figures 2–4 show the sorption isotherms for several gases in PNB, PFMNB, and POFMNB. The isotherms obtained for PNB have a form typical of rubbers. For gases with lower solubility coefficients (He, $N_2$, Ar, and $CH_4$), the isotherms are linear up to very high pressure. The $CO_2$ and $C_2H_6$ isotherms are concave with respect to the concentration axis in the range of higher pressures. At pressures below 10 atm, a kind of *inflection point* can be observed. Such behavior is in agreement with the fact that the glass transition temperature of PNB is only a few degrees higher than the measurement temperature $T$ (25 °C). Under such circumstances, only a very low concentration of solute molecules is required to plasticize the polymer, reduce its glass transition temperature, and transform it into the rubbery state at 25 °C.

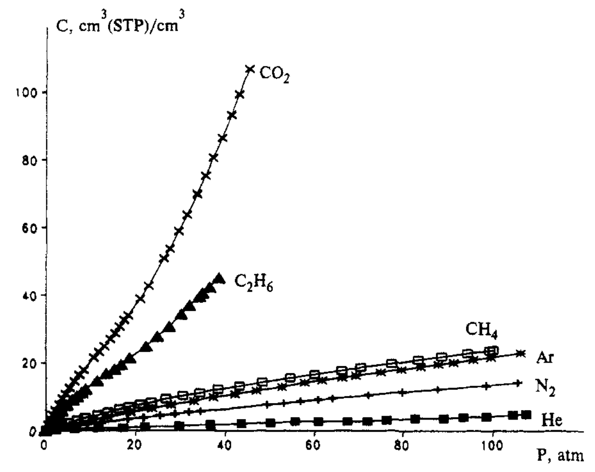


**Figure 4.** Sorption isotherms in POFPNB at 25 °C.

The same phenomena are more clearly seen for both fluorine-containing polymers in the shape of their sorption isotherms. Figure 3 shows the sorption isotherms for PFMNB. The isotherms obtained for all the gases (except the $CO_2$ isotherm at higher pressures) are concave with respect to the pressure axis. Such isotherms are characteristic of glassy polymers. For many years the dual-mode sorption model has been used to describe gas sorption in amorphous glassy polymers. The main premise of this model is that two populations of solute molecules exist in the sorbed state. One population ($C_D$) is viewed as arising from pure physical dissolution which can occur both above and below $T_g$. Such dissolved molecules should obey Henry's law. The second population ($C_H$) is considered as arising from the trapping or condensation of solute molecules in "microcavities", regions of a decreased local density, or on unspecified "fixed sites" within glassy polymers. Such microcavities or regions are regarded to be related to the nonequilibrium nature of glassy polymers (the existence of "excess" free volume). The behavior of this second population should be described by a Langmuir isotherm. Hence, the equation of the dual-mode sorption model is as follows:

$$C = C_D + C_H = k_D p + C'_H bp/(1 + bp) \qquad (2)$$

where $k_D$ (cm$^3$(STP)/(cm$^3$ atm)) is the Henry's law solubility constant, $b$ (atm$^{-1}$) is the Langmuir affinity constant, and $C'_H$ is the Langmuir capacity parameter. The parameters $k_D$ and $b$ have a significance of sorption–desorption equilibrium constants for the two populations. $C'_H$ describes the adsorption capacity of a polymer with respect to a specific gas at a specific temperature $T < T_g$. It has been shown[28] that $C'_H$ values fall off with decreases in $T_g - T$.

The $CO_2$ sorption isotherm shows an inflection point at a much higher pressure and solute concentration than do the PNB isotherms. The reason for this is the much higher $T_g$ of PFMNB. It has been shown by Sanders[29] that different polymers appear to be plasticized to a similar extent by dissolved $CO_2$. Therefore, one would expect the coordinate of the *inflection point* ($p_g$,$C_g$) to be higher the larger the difference between the $T_g$ of a pure polymer and the $T$. The shape of the $CO_2$ sorption isotherm in POFPNB is in agreement with this expectation. POFPNB

**Table 9. Dual-Mode Sorption Model Parameters**[a]

| polymer | parameter | gas $N_2$ | $Ar$ | $CH_4$ | $CO_2$ | $C_2H_6$ |
|---|---|---|---|---|---|---|
| PFMNB | $k_D$ | 0.109 | 0.177 | 0.183 | 1.310 | 0.850 |
| | $C'_H$ | 24.8 | 30.3 | 29.3 | 40.8 | 27.9 |
| | $b$ | 0.019 | 0.021 | 0.043 | 0.171 | 0.300 |
| POFPNB | $k_D$ | 0.085 | 0.153 | 0.149 | 1.210 | 0.817 |
| | $C'_H$ | 8.20 | 10.4 | 12.1 | 14.4 | 7.64 |
| | $b$ | 0.014 | 0.016 | 0.028 | 0.136 | 0.197 |
| PTMSNB | $k_D$ | 0.04 | 0.055 | 0.13 | 0.50 | 0.95 |
| | $C'_H$ | 10 | 18 | 18 | 27 | 14 |
| | $b$ | 0.015 | 0.014 | 0.040 | 0.098 | 0.72 |

[a] Units: $k_D$, cm$^3$(STP)/(cm$^3$·atm); $C'_H$, cm$^3$(STP)/cm$^3$; $b$, atm$^{-1}$.

has a $T_g$ value which is intermediate between the $T_g$'s of PNB and PFMNB. Indeed, the inflection point of the sorption isotherm for this polymer is observed at intermediate pressures of $CO_2$.

Table 9 gives the parameters for PFMNB, POFPNB, and PTMSNB calculated by a nonlinear least squares treatment of eq 2. It is seen that the structure of the side chain strongly influences the parameters of the dual-mode sorption model.

Let us consider the general effects of fluorine-containing moieties on the transport and sorption characteristics of different polymers, including the polynorbornenes studied in the present paper. First, it has been demonstrated that the introduction of a bulky $-C(CF_3)_2-$ linkage in various main chains (polycarbonates, polyimides, etc.) tends to inhibit dense packing of the chains, thus making the polymer matrix more "opened".[3,27] This effect is manifested in the larger permeability, diffusion, and solubility coefficients of such polymers. These increases are not typically accompanied by significant losses in selectivity $\alpha_{ij}$. Actually, in some cases separation factors increase. Similar effects take place when fluorine-containing groups are introduced as side chains. This is shown in the higher glass transition temperatures and free volume of PFMNB and POFPNB compared to PNB.

Another consequence of introducing fluorine-containing moieties into polymers is related to the unique solvent properties attributed to such polymers as well as to low molecular weight fluorine-containing organic compounds. It has been shown[30-34] that the increased solubility of many molecules in perfluorinated compounds is caused by the especially low surface tension and cohesive energy density of fluorinated materials. In fluorinated polymers this should result in a relatively nonselective increase in permeability with respect to different gases. As for the parameters of the dual-mode sorption model, it is reasonable to expect that this effect will be exhibited in the Henry's law population of solute molecules, i.e., in $k_D$ parameters.

Since the polarity of C–F bonds is comparable to those of C–Cl and C–Br bonds,[35] specific dipole–dipole interactions should be expected for polar penetrants or even nonpolar ones which contain polar bonds (e.g., C–O) or have a strong quadrupole moment like $CO_2$. There are some indications of such effects in the literature, (see, e.g., ref 34). However, it is difficult to isolate the role of such specific interactions from many other factors which also influence solubility and diffusivity.

Inspection of the data of Table 9 clearly reveals that the Henry's law solubility coefficients $k_D$ of both fluorine-containing polynorbornenes are higher than those of PTMSNB, in agreement with the predictions of refs 28 and 29. However, since $k_D \ll C'_H b$, the effect of the Henry's law population of sorbed molecules is small in comparison with the Langmuir population of sorbed molecules.

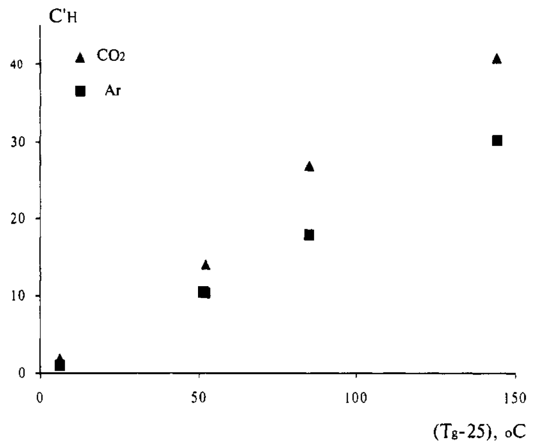


**Figure 5.** Dependence of the Langmuir capacity parameter $C'_H$ in norbornene polymers on the difference ($T_g$ – 25) (°C).

The influence of fluorine-containing moieties on $T_g$, on free volume, and, through these parameters, on $S$ and $P$ is more complicated. It is seen from Table 9 that the Langmuir capacity parameter $C'_H$ increases with $T_g$ or with the difference $T_g - T$ ($T$ = 25 °C). Figure 5 shows that this dependence is linear, in agreement with reports in the literature.[28] On the other hand, the affinity parameter $b$ is almost constant for all the polymers listed in Table 9. Therefore, the solubility coefficients $S = k_D + C'_H b$ are highest for PFMNB among the three norbornene polymers listed in this table. The high permeability coefficients of this polymer are related to its strong nonequilibrium character as manifested by its high $T_g$ and large value of $C'_H$.

An interesting feature of the results of sorption studies is that, for both fluorine-containing polymers, ethane's sorption isotherms lie below those of carbon dioxide (Figures 3 and 4). On the other hand, the position of the sorption isotherms in PNB is opposite: the ethane's isotherm lies above the one of carbon dioxide (Figure 2). If one addresses other polymers containing no strongly polar bonds, e.g., silicon-containing polynorbornenes,[10] poly(vinyltrimethylsilane),[37] and poly(trimethylsilyl)propyne),[38] one finds the same order of sorption isotherms as in the case of PNB. Furthermore, poly(tetrabromophenolphthalein phthalate) containing polar C–Br bonds exhibits an inverse order of the sorption isotherms of $C_2H_6$ and $CO_2$— the former is situated below the latter.[39]

One can assume that such a behavior is a manifestation of higher solubility of carbon dioxide owing to the presence of polar C–F bonds in PFMNB and POFPNB. Although $CO_2$ is a nonpolar molecule, it has a quadrupole moment, and C–O bonds are strongly polar, so local dipole–dipole interactions are possible. Earlier, indications of enhanced solubility of $CO_2$ were reported for fluorine- and chlorine-containing polymers.[36,40-42]

The question still to be answered is why the diffusion coefficients of PFMNB do not differ substantially from those of PNB in spite of the fact that there are significant differences in free volume between the two polymers. According to Iwin,[43] materials obtained by ring-opening polymerization are frequently not characterized by a statistical sequence of different cis/trans isomers of repeat units but rather consist of blocks of cis- and/or trans-configurations having different specific chain lengths. Such blocks tend to result in micro phase separation. We assume that such two-phase morphology can make diffusion pathways more turtuous and thus decrease the observed gas diffusion coefficients. Some qualitative confirmation of this hypothesis was obtained in spin probe experiments which revealed two frequencies of rotation $\nu_c$ of TEMPO stable free radical and, hence, phase microstructure in PFMNB. Although the values of $\nu_c$ and the observation of two phases do not explain completely the observed diffusivity of PFMNB, this result makes further tests of this hypothesis desirable, and corresponding studies are now in progress.

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