

# Gas Transport Properties of Polycarbonate–Polyurethane Membranes

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## SYNOPSIS

Polyurethanes (PU) were prepared using polymeric diols, containing polar groups, as —O—C(O)—O— (carbonate) groups, carbonate and ether (—O—) groups, or carbonate and ester groups [—C(O)—O—]. PUs were prepared by the prepolymer two-step technique using ethyl acetate (EA) as the solvent; the diol was reacted at about +80°C with TDI (ratio 1 : 2) to give the prepolymer terminated with NCO, which was then cross-linked with triisopropanolamine (TIPA). The membranes were prepared using a Gardner knife and were characterized by differential thermal analysis (DSC). Most of the polymers prepared from low and medium molecular weight diols were amorphous and elastomeric at the temperature of gas transport measurement (35°C). The permeabilities (*P*) and the diffusion coefficients (*D*) of different gases (O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, CO) were measured by a modified Lyssy apparatus, the solubility coefficient (*S*) was also calculated. The water-vapor transport properties *D* and *S* were measured according to ASTM. Diffusivity data follow the Fujita model and the solubility coefficients the regular solution theory, as developed by Prausnitz and Shair. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Polyurethanes (PU) are characterized by the presence of urethane (—NHCOO—) groups and other functional groups, the presence of both groups determining the properties of the polymers. Recently, we studied PUs based on toluene diisocyanate (TDI) and polyether or polyester diols with the aim of studying correlations between the structure of the polymer and their gas transport properties.<sup>1–3</sup> To reduce the formation of crystalline domains that limit permeability, a mixture of TDI isomers, linear diols, often not stereoregular, and a polyfunctional cross-linking agent for the extension of the prepolymer were used. With these reagents, amorphous polymers are usually obtained, the exception being the formation of some stereoregular, high molecular weight diols. This work deals mainly with polycarbonate PUs containing, besides carbonate groups,

methylene and ether, or methylene and ester, groups. However, data from polyester–PUs are discussed for the sake of comparison. A general relationship was found to exist among polymer composition, diffusivity, and solubility.

## EXPERIMENTAL

### Materials

- (•) Polycarbonate diols containing the —OC(O)O— group and, respectively, either the tetramethylene (PTMC) or the hexamethylene group (PEMC) or both pentamethylene and hexamethylene (PPMEMC).
- (a) Polycarbonate diols containing the —OC(O)O— group and, respectively, either the tetramethylene (PTMC) or the hexamethylene group (PEMC) or both pentamethylene and hexamethylene (PPMEMC).
- (b) Polycarbonate diols containing both the —OC(O)O— group and the —O—

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Table I Polymeric Diols Used

Abbreviation	Formula	Extended Name
<u>Polycarbonate diols</u>		
PTMC	$\text{HO}(\text{CH}_2)_4 \left[ \text{O} - \overset{\text{O}}{\parallel} \text{CO}(\text{CH}_2)_4 \right]_n \text{OH}$	Poly(tetramethylene carbonate) diol MW 670, 1093, 2600
PEMC	$\text{HO}(\text{CH}_2)_6 \left[ \text{O} - \overset{\text{O}}{\parallel} \text{CO}(\text{CH}_2)_6 \right]_n \text{OH}$	Poly(hexamethylene carbonate) diol MW 565, 840, 1025, 1900, 2370
PPMEMC	$\text{HO}(\text{CH}_2)_6 \left[ \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{O}(\text{CH}_2)_5 \right]_m \left[ \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{O}(\text{CH}_2)_6 \right]_n \text{OH}$	Poly(pentamethylene-hexamethylene carbonate) diols MW 1700
<u>Polyethercarbonate diols</u>		
PTEGC	$\text{HO}(\text{CH}_2 - \text{CH}_2\text{O})_2 \text{CH}_2 - \text{CH}_2 - \left[ \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{O}(\text{CH}_2\text{CH}_2\text{O})_2 \text{CH}_2 \text{CH}_2 \right]_n \text{OH}$	Poly(triethylene glycol carbonate) diol MW 2537
PDPGC	$\text{HO} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \left[ \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{O} \right]_n \text{OH}$	Poly(dipropylene glycol carbonate) diol MW 2100
PDPGPPGC	$\text{HO} - \underset{\text{CH}_3}{\text{CH}} - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{O} - \left( \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{O} \right)_n \left[ \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{O} \right]_m \text{OH}$	Poly(dipropylene glycol)poly(propylene glycol carbonate) diol MW 1545
or HO OCOO P OCOOD - OCOO - D - OCOO P ... OCOO D OH, where P = polypropyleneglycol and D = dipropyleneglycol		
<u>Polyestercarbonate diols</u>		
P(C-ES)	$\text{HO}(\text{CH}_2)_6 \left[ \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{O}(\text{CH}_2)_6 \right]_n \left[ \text{O} - \overset{\text{O}}{\parallel} \text{C}(\text{CH}_2)_5 \right]_m \text{OH}$	Poly(hexamethylene carbonate pentamethylene ester) diol MW 2000
<u>Polyester diols</u>		
PTMA	$\text{H} \left[ \text{O} - (\text{CH}_2)_4 - \text{O} - \overset{\text{O}}{\parallel} \text{C} - (\text{CH}_2)_4 - \text{C} \right]_n \text{OH}$	Poly(tetramethylene adipate) diol MW 600, 1000, 1600

(ether) group: poly(triethylene glycol carbonate)diol (PTEGC); Poly(dipropylene glycol carbonate) diol (PDPGC); and Poly(dipropylene glycol)-poly(propylene glycol carbonate) diol (PDPGPPGC).

(c) Poly(ester carbonate) diols [P(C-ES)] containing the carbonate  $-\text{OC}(\text{O})\text{O}-$  group and the ester  $-\text{C}(\text{O})\text{O}-$  group. These were obtained by reacting dimethylcarbonate with hexanediol and caprolactone.

- Diisocyanate: toluene diisocyanate (TDI), a mixture of the toluene-diisocyanate 2.4 and 2.6 isomers in 80/20 ratio (Bayer product).
- Cross-linking agent: triisopropanolamine (TIPA) (Fluka product)  $\text{N}-[\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}]_3$ .
- Solvent: dehydrated ethyl acetate (EA) b.p. = 77°C (RP Carlo Erba product).

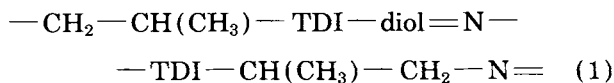
### Membrane Preparation

The PU synthesis was carried out according to a two-step process.<sup>1</sup> The polycarbonate diols were dried at 50°C at reduced pressure and then dissolved under nitrogen in anhydrous EA in a reactor supplied with a condenser.

After adding TDI, with molar ratio  $\text{NCO}/\text{OH} = 2.1$ , the system was heated up to 80°C and maintained for 3 h under stirring. The conversion of the reagents was followed by determining the amount of NCO groups according to the ASTM D-2572 method.<sup>4</sup> In the second step, a mixture of the prepolymer and the cross-linking agent, dissolved in EA, was prepared, keeping the  $\text{OH}/\text{NCO}$  molar ratio = 1.1 and the temperature at 45–50°C, so as to have a homogeneous solution. After adding the cross-linking catalyst (15–20 drops of stannous octoate 15% solution by weight in EA solvent), the reacting mixture was spread with a Gardner knife on a glass plate thermostated at 45–50°C. To prevent the formation of bubbles, or holes in the membranes, the casting solution was degassed and the evaporation rate of the solvent kept sufficiently low by covering the system with a glass cup. The cross-linking rate and consequent viscosity increase were controlled by spreading the film under controlled temperature and atmosphere. The thickness of the dry film could be changed from 50 to 200  $\mu\text{m}$ .

### Properties of the PUs and of the Membranes

The general stoichiometric formula of the repeating unit of the PUs is the following:



Density was measured with an analytical balance by weighing the samples, at room temperature  $T$ , in air and in distilled water.<sup>5</sup> The glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ) were measured with a DSC Mettler TA 3000 within the temperature range of  $-170^\circ\text{C}$  to  $+250^\circ\text{C}$  and with a heating rate of  $10^\circ\text{C}/\text{min}$ . Table II reports the internodal molecular weight, the density, the glass transition temperature ( $T_g$ ), the melting point ( $T_m$ ), when present, and the solubility parameter ( $\delta$ ).

The molecular weight ( $M_c$ ) was calculated on the basis of eq. (1), taking into account TIPA with a fraction  $\frac{2}{3}$  of its molecular weight and the molecular weight of the different diols indicated in Table I. The solubility parameters were calculated by the method of group contributions, according to Fedors,<sup>6</sup> on the basis of the stoichiometry.

### Gas Transport Properties

Measurements of the permeability and the diffusion coefficient were carried out using a Lyssy permeameter, modified in the laboratory. The method of accumulation was used. A detailed description of the permeameter and methodologies of measurement is reported in Ref. 3. Initially, both the upper and lower semicells were full of helium. A rapid and complete substitution of the helium in the upper semicell by the sample gas was then carried out. The gas then permeated into the lower semicell where it was circulated by a pump together with the helium in the closed lower circuit. Every now and then, at given intervals, samples of this gas were taken and analyzed by GC. The amount ( $Q$ ) of the permeated gas could be measured as a function of time. Permeability ( $P$ ) of the membrane was evaluated in steady-state conditions, i.e., when  $dQ/dt$  is constant.

The diffusion coefficient was calculated with the method of time lag  $\tau$  by extrapolation along the abscissa ( $t$ ) of the tangent of the steady part of curve  $Q(t)$ . From the  $\tau$  value,  $D$  was calculated using  $D = l^2/6\tau$ .

The solubility coefficient ( $S$ ) was evaluated by the equation  $S = P/D$ . The values reported in this work are the average values of many experimental runs. The largest experimental errors are lower than  $\pm 10\%$  for  $P$  and  $D$ .<sup>3</sup>

### Water-vapor Transport

Permeability tests were done according to ASTM E 96 (Ref. 7) at 23°C by periodic weighing (every 24

**Table II Polyurethane Chemical-Physical Properties (Molecular Weight, Density, Glass Transition, Melting Point, Solubility Parameter)**

Membrane	$M_c$	Density (g/cm <sup>3</sup> )	$T_g$ (°C)	$T_m$ (°C)	$\delta_p$ (cal/cm <sup>3</sup> ) <sup>1/2</sup>
PEMC 565-PU	1040	1.29	38.5	a	13.2
PEMC 840-PU	1320	1.25	23.2	a	10.4
PEMC 1025-PU	1500	1.20	9.0	a	10.3
PEMC 1900-PU	2380	1.18	-14	b	10.1
PEMC 2370-PU	2860	1.18	-20	41	10.0
PTMC 670-PU	1150	1.29	29.5	a	10.9
PTMC 1093-PU	1570	1.27	8.2	a	10.7
PTMC 2600-PU	3070	1.21	-15.9	42.4	10.4
PPMEMC 1700-PU	2170	1.18	-13.5	a	9.9
PTEGC 2100-PU	2580	1.20	-10	a	10.1
PDPGC 2537-PU	3010	1.19	5.3	a	9.64
PDPGPPGC 1545-PU	2020	1.16	-3.7	a	9.42
PC-ES 2000-PU	2470	1.17	-27	a	11.1
PTMA 600-PU	1050	1.20	14.8	a	12.1
PTMA 1000-PU	1510	1.19	-9.6	a	11.6
PTMA 1600-PU	2100	1.18	-34.1	b	11.1

<sup>a</sup> No melting point.

<sup>b</sup> Samples crystallize only after long times.

h) of a standard cell, sealed by the membrane, the interior of which was maintained anhydrous with CaCl<sub>2</sub>. The environmental humidity outside was kept constant by a saturated solution of KCl (85.4% relative humidity). Water permeability was calculated from the weight increase rate of the desiccator, taking into consideration its equivalent in N cm<sup>3</sup>, the geometry of the membrane, and the water partial pressure difference.

Even if the ASTM cup method is uncertain, the amount of permeated water is so large, compared to the gas permeability, that the reported figures are quite adequate for comparison. The solubility coefficient ( $S$ ) was evaluated by measuring the equilibrium water-vapor absorption of the membranes in a 97.5% RH atmosphere at 23°C.<sup>8</sup>

## ANALYSIS AND DISCUSSION

To obtain an overall view of PU behavior in transport phenomena, the data obtained from polyesters as poly(tetramethylene-adipate) diols (PTMA) are also reported for comparison purposes.

### Density and Thermal Properties of PU

From Table II it can be seen that the PU density varies from 1.16 g/cm<sup>3</sup> for the copolymer

PDPGPPGC-PU to 1.29 g/cm<sup>3</sup> for the PTMC-PU. In the PTMC and PEMC-PU series, a decrease in density with increase in chain length can be observed. For the same PUs, it can be observed that  $T_g$  also decreases with increase in chain length. This corresponds to the concept of an increase in free volume.

$T_g$  depends both on the intrinsic flexibility of the chain and on the interaction between different chains. This latter appears to be the most important factor. In fact, a decrease in the weight percentage of TDI, which acts as a stiffening element due to the hydrogen bonds of the urethane groups generated by the same TDI, always causes a decrease in the  $T_g$  of the corresponding PUs (Table II). The decrease of TDI % corresponds to an increase in the diol molecular weight; in other words, by increasing the molecular weight of the diols, the  $T_g$  of PU decreases even though the  $T_g$  is influenced slightly by the starting diols. Thus, for these PUs, the diol structure and composition seem to have a less influence on the variation of  $T_g$ , especially where copolymeric diols are concerned. For example, in the case of PEMC 1900-PU, containing six methylenic units, and PPMEMC 1700-PU, containing both five and six methylenic units, at comparable  $M_c$ , we can observe that the two  $T_g$ 's are almost equal. Even when methylene groups are partially substituted by

—O— groups (ether), which could, in principle, interfere with the hydrogen-bond distribution, the  $T_g$  of the corresponding PU does not change appreciably. For example, PTEGC 2100-PU and PEMC 1900-PU, which have a similar  $M_c$ , differ only in that in the former case there are six methylenes with three interposing oxygens between two successive carbonate groups, whereas in the latter, there are only six methylene groups. The insertion of the oxygen atoms produces only small variations of the  $T_g$  (from  $-14$  to  $-10^\circ\text{C}$ ). In some cases, an influence of the structure of the diol chain on  $T_g$  seems to be present. For instance, substituting a hydrogen with a methyl group in the ethylene oxide introduces a rotational rigidity (steric hindrance) of the chain, which is in accordance with the slight increase of  $T_g$  of PDPGC 2537-PU with respect to that of PTEGC 2100-PU. Moreover, copolymerization, which substitutes blocks of polypropylenglycol for the propylenglycol dimers, reduces the  $T_g$  (PDPGPPGC 1545-PU).

The substitution of half the carbonic groups with ester groups leads to a reduction of  $T_g$ . The P(C-ES) 2000 PU is a copolymer similar to PPMEMC-PU, as for the copresence of pentamethylene and hexamethylene groups, but it differs in the fact that about half the carbonic groups are substituted by ester groups. The  $T_g$  of P(C-ES)-PU is lower than that of the analogous copolymer PPMEMC-PU; this, however, could be attributed to the reduction of polarity (the ester group has one oxygen atom less) and to a consequent minor interaction between the chains, and not to a higher internal flexibility.

All these considerations show that  $T_g$  depends mainly on the interchain forces due to the hydrogen bonds connecting the NH of the urethane groups to the electron donor atoms (e.g., oxygen), belonging to both the urethane groups and the diol chains.

### Crystallinity

By decreasing the weight percentage of TDI, the hydrogen-bond density also decreases; when this density goes below a certain value, in the case of regular sequences in the units of the high molecular weight diols, secondary van der Waals forces among the chains may induce crystallization.

Polycarbonate diols containing methylenic groups in the chain are generally crystalline at room temperature; instead, the PUs prepared from them are crystalline only when high molecular weight polycarbonate diols are used. The crystallization seems favored by the packing of the "soft" methylene-rich parts of the PU chain; the longer the diol chains, the easier the packing. On the contrary, with copolymeric diols like PTEGC, PDPGC, PDPG, PDPGPPGC, and P(C-ES), which are viscous liquids at room temperature, no melting point is present in the synthesized PUs.

### Transport Properties and Molecular Structure

Tables III-VI report the transport properties ( $P$ ,  $D$ ,  $S$ ) of gases and water vapor through the prepared PU membranes. The permeabilities, the diffusion coefficients, and the solubilities of the gases differ according to the diols used.

**Table III Gas Transport Properties of PES-PU Membranes: Permeability, Diffusion Coefficient and Solubility Coefficient**

Membrane	Type <sup>a</sup>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO	Water Vapor
<u>Permeability: Exp. (10) [N cm<sup>3</sup> cm/(cm<sup>2</sup> s cmHg)]</u>							
PTMA 600-PU	a	0.13	<sup>b</sup>	0.047	0.7	0.037	5,200
PTMA 1000-PU	a	0.75	0.15	0.51	6.4	0.26	7,900
PTMA 1600-PU	a (- > c)	2	0.80	1.6	20	1.2	9,900
<u>Diffusivity: Exp. (8) (cm<sup>2</sup>/s)</u>							
PTMA 600-PU	a	7.60	<sup>b</sup>	2.700	2.7	3.9	4.1
PTMA 1000-PU	a	16	5.3	5.8	5.7	7.4	5.5
PTMA 1600-PU	a (- > c)	39	22	17	13	11	7.8
<u>Solubility: Exp. (4) [N cm<sup>3</sup>/(cm<sup>3</sup> cmHg)]</u>							
PTMA 600-PU	a	1.7	<sup>b</sup>	1.7	26	0.95	127,000
PTMA 1000-PU	a	4.7	2.8	8.8	110	3.5	145,000
PTMA 1600-PU	a (- > c)	5	3.6	10	87	10	127,000

<sup>a</sup> a = amorphous; c = crystalline.

<sup>b</sup> Values out of range (low).

**Table IV Gas Transport Properties of PC-PU Membranes: Permeability, Diffusion Coefficient and Solubility Coefficient**

Membrane	Type <sup>a</sup>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO	Water Vapor
<b>Permeability: Exp. (10) [N cm<sup>3</sup> cm/(cm<sup>2</sup> s cmHg)]</b>							
PTMC 670-PU	a	0.14	0.041	0.05	0.9	0.07	1,100
PTMC 1093-PU	a	0.19	0.088	0.14	1.8	0.14	2,800
PTMC 2600-PU	c	0.41	0.12	0.13	3.3	0.19	2,500
<b>Diffusivity: Exp. (8) (cm<sup>2</sup>/s)</b>							
PTMC 670-PU	a	2.9	1.9	0.8	1.2	1.0	1.2
PTMC 1093-PU	a	5.4	5.0	1.9	1.7	3.3	2.0
PTMC 2600-PU	c	7.2	2.6	1.5	2.6	4.3	3.0
<b>Solubility: Exp. (4) [N cm<sup>3</sup>/(cm<sup>3</sup> cmHg)]</b>							
PTMC 670-PU	a	4.9	2.2	6.3	72	7.0	96,300
PTMC 1093-PU	a	3.5	1.4	7.2	100	4.2	141,000
PTMC 2600-PU	c	6.3	4.6	9.0	130	4.6	81,900

<sup>a</sup> a = amorphous; c = crystalline.

**PU from Polydiols Containing  
—O—(CO)—O— and CH<sub>2</sub> Groups  
(PTMC, PEMC) and, for Comparison,  
—(CO)—O— and CH<sub>2</sub> Groups (PTMA)**

The sequences of the methylenic CH<sub>2</sub> groups in the soft part of the PU chains are the following:

- For PTMA: —(CH<sub>2</sub>)<sub>4</sub>— and —(CH<sub>2</sub>)<sub>6</sub>— interconnected by the ester groups.
- For PTMC: —(CH<sub>2</sub>)<sub>4</sub>— interconnected by the carbonate groups.
- For PEMC: —(CH<sub>2</sub>)<sub>6</sub>— interconnected by the carbonate groups.

**Table V Gas Transport Properties of PC-PU Membranes: Permeability, Diffusion Coefficient and Solubility Coefficient**

Membrane	Type <sup>a</sup>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO	Water Vapor
<b>Permeability: Exp. (10) [N cm<sup>3</sup> cm/(cm<sup>2</sup> s cmHg)]</b>							
PEMC 565-PU	a	0.25	0.06	0.05	1.4	0.06	1,100
PEMC 840-PU	a	0.30	0.11	0.09	2.7	0.2	1,400
PEMC 1025-PU	a	0.83	0.23	0.22	3.8	0.3	2,100
PEMC 1900-PU	a-> c	2.2	0.76	1.10	15	1.0	4,600
PEMC 2370-PU	c	2.9	1.20	1.60	12	1.3	5,600
PPMEMC 1700-PU	a	1.1	0.37	0.64	10	0.59	3,300
<b>Diffusivity: Exp. (8) (cm<sup>2</sup>/s)</b>							
PEMC 565-PU	a	2.2	1.7	0.41	2.2	1.5	1.3
PEMC 840-PU	a	2.6	3.7	1.2	2.9	3.9	1.5
PEMC 1025-PU	a	12	7.6	1.9	3.8	5.6	1.7
PEMC 1900-PU	a-> c	19	17	11.0	21	14	7.0
PEMC 2370-PU	c	22	24	12.0	27	23	7.6
PPMEMC 1700-PU	a	7.9	7.9	3.8	8.9	7.4	3.4
<b>Solubility: Exp. (4) [N cm<sup>3</sup>/(cm<sup>3</sup> cmHg)]</b>							
PEMC 565-PU	a	11	3.5	11.0	93	4	91,000
PEMC 840-PU	a	11	3.0	7.5	94	5	96,400
PEMC 1025-PU	a	7	3.0	12.0	100	6	12,300
PEMC 1900-PU	a-> c	11	4.5	10.0	71	7	66,300
PEMC 2370-PU	c	13	4.8	13.0	45	6	74,600
PPMEMC 1700-PU	a	14	4.7	17.0	110	8	96,200

<sup>a</sup> a = amorphous; c = crystalline.

**Table VI Gas Transport Properties of PC-PU and PCES-PU Membranes: Permeability, Diffusion Coefficient and Solubility Coefficient**

Membrane	Type <sup>a</sup>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO	Water Vapor
Permeability: Exp. (10) [N cm <sup>3</sup> cm/(cm <sup>2</sup> s cmHg)]							
PDPGC 2537-PU	a	0.53	0.11	0.14	3.6	0.18	2,700
PDPGPPGC 1545-PU	a	1.30	0.37	0.76	9.7	0.78	4,000
PTEGC 2100-PU	a	0.35	0.11	0.20	4.2	0.19	13,000
PC-ES 2000-PU	a	2.00	0.80	1.70	27.0	1.00	8,700
Diffusivity: Exp. (8) (cm <sup>2</sup> /s)							
PDPGC 2537-PU	a	8.1	4.0	2.1	3.5	3.3	1.9
PDPGPPGC 1545-PU	a	23	13	4.8	6.1	16.0	2.0
PTEGC 2100-PU	a	7.9	7.4	3.7	5.0	6.3	3.4
PC-ES 2000-PU	a	24	18	14	16	24.0	11.0
Solubility: Exp. (4) [N cm <sup>3</sup> /(cm <sup>3</sup> cmHg)]							
PDPGC 2537-PU	a	6.5	2.8	6.6	100	5.4	144,000
PDPGPPGC 1545-PU	a	5.6	2.9	16	160	5.0	200,000
PTEGC 2100-PU	a	4.4	1.5	5.4	84	3.0	340,000
PC-ES 2000-PU	a	8.4	4.4	12	170	4.2	790,000

<sup>a</sup> a = amorphous; c = crystalline.

The chains that contain  $-(CH_2)_n-$  connected to the ester groups show lower  $T_g$  than do those connected to carbonate groups. For amorphous polymers, like those reported in Tables III-V, this indicates a larger free volume. Accordingly, in the case of a comparable  $M_c$ , the diffusivity is in the order PTMA 600 > PTMC 670 > PEMC 565. Moreover, the diffusivity of gases increases with  $M_c$ , which can be related to the decrease of  $T_g$  and, again, to the corresponding increase of free volume. Diffusivity decreases with the increase in the gas molecule diameter.

The solubility coefficients ( $S$ ) of the permanent gases are lower in the case of shorter methylenic chains. Polyester PU like PTMA-PU shows  $S$  not unlike that of the corresponding PTMC-PU. Easily condensable gases, such as CO<sub>2</sub>, show an  $S$  value usually much higher than that of permanent gases; this is due to the high  $\Delta H$  of condensation. For membranes with low  $M_c$ , the solubility of CO<sub>2</sub> increases in the order PTMA-PU < PTMC-PU < PEMC-PU. By increasing  $M_c$ , the solubility of CO<sub>2</sub> increases and reaches values of the same order for all amorphous PUs of the three series. Permeability to gases is greater for higher  $M_c$ , for longer methylene chains, and for equal methylene chains when polyester groups are present.

Permeability to water vapor is orders of magnitude higher than that of the gases. This is due mainly to the extremely high solubility of water in the PUs since the vapor-diffusion coefficients are of the same

order of magnitude as are the diffusion coefficients of gases, and they change little with the type of polymer. The solubility of water vapor appears to be at least 10,000 times greater than is the solubility of permanent gases. This high solubility is due to the strong interaction of water with the urethane groups, as has been possible to verify by IR.<sup>9</sup> Water solubility decreases when the molecular weight of the diols is so high that crystallization can take place. The water vapor permeability of the membranes based on polyester diols PTMA is higher than that based on polycarbonate diols.

#### **PU of Copolymeric Polydiols PPMEMC and P(C-ES) (Tables V and VI)**

These copolymers are amorphous and elastomeric and have both penta and hexa methylene groups: P(C-ES)-PU contains both the  $-C(O)-O-$  ester group and the  $-O-C(O)-O-$  carbonate group, whereas PPMEMC contains  $-O-C(O)-O-$  groups. The greater flexibility of the P(C-ES)-PU is evidenced by the  $T_g = -27^\circ\text{C}$ , compared with the value  $T_g = -13.5^\circ\text{C}$  of PPMEMC-PU; this is in agreement with the existence of a greater free volume. Accordingly, we observe a diffusion coefficient that is two or three times higher (to various gases and water vapor) in the case of P(C-ES)-PU. The solubility coefficient in the two polymers is comparable for a given gas and also for the water vapor, which presents very high values for the reason explained earlier. The solubility

coefficient of CO<sub>2</sub> is a little higher in the case of P(C-ES)-PU. Permeability is, in general, higher for the P(C-ES)-PU.

#### **Polyurethanes Containing —OC(O)O— and —O— Groups (Table VI)**

These PUs, prepared from diols PDPGC and PTEGC or copolymeric diol PDPGPPGC (Table I), are amorphous and elastomeric. The PTEGC-PU, less hindered in rotation due to the lack of lateral CH<sub>3</sub>, has the minimum  $T_g$  ( $T_g = -10^\circ\text{C}$ ). Furthermore, it packs easily and has the highest density (1.2 g/cm<sup>3</sup>) and the lowest diffusivity, the other two PUs, being characterized by CH<sub>3</sub> pending lateral groups. The polymer with the lowest  $T_g$  ( $-3.7^\circ\text{C}$ ) is the block polymer PDPGPPG-PU, which also presents the highest diffusion coefficients.

The solubility coefficient of the permanent gases and CO<sub>2</sub> is lowest in the case of the polymer containing the oxyethylene groups; of the other two copolymers, it is slightly higher in the case of the block copolymer. As a final result, the permeability to gases is lowest for the PU containing polyoxyethylene groups and is, on the average, higher for polymers based on polyoxypropylene groups. As usual, the permeability to CO<sub>2</sub> or to water is noticeably higher than is the permeability to the gases. As for the other PUs, the very high permeability to water vapor must be attributed mostly to their high solubility. The maximum solubility coefficient is reached in the PTEGC 2100; this could be explained

by the lack of hydrophobic CH<sub>3</sub> groups and, therefore, to the greater ratio of the O/C atoms, which is 1/2 instead of 1/3 in the case of the polyoxypropylene glycol, where oxygen is the electron donor that can associate water.

#### **Separation Factor and Molecular Structure**

The separation factors are reported in Table VII for the combination of gases: O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, and H<sub>2</sub>O/CH<sub>4</sub>, together with the permeabilities of O<sub>2</sub>, CO<sub>2</sub>, and water vapor in the given membrane. For the O<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>O/CH<sub>4</sub> systems, the more permeable the membranes, the less selective they are. The physical properties of nitrogen and oxygen, their molecular dimensions, and their interaction with polymers are similar; however, the oxygen atom is more electronegative than is nitrogen; the C and H belonging to the polymer chains are less electronegative.<sup>10</sup> This could be considered an important argument in the effort to understand the reason for the higher solubility of O<sub>2</sub>, compared to N<sub>2</sub>, in almost all the PUs that we studied. Diffusivity depends on the polymer free volume, on the gas molecule dimensions, and also on the "hole" size distribution. The higher diffusivity ratios are found in the case of the lowest molecular weight ( $M_c$ ) PUs, those endowed with the higher  $T_g$  (which are glassy at room temperature). We believe that the existence of a low fraction of free volume and a tight distribution of its cells could be important factors in determining selectivity.

**Table VII Transport Properties and Separation Factors of Some PU Membranes<sup>a</sup>**

Membrane	$P_{\text{O}_2}$	$\alpha_{\text{O}_2/\text{N}_2}$	$P_{\text{CO}_2}$	$\alpha_{\text{CO}_2/\text{CH}_4}$	$P_{\text{H}_2\text{O}}$	$\alpha_{\text{H}_2\text{O}/\text{CH}_4}$
PTMA 600-PU	0.13	—	0.7	14	5,200	110,000
PTMA 1000-PU	0.75	5.0	6.4	12	7,900	15,000
PTMA 1600-PU	2	2.5	20	12	9,900	6,500
PTMC 670-PU	0.14	3.4	0.9	18	1,100	23,000
PTMC 1093-PU	0.19	2.1	1.8	12	2,700	20,000
PTMC 2600-PU	0.41	2.0	3.3	25	2,500	19,000
PEMC 565-PU	0.25	4.2	1.4	28	1,100	23,000
PEMC 840-PU	0.30	2.7	2.7	30	1,400	16,000
PEMC 1025-PU	0.83	3.6	3.8	17	2,100	9,600
PEMC 1900-PU	2.2	2.9	15	13	4,500	4,200
PEMC 2370-PU	2.9	2.5	12	7.5	5,600	3,500
PPMEMC 1700-PU	1.10	3.1	10	16	3,300	5,100
PDPGC 2537-PU	0.53	4.7	3.5	26	2,700	20,000
PDPGPPGC 1545-PU	1.3	3.5	9.6	13.	4,000	5,300
PTEGC 2100-PU	0.35	3.2	4.2	21.	12,600	63,000
PC-ES 2000-PU	2.0	2.5	27	15	8,700	5,000

<sup>a</sup> Permeability  $P \times 10^{10}$  [N cm<sup>3</sup> cm/(cm<sup>2</sup> s cmHg)].



In the case of the H<sub>2</sub>O/CH<sub>4</sub> system, the separation factor  $\alpha$  is determined mainly by the water solubility coefficient, which is very large compared to that of CH<sub>4</sub>, while the diffusivities of H<sub>2</sub>O and CH<sub>4</sub> are of the same order:  $\alpha$  decreases with decrease in the number of the water-sorption centers (urethane groups) per unit volume, i.e., with the increase in  $M_c$ . A similar explanation can be given for the relationship  $P$ ,  $\alpha$  in the case of CO<sub>2</sub>/CH<sub>4</sub>: The higher solubility of CO<sub>2</sub> and the low fraction of the free volume (polymers with higher  $T_g$ ) are mainly responsible for these results.

### General Considerations on Diffusion and Solubility Coefficients with Particular Reference to the Membranes in the Elastomeric State

The polymers presented in this work are elastomeric at 35°C, at which the transport properties were measured with the exception of PEMC 565-PU. Therefore, a general interpretation of diffusivity and solubility coefficients, valid for this type of elastomeric polymers, could be of interest. It is known that the diffusion coefficient ( $D$ ) depends on the molecular dimensions of the gas, on the free volume of the polymer (and, hence, on its  $T_g$ ), and also on the size distribution of the free-volume holes. From this point of view, membranes with lower density and lower  $T_g$  should have a higher  $D$ . Moreover, for a given membrane, the diffusion coefficient decreases by increasing the size of the permeant.

When the amorphous polymers are at a temperature higher than  $T_g$ , the chains are continuously oscillating, there are no permanent holes, and the permeate moves as in a liquid. It is possible to assume that the diffusion coefficient may be related to the free volume of the polymers. Its experimental determination is quite difficult.<sup>11</sup> Therefore, a theoretical evaluation has to be performed. According to the W.L.F. theory,<sup>12</sup> the fraction of free volume can be calculated with the relation

$$f = 0.025 + 4.8 \times 10^{-4}(T - T_g) \quad (2)$$

valid when the permeant does not swell the polymer. As an empirical relation, we propose the following:

$$f \log D = Af - B \quad (3)$$

which agrees with the Fujita model.<sup>13</sup> Using the  $T_g$  and  $D$  data of an analogous series of PUs based on PTMA, PTMC, and PEMC of different molecular weights and using O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> (see Figs. 1 and 2), it can be seen that the experimental data can be correlated, as a first approximation, to

the free volume even if due to the small number of experimental data it is not possible to perform a statistical evaluation of the correlation.

If for the same membranes PTMA-PU, PTMC-PU, and PEMC-PU the logarithm of the diffusion coefficient is plotted as a function of the collision diameter ( $\sigma$ ), calculated by the viscous and kinetic behavior, a nonlinear trend is obtained, the tendency being for  $D$  to decrease with the growth of the cross section of the permeate. This suggests that the diffusion depends not only on molecular size but also on the interactions between the gas molecules and the membranes.

### Analysis of Solubility Data According to Prausnitz and Shair

Prausnitz and Shair proposed an interesting procedure to analyze data on the solubility of gases in solvents.<sup>14</sup> It has been demonstrated that this type of correlation can be applied to the gas/rubber polymer systems.<sup>15</sup> With this approach, the solution is considered as a two-step process: The first is the condensation of the gas into a pseudoliquid whose properties are calculated from the corresponding state theory. The second step is the dissolution of the pseudoliquid into the polymer that acts as a solvent. The variation of the free energy of the two-step process is

$$\Delta G = RT \ln \{ f_i^L / f_i^0 \} + RT \ln \gamma_i X_i \quad (4)$$

where  $\gamma_i$  is the activity coefficient of the gas  $i$  and  $X_i$  is the molar fraction of the corresponding dissolved liquid. From the theory of regular solutions, it can be written that

$$RT \ln \gamma_i = V_i^L (\delta_p - \delta_i)^2 \Phi_p^2 \quad (5)$$

where  $\Phi_p$  is the polymer volume fraction,  $V_i^L$  the molar volume of component  $i$  in the liquid state, and  $\delta_i$  its solubility parameter.

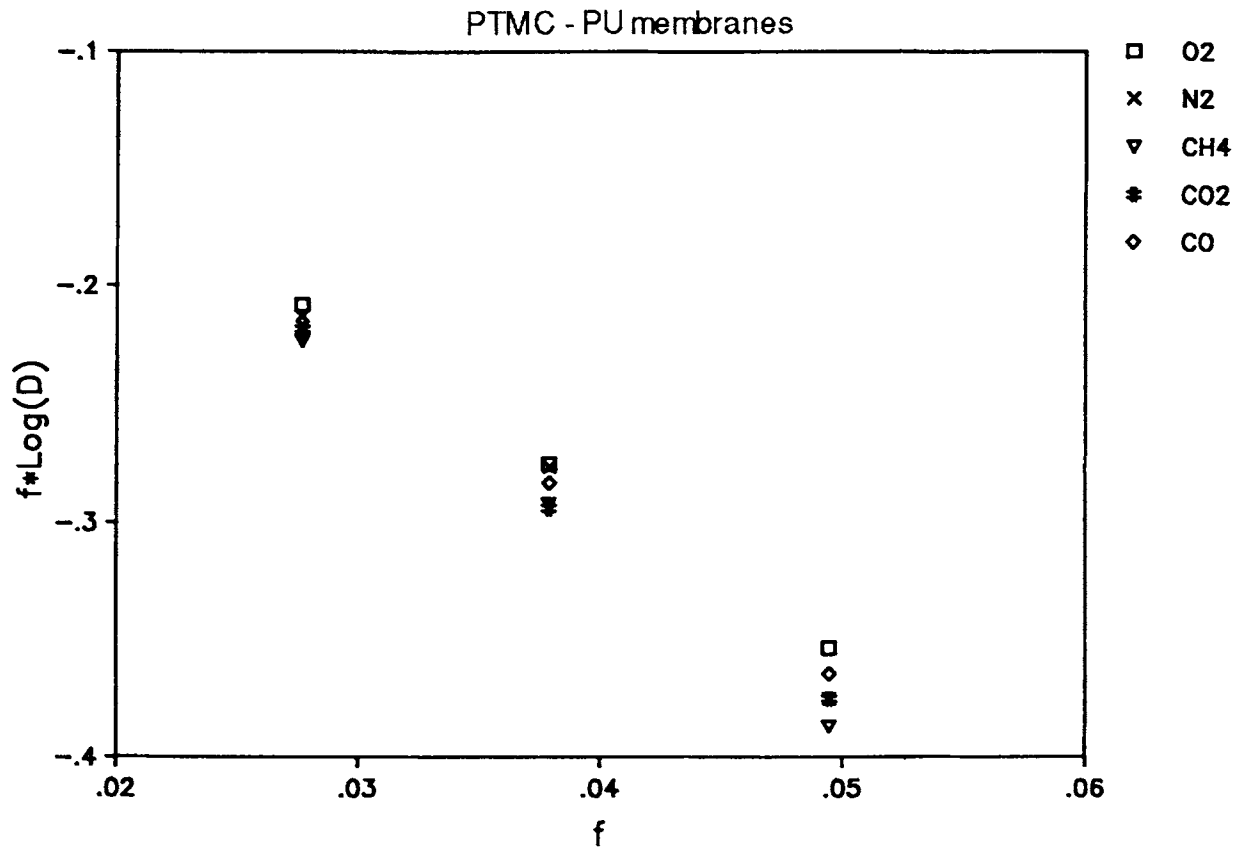
At equilibrium,  $\Delta G = 0$ , for which

$$\frac{1}{X_i} = \frac{f_i^L}{f_i^0} \exp \frac{V_i^L (\delta_p - \delta_i)^2 \Phi_p^2}{RT} \quad (6)$$

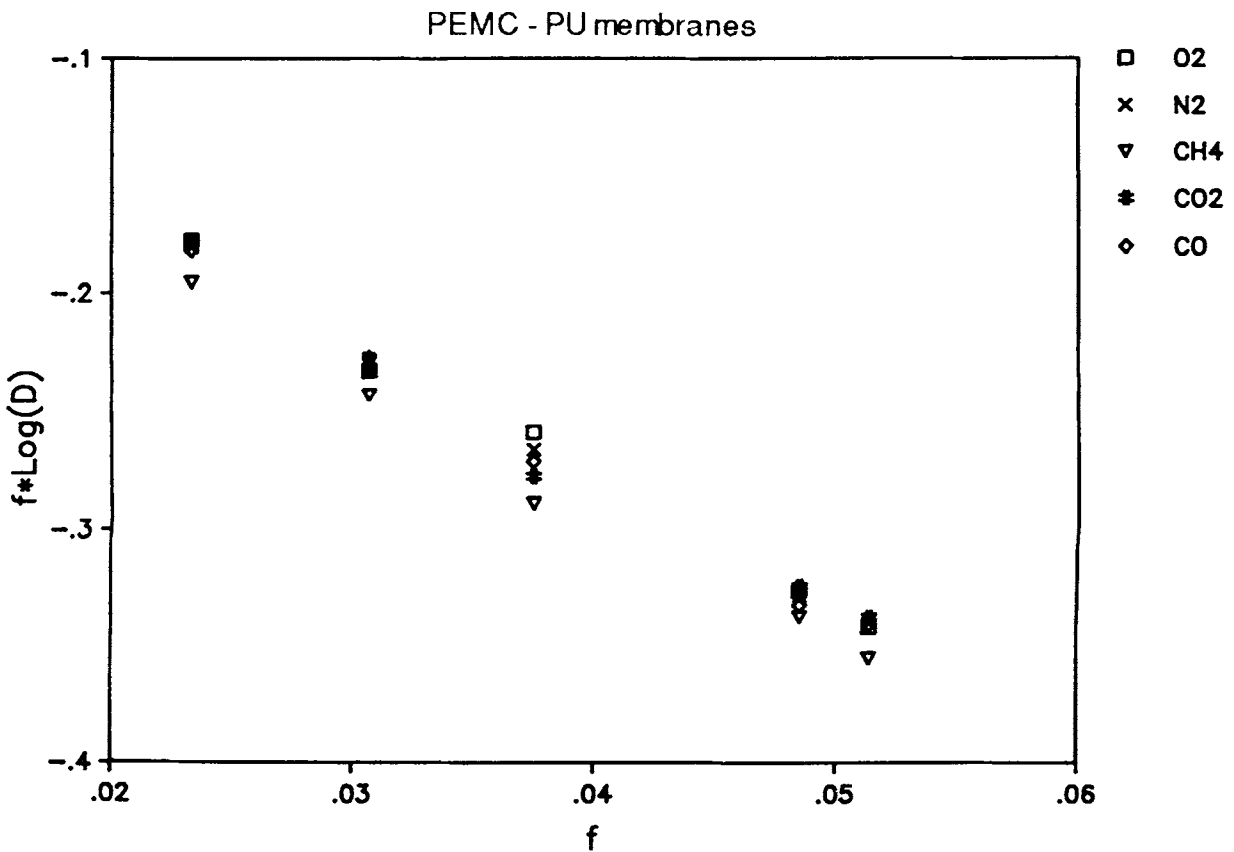
By setting  $S_i' = X_i / f_i^0$ , we write

$$-\ln S_i' = \ln f_i^L + \frac{V_i^L (\delta_p - \delta_i)^2}{RT} \quad (7)$$

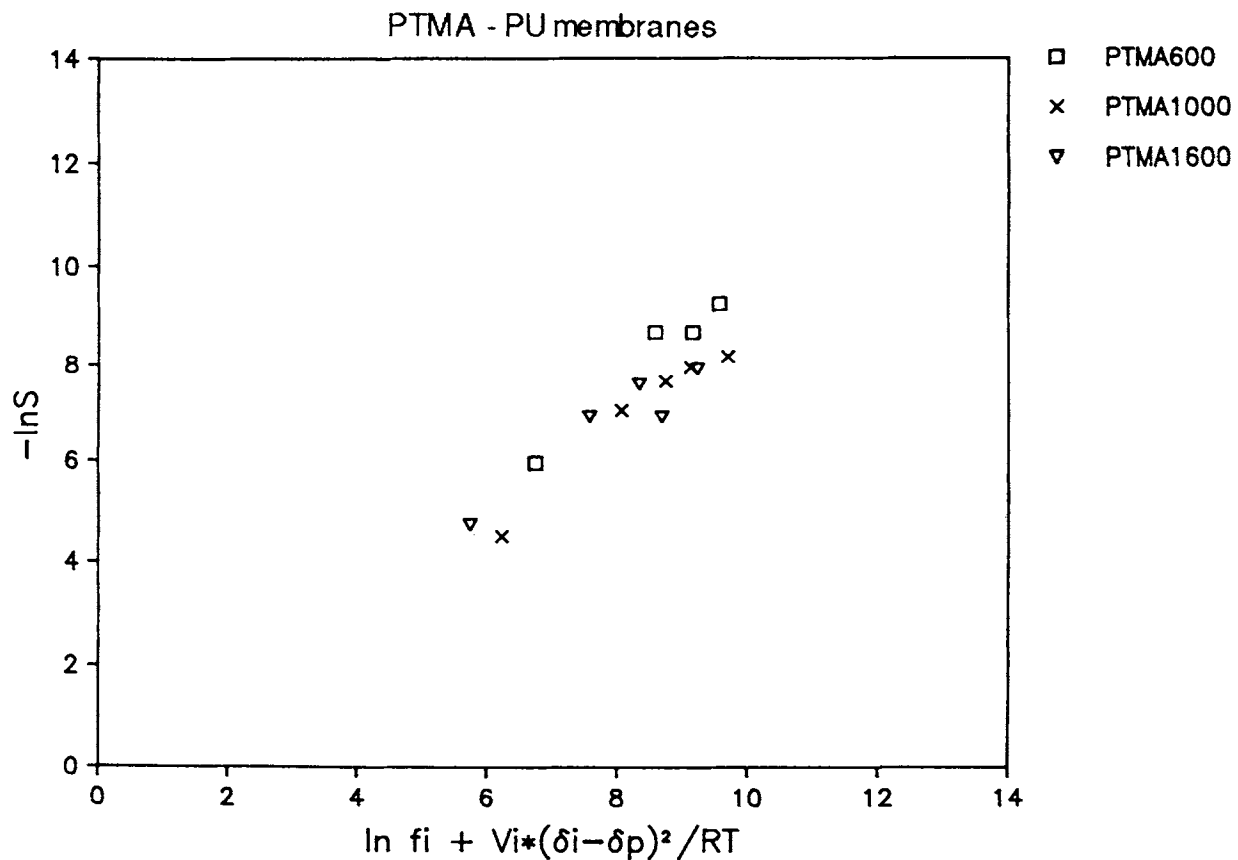
where the reference fugacity  $f_i^0 = 1$  atm has been assumed. The fugacity  $f_i^L$  of the hypothetical liquid



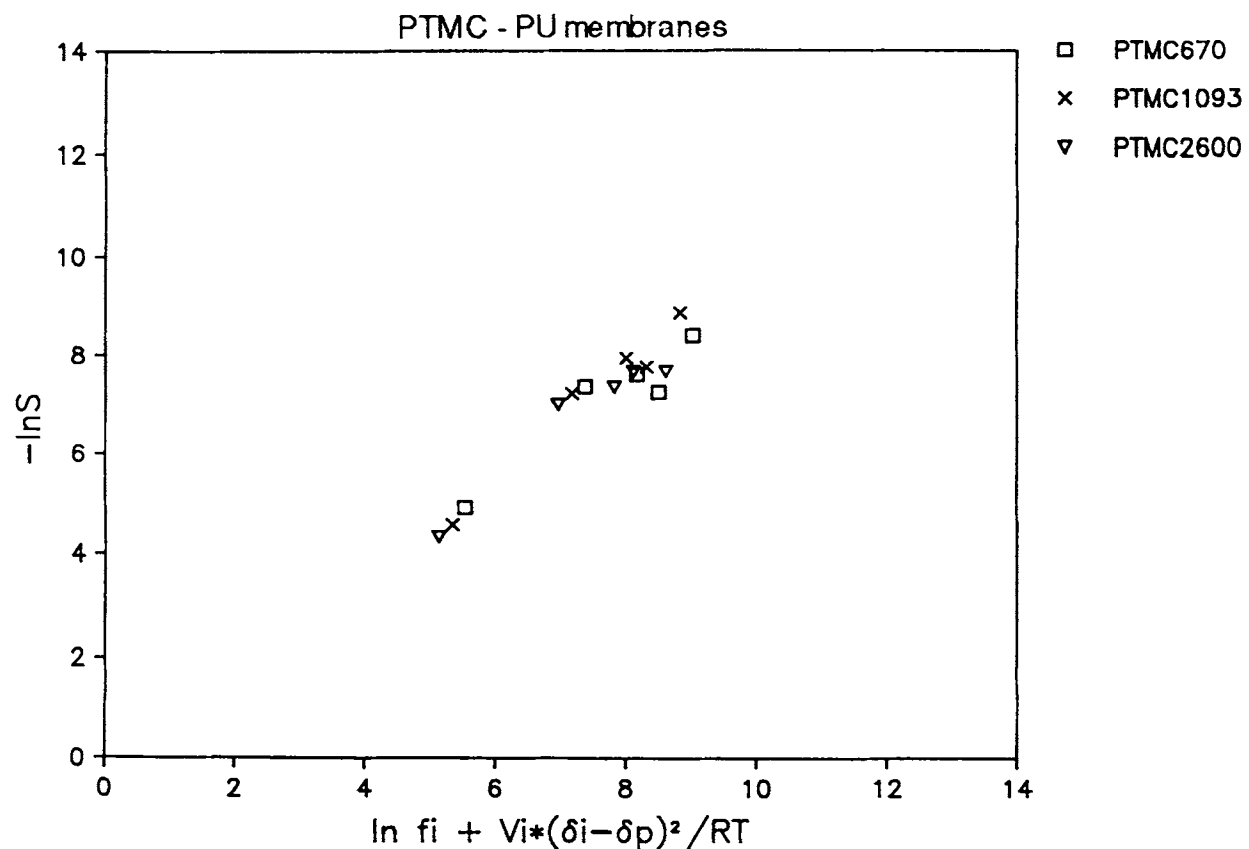
**Figure 1**  $f \log D$  vs.  $f$  of  $O_2$ ,  $N_2$ ,  $CO$ ,  $CO_2$ , and  $CH_4$  in PTMC-PU of different molecular weights.



**Figure 2**  $f \log D$  vs.  $f$  of  $O_2$ ,  $N_2$ ,  $CO$ ,  $CO_2$ , and  $CH_4$  in PEMC-PU.



**Figure 3** Logarithmic solubility coefficient  $-\ln S$  of the same gases as in Figures 1 and 2 vs. the second term of eq. (7) in PTMA-PU of different molecular weights.



**Figure 4**  $-\ln S$  of the same gases as in Figures 1 and 2 vs. the second term of eq. (7) in PTMC-PU of different molecular weights.

at atmospheric pressure is independent of the polymer property; Prausnitz and Shair demonstrated that the reduced fugacity is a universal function of the reduced temperature.

In Figures 3 and 4, the logarithm of experimental  $S$  is reported vs. the solubility calculated according to eq. (7). It can be observed that the experimental coefficients of solubility reported in the figures are given in  $\text{N cm}^3/\text{cm}^3 \text{ cmHg}$ , whereas those of eq. (7) are expressed as molar fractions/atm; so there is a factor to pass from one solubility value to the other.

The trend of experimental vs. calculated solubility data is linear for all membranes: The slopes of the regression lines are very close to unity; this demonstrates that the theory proposed by Prausnitz and Shair interprets the solubility of all the gases tested in all the elastomeric membranes quite well. The glassy membrane PEMC 565-TIPA ( $T_g = 39^\circ\text{C}$ ) could not be studied with the previous theory but only with the "dual mode absorption" theory.<sup>16</sup> Nevertheless, since the measurements were done very near the membrane  $T_g$  ( $39^\circ\text{C}$ ), the results were not appreciably far from what was foreseen by eq. (7). When membranes of high  $M_c$  contain zones of crystallization, the preceding theory cannot be used.

## CONCLUSIONS

PU membranes are particularly suitable for the study of the relations between their chemical nature and structure and their transport properties, it being quite easy to prepare PU membranes with different chemical composition and structure. The studied polycarbonate PUs are mainly amorphous. Their transport properties, evaluated at  $35^\circ\text{C}$ ,  $\Delta P = 1 \text{ atm}$  for  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  and at  $23^\circ\text{C}$  for water vapor, suggest the following conclusions:

- (a) The diffusion coefficient can be related to the free volume of the membrane or to its  $T_g$  and increases with the lowering of  $T_g$ . This parameter may be easily changed by synthesis.

- (b) The solubility data can be described well by the Prausnitz-Shair model of regular solutions except for water. This suggests how to modify the chemical composition of a membrane to decrease the difference  $\delta_p - \delta_g$  and to increase the chosen gas solubility. This suggests also how to operate in order to increase the difference in the solubility coefficients between two gases to obtain a better selectivity factor.

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