

Polyurethane Membranes from Polyether and Polyester Diols for Gas Fractionation

M. PEGORARO,* L. ZANDERIGHI, A. PENATI,[†] F. SEVERINI, F. BIANCHI, NANYUN CAO, R. SISTO,¹ and C. VALENTINI¹

Dipartimento di Chimica Industriale e Ingegneria Chimica, "G.NATTA," Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy, and ¹ENI Ricerche, Monterotondo, Italy

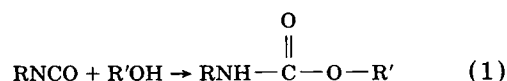
SYNOPSIS

Polyurethane prepolymers were prepared in ethylacetate from TDI and poly(oxypropylene)glicols (PE-PU) or poly(tetramethyleneglycoladipate)diols (PES-PU) of different molecular weights (M). Homogeneous membranes were prepared by spreading the prepolymer solution added with a three, four or pentafunctional crosslinking agent, in the presence of stannous octoate as a catalyst. On increasing M, the PUs T_g decreases regularly in the range +30 to -47°C. PU's are amorphous with the exception of PES-PU obtained from highest M polyester diols. Permeability P, diffusivity D, solubility coefficient S of N₂, O₂, CO₂, CH₄, CO were measured at T = 35°C (>T_g). P, D, S do not depend on the crosslinker functionality, but mainly on M. P and D in PE-PU are linear function of T-T_g, while in PES-PU the function is not linear. Gas solubility fulfills in general the regular solution theory. P, D, S of water vapor is also given. Permeability decreases in the order H₂O > CO₂ > O₂ > CH₄ > CO > N₂. Some practical application based on particular selectivities is suggested.

INTRODUCTION

Polyurethanes (PUs) are well known and widely used in many fields as they are suitable for the production of foams, filaments, and films.¹ The study of transport properties of fluids through PU membranes is particularly interesting because the molecular structure of the polymer chain can be easily changed in a wide range by changing the reagents, which are generally polyisocyanates and polyhydroxyl or amino-terminated compounds.

In the present work, difunctional isocyanate in the form of prepolymers, of different molecular weight, reacted with crosslinking agents containing OH groups with different functionality, have been used to prepare new membranes. The formation reaction of PU involves the isocyanate and the hydroxyl groups according to:



where the urethane link is shown.

As secondary reactions, which give allophanate and biuret groups^{2,3} responsible for branching and crosslinking, are favoured at high temperatures, the polymerization reactions were therefore performed at sufficiently low temperature.⁴

The polymers were prepared in two stages: prepolymer and network forming. This is a procedure that allows better control of the network structure than in the "one-shot" procedure as described in a preceding paper.⁵

The aim of this work was the study of the relationships between the structure of the membranes and the gas transport properties.

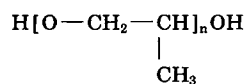
EXPERIMENTAL

Materials

Dow Chemical poly(oxypropylene) glicols (PPG) having the general formula

* To whom correspondence should be addressed.

[†] Present address: Dept. of Engineering, University of Trento, Trento, Italy.



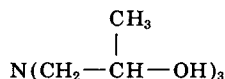
and different molecular weights (Voranol 400, 1200, 2000) were used. The mean molecular weights, estimated on dry polyols by titration of the hydroxyl groups (OH number) with phthalic anhydride in pyridine,⁶ were respectively 430, 1230, and 2180. The polyols are liquids at room temperature; their transition temperatures and other physical and chemical properties are shown in Table I.

The COIM Co. tetramethyleneglycol and adipic acid (PTMA 600, 1000, 1600, 2200, 3000) polyester diols were used. Their molecular weights were respectively 575, 1035, 1620, 2200, and 2980 as determined by the OH number method.⁶ These polyols are solid at room temperature. Their glass transition temperature and melting points determined by DSC analysis are reported in Table I.

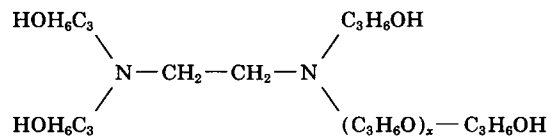
TDI (2, 4 and 2, 6 toluene diisocyanate $\text{CH}_3-\text{C}_6\text{H}_3(\text{NCO})_2$ (80 : 20) was a BAYER product.

The following crosslinking agents with different functionality have been used:

1. Triisopropanolamine (TIPA) by Fluka as a trifunctional agent:

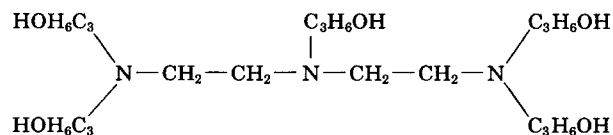


2. Tetrapropanol-ethylenediamine (EDA-PO) (Pressindustria)



as a tetrafunctional agent. It was obtained by condensation of ethylenediamine and propylene oxide. Stoichiometric molecular weight ($x = 1$) is 350.5 and the molecular weight, from the hydroxyl number, is 357.3.

3. Penta propanol diethylentriamine (DETA-PO) (Pressindustria)



as a pentafunctional agent. It is obtained by condensation of diethylentriamine and propylene oxide. The stoichiometric molecular weight is 392 and the molecular weight from OH number is 402.

4. (Stannous octoate) $(\text{C}_7\text{H}_{15}\text{COO})_2\text{Sn}$ was used as catalyst in the crosslinking stage.
5. Ethylacetate (EA) $\text{CH}_3\text{COOC}_2\text{H}_5$ (BP = 77°C), RP Carlo Erba product was used as solvent both

Table I Specification of Raw Materials

Polyols	Nominal Molecular Weight (g/mol)	Experimental Molecular Weight (g/mol)	Physical State	Acidity (mg KOH/g)	OH Number (mg KOH/g)	Water Content ^a (g/g)	T_g^b (°C)	T_m^c (°C)
Polyether (PPG) ^d	VR 400	430	Viscous liquid	0.17	260	0.56 10 ⁻³	-72	—
	VR 1200	1230	Viscous liquid	0.34	91.2	0.48 10 ⁻³	-68	—
	VR 2000	2180	Viscous liquid	0.10	51.4	0.14 10 ⁻³	-67	—
Polyester (PTMA) ^e	PTMA 600	575	Waxy solid	1.09	195	2.16 10 ⁻³	-92	41
	PTMA 1000	1040	Waxy solid	0.38	108	1.11 10 ⁻³	-74	51
	PTMA 1600	1620	Waxy solid	0.37	69.2	1.66 10 ⁻⁴	-68	53
	PTMA 2200	2200	Waxy solid	0.53	50.9	0.42 10 ⁻³	-67	53.4
	PTMA 3000	2980	Waxy solid	0.38	37.6	0.20 10 ⁻³	-62	55.6

^a Water content after vacuum treatment (≈ 12 tor at 50°C for 8 h).

^b T_g , glass transition temperature.

^c T_m , melting point.

^d PPG = $\text{H}-\text{O}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{OH}$.



^e PTMA = $\text{H}-\text{O}-(\text{CH}_2)_4-\text{O}-\overset{\text{O}}{\parallel}(\text{CH}_2)_4-\overset{\text{O}}{\parallel}\text{C}-(\text{CH}_2)_4-\text{O}-(\text{CH}_2)_4-\text{OH}$.

in the prepolymer preparation and in the cross-linking step.

All substances were accurately dried both under reduced pressure (for high boiling reagents) and with molecular sieves; water content of the dried product was analyzed according to K. Fischer method.⁷

Permeability Measurements

The measurements of permeability to water vapor have been carried out at 22°C according to ASTM.⁸ Water solubility was measured as limiting value of the weight increase of membranes after their immersion in water. The measurements of permeability to gases have been carried out at 35°C with a modified Lyssy permeameter.⁹ Diffusion coefficients, which are the kinetic terms of the permeability, have been evaluated from time lag H of the gas transport according to the relation: $D = l^2/6H$ where l is the membrane thickness. The solubility data, which are the thermodynamic terms of permeability, have been calculated with the equation: $S = P/D$. Of course, all experimental errors on P and on D propagate in these last one data.

DSC Analysis

A Mettler T 3000 DSC apparatus was used with a temperature scanning rate of 10° K/min and samples having mass of 12–16 mg. The temperature range was -150 +250°C.

POLYMER AND FILM PREPARATION

First Stage: Prepolymer Preparation

The NCO-terminated prepolymers were obtained by refluxing under nitrogen an ethylacetate solution of PPG or of PTMA and TDI, in the molar ratio 1/2.1. The reaction was carried out for 5 h at the solution boiling temperature: The polyaddition proceeds completely even with higher molecular weight polyols, as it has been verified by evaluating the NCO content according to the ASTM D 2572-70 method.¹⁰

The reaction temperature (around 80°C) avoids the formation of allophanates, biurets, and secondary compounds.³

The solution of PPG prepolymers prepared with the described procedure is stable up to eight months in absence of water. On the contrary, after cooling at room temperature the solution of PTMA pre-

polymers, a precipitate is obtained, but it can be dissolved again by heating the solution.

Lower molecular weight PPG and PTMA react more quickly due to the higher hydroxyl groups concentration C_{OH} , ($C_{OH} = 2W/VM$, where V is the solution volume and W and M are the weight and the molecular weight of the polyol). The choice of the reacting mixture molar ratio $m = TDI/Polyol = 2.1$ has been suggested by the opportunity of terminating all the prepolymer chains with NCO groups. A statistical calculation of the molecules distribution carried out according to Flory¹¹ shows that for $m = 2$, no OH groups are present at the end of the polymer chain, while NCO-terminated molecules are of the type T, TPT, TPTPT, and TPTPTPT, where T is the TDI and P is the diol. The molar fraction of the TPT units is calculated to be maximum for $m = 2$. Some free unreacted TDI is present in this condition.

Second Stage: Crosslinking Polymerization

The following procedure has been used: About 10 g EA solution (66% by weight of prepolymer) were diluted to 50% polymer concentration with dry solvent (EA) in a 100-mL beaker. An amount of EA solution of the chosen crosslinking agent (25% concentration) was added by means of a syringe and under slow stirring, so as to obtain an OH/NCO ratio between the hydroxyl groups of the crosslinking agents and the NCO groups of the prepolymer equal to 1.1/1. After elimination of any gas bubbles by gentle heating, the solution was cooled to room temperature and stannous octoate was added in the amount of about five parts per thousand of the prepolymer solution. As soon as the solution began to crosslink (after about 5 min), it was poured on a flat glass previously cleaned with EA and dried. The membrane was prepared by spreading the polymer with a Gardner knife and allowing a very slow evaporation of EA. After complete gelation and solvent evaporation, the film was detached from the glass by immersion into water. Films, having a thickness from 20–100 microns, were stored between filter papers. With PTMA-based prepolymers, no cooling was performed after the gas bubble elimination.

STRUCTURE AND PHYSICAL PROPERTIES OF PU

In the second stage, the polymer chains grow branching and become richer in the active and reactive terminal groups, the bulk viscosity increases

Table II Physicochemical Properties of Polyurethane Membranes^a

Symbol	Density (g/cm ³)	T_g (°C)	Melting Point (°C)	Solubility Parameters δ_p (cal/cm ³) ^{1/2}
VR400	1.18	30	No m point	12.50 ^b
VR1000	1.10	-21.7	No m point	10.20 ^b
VR2000	1.07	-46.5	No m point	9.6 ^b
PTMA600	1.20	14.8	No m point	12.10
PTMA1000	1.19	-9.6	No m point	11.61
PTMA1600	1.18	-34.1	No m point	11.10
PTMA2200	1.17	-35.8	50.9	
PTMA3000	1.18	-39.4	61.5	

^a Values of the membrane thickness were 100–200 μm .

^b Reported values are average of the three types of crosslinking agents.

rapidly, and after a certain conversion the reacting system turns on insoluble gel. Flory gave the expression of the distribution of the monomers in the polymer chain vs. the conversion for the ordinary polyfunctional condensations.

A statistical calculation of the distribution of the growing chains, extracting by chance molecules of the crosslinking agent and of the prepolymer and building the branched structure, has been performed.¹² The obtained distribution agrees with that foreseen by Flory. All the statistical models bring in any way to a picture of the growing system that contains branches and segments, each made of a distributed statistically number of ether or ester units. Branching and the length distribution of the polyol segments, named usually "soft" segment, generate a disordered structure, which favours an amorphous state. Moreover, in the case of the PU obtained by poly oxypropylene diols, the polyol units can enter in the chain of the polyol in different ways, so enhancing the probability to obtain the amorphous state. In fact, in the case of the polyether PU we could never find evidence of crystallinity both at X-rays and at DSC analysis.

The polyester units in PES-PU polymers are on the contrary stereoregular, and by increasing the molecular weights of polyesters the probability of crystallization of the "soft" segments increases. By using polyester diols having M of 3000, the crystallization has been observed at once and some time after the preparation when using M of 2200.

Even when PU results amorphous at X-rays and DSC analysis, a short-range order could be still possible in the systems due to the hydrogen bonds interactions typical of the urethane groups¹³ of different chains, which could, eventually, segregate into

"hard" domains. The hard segments of a given chain contain mainly the urethane groups, belonging to one or more sequences made of the diisocyanate and of the low molecular weight crosslinking agent, molecules, which play the role of extenders. In the present case, the extender is a polyfunctional alcohol (TIPA, EDA, DETA), that may introduce disorder in the building of the polymer chain owing to branching. Moreover, the low symmetry of the used diisocyanate and the presence of two isomers reduces the possibility of interaction between the hard segments. The irregular structure of these blocks should decrease the probability of the ordered regions.

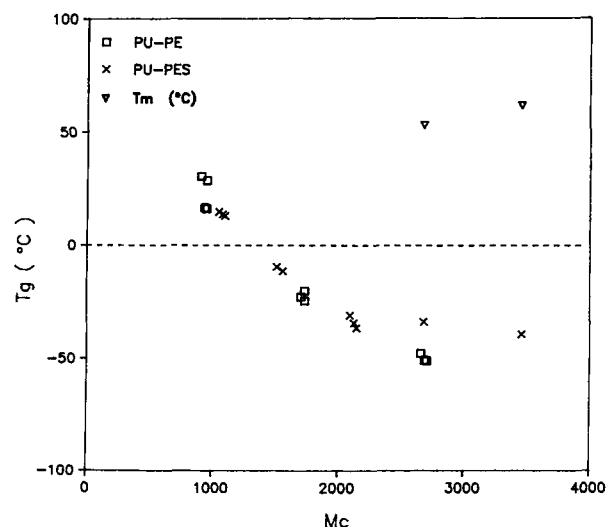


Figure 1 Glass transition temperature (T_g) vs. stoichiometric molecular weight (M_c) of the chains between the crosslink. The melting point T_m of PTMA 2200 and of PTMA 3000 are also reported.

Table III Water Vapor Transport Properties in PE-PU and in PES-PU at 22°C

Film	$P \cdot 10^7$ $\left(\frac{\text{Ncm}^3 \text{ cm}}{\text{s cm}^2 \text{ cmHg}}\right)$	S $\left(\frac{\text{Ncm}^3}{\text{cm}^3 \text{ cmHg}}\right)$	$D \cdot 10^8$ $\left(\frac{\text{cm}^2}{\text{s}}\right)$
VR400	1.8	32.0	0.6
VR1200	10.8	25.1	4.3
VR2000	23.4	20.1	11.7
PTMA600	5.2	18.7	2.8
PTMA1000	7.9	17.2	4.6
PTMA2200	10.6	7.7	13.8

$S = A\rho \frac{22400}{18 \cdot 1.98}$, where A is the specific water sorption (g H₂O/g membrane), ρ is the membrane density, and 1.98 is the water vapour pressure at 22°C (cm Hg).

DSC RESULTS

The polyglycol's chain length has a significant influence on the glass transition temperature (T_g) of PU-PE membranes: By increasing the molecular weight of PE diols from 430 to 2,180 daltons, T_g decreases from about 300 to 227 K. No important effect of the functionality of crosslinking agents on PU's T_g has been found, particularly in the case of mean and large M of polyglycols crosslinked with TIPA, EDA, or DETA. In all PE-PU polymers, no evidence of a melting transition has been found; therefore, these membranes can be considered amorphous and in the rubberlike state, as to the gas transport properties, which were measured at $T > T_g$.

The T_g of PES-PU membranes behave in the

same way: it depends on the PES molecular weight but practically not on the crosslinking agent functionality. The presence of a well-defined endothermic transition in these polymers prepared with higher molecular weight of polyester diols ($M > 2,200$) indicates the presence of crystallized regions. At M 1600, a long time is needed at room temperature before crystallization takes place. The gas transport properties presented in this work were any way obtained using amorphous samples.

The T_g values of PE-PU reported in Table II and used in the following are mean values among the values obtained with the three type of crosslinking agents. For the sake of completeness in Figure 1, the experimental T_g values for PE-PU and for PES-PU membranes with different crosslinking agents are reported as a function of the theoretical molecular weight (M_c) of the chains between the cross-

Table IV Transport Properties of Some Gases in PE-PU Membranes at 35°C

Gas	O ₂	N ₂	CO ₂	CH ₄	CO
Permeability $P \cdot 10^{10}$ (Ncm ³ cm/(cm ² s cmHg))					
VR400	0.15	0.04	0.95	0.055	0.05
VR1200	2.9	0.9	19.	1.8	3.4
VR2000	7.8	2.8	72.	9.0	9.2
Diffusion coefficient $D \cdot 10^8$ (cm ² /s)					
VR400	5.1	2.7	2.8	1.5	2.
VR1200	41	39	23	16	28.
VR2000	110	150	150	50	58.
Solubility coefficient $S \cdot 10^4$ (cmHg) ⁻¹					
VR400	3	1.7	34.	3.5	2.5
VR1200	7.	2.2	84.	10.	12.
VR2000	7.1	1.8	125.	18.	16.

Table V Gas Transport Properties in PES-PU Membranes at 35°C

	O ₂	N ₂	CO ₂	CH ₄	CO
Permeability $P \cdot 10^{10}$ (Ncm ³ cm/(cm ² s cmHg))					
PTMA600	0.13	^a	0.7	0.047	0.037
PTMA1000	0.75	0.15	6.4	0.51	0.26
PTMA1600	2.	0.8	20.	1.6	1.2
Diffusion coefficient $D \cdot 10^8$ (cm ² /s)					
PTMA600	7.6	^a	2.7	2.7	3.9
PTMA1000	16.	5.3	5.7	5.8	7.4
PTMA1600	39.	22.	13.	17.	11.
Solubility coefficient $S \cdot 10^4$ (cmHg) ⁻¹					
PTMA600	1.7	^a	26	1.7	0.95
PTMA1000	4.7	2.8	110	8.8	3.5
PTMA1600	5.	3.6	87.	10.	10.

^a Undetectable.

links. M_c is the sum of the diol molecular weight (M_D), of the TDI (two units), and of the fraction of the crosslinking agent of functionality f entering in the chain: $M_c = M_D + 2M_{TDI} + 2M_{CA}/f$. It has

been observed that when the lowest molecular weights are prepared at room temperature the T_g values, are higher; this case doesn't interest the present work.

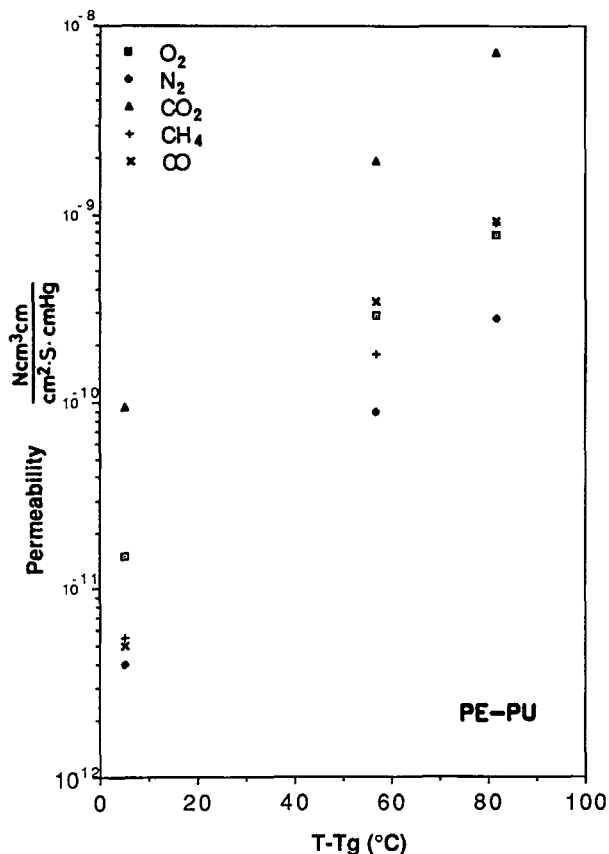


Figure 2 Permeability data of PE-PU membranes vs. the difference between the temperature of the permeation measurements (35°C) and the glass transition temperature of the membranes.

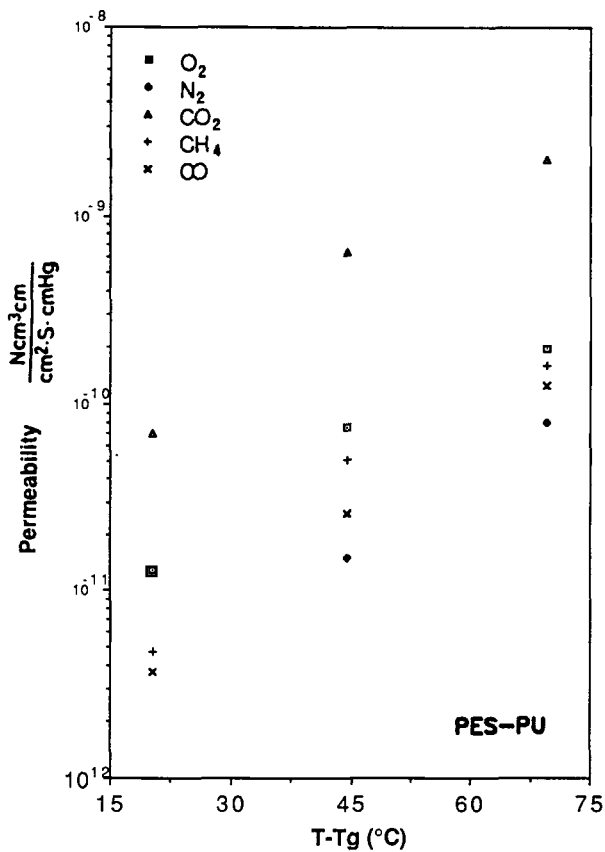


Figure 3 Permeability data of PES-PU membranes vs. the difference between the temperature of the permeation measurements (35°C) and the glass transition temperature of the membranes.

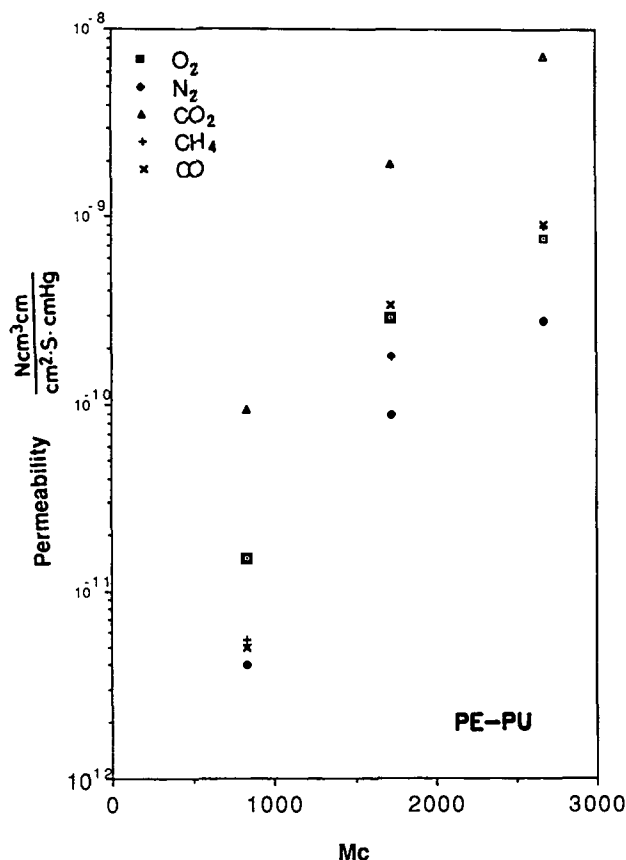


Figure 4 Permeability data of PE-PU membranes vs. the theoretical molecular weight (M_c) of the chains.

MEMBRANE TRANSPORT PROPERTIES

Transport of Water

Water is a high-polar substance condensable at room temperature whose transport properties strongly involve the urethane polar groups. Due to the easy condensation, we preferred to measure permeability according to ASTM,⁸ and the solubility coefficient, obtained by water sorption. Diffusivity was evaluated by the ratio P/S . Table III shows the water transport properties for the different PE-PU and PES-PU. While the diffusion coefficient increases with M_c even more than one order of magnitude, the solubility coefficient decreases slowly, due to the decrease of the urethane groups density; therefore, permeability increases with M_c . No effect of functionality of the crosslinking agents has been found, while the chain length has a large effect.

Transport of Gases

Permeability (P), diffusion coefficient (D), and solubility coefficient (S) of N_2 , O_2 , CO_2 , CH_4 , and

CO in PE-PU and PES-PU membranes are reported in Tables IV and V, respectively. Similarly to what was found for the glass transition temperature, the transport properties also depend on the molecular weight of polyols but not on the functionality of the crosslinking agents. Therefore, the data reported in Table IV are the mean values obtained using membranes prepared with different crosslinking agents. The measurements of Table V were obtained using PES-PU crosslinking with TIPA only.

The aim of the present work is to find some relation among the transport properties and the characteristic parameters of the polymer. Before starting a detailed theoretical analysis, which will be done in a following paper, a preliminary and empirical investigation has been made by plotting the experimental data as a function of different physical parameters.

Permeability Data

The data reported in this work were obtained using PE-PU and PES-PU films that appeared to be

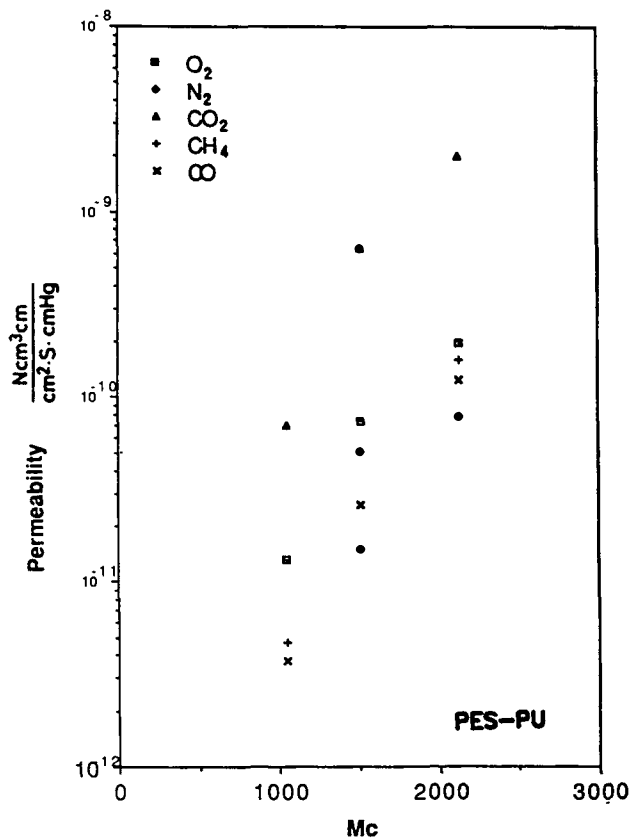


Figure 5 Permeability data of PES-PU membranes vs. the stoichiometric molecular weight (M_c) of the chains.

amorphous at DSC analysis. The temperature of the permeability tests was kept at 35°C, which allows us to consider our materials rubberlike ($T > T_g$). The data have been plotted either as a function of the difference between the permeation temperature (T) and the glass transition temperature (T_g) (Figs. 2 and 3) or as a function of the molecular weight (M_c) of the network chain (Figs. 4 and 5). Both these parameters may be related somehow to the free volume of the membranes polymers.

A fairly good linear relationship P vs. $(T - T_g)$ is found for PE-PU membranes (Fig. 2); moreover, oxygen and nitrogen seem to have the same slope. Methane has a different slope. Most likely the permeability data of nitrogen in the lowest range of permeability, that is at low $T - T_g$ and M_c , have a large experimental error due to the long time of measurements and the unavoidable leakage of air in the apparatus that, even if small, has a certain weight on the lowest permeability data.

A linear relationship permeability vs. $T - T_g$ is

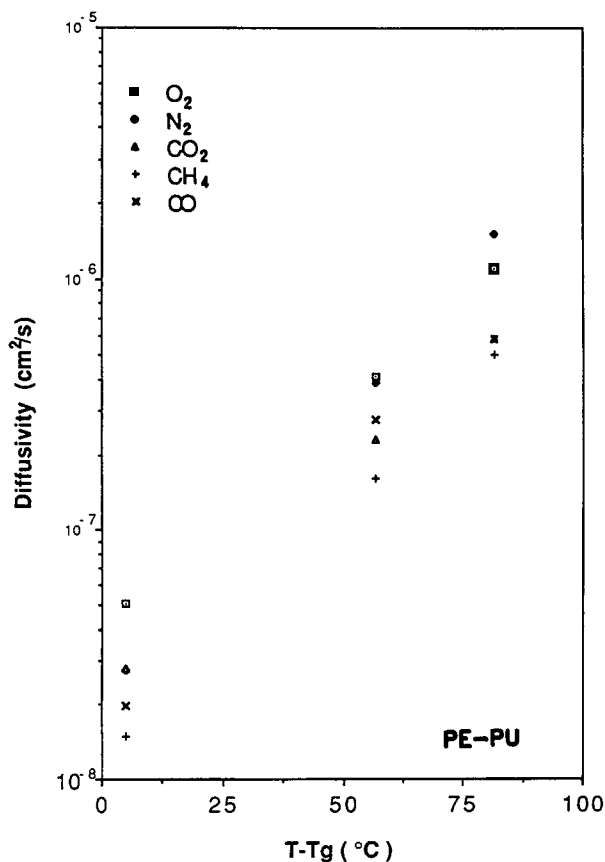


Figure 6 Diffusion coefficients of different gases through PE-PU membranes vs. the difference between the temperature of the permeation measurements (35°C) and the glass transition temperature of the membranes.

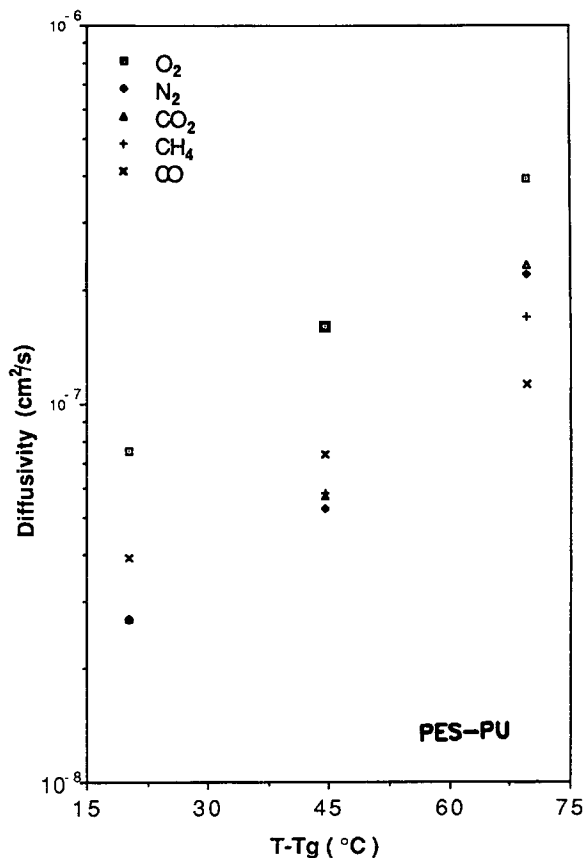


Figure 7 Diffusion coefficients of different gases through PES-PU membranes vs. the difference between the temperature of the permeation measurements (35°C) and the glass transition temperature of the membranes.

not evident with PES-PU membranes (Fig. 3). The slope decreases particularly for the higher ($T - T_g$) values, e.g., for the PTMA-1600 membrane ($M_c = 2,125$). The lowest slope might be ascribed to the presence of a significant amount of ordered and tighter regions, where the gas permeability is lower. As said above, we observed that after some week elapsed from the preparation of the membrane PTMA 1600 a melting point could be observed at DSC. This demonstrates the existence of preordered regions that can evolve into crystallites.

Looking at the permeability vs. (M_c) diagrams (Fig. 4) PE-PU and (Fig. 5) PES-PU, a general increase of permeability with the molecular weights M_c is observed. For what concerns the gases, the permeability data are in the following order: $\text{CO}_2 > \text{O}_2 > \text{CH}_4 > \text{CO} > \text{N}_2$, with all PE-PU and PES-PU polymers.

Diffusion Coefficients

The kinetic term of permeability has been plotted as a function of $(T - T_g)$ (Figs. 6 and 7) and of the

cross-section σ^2 of the permeating molecules (Figs. 8 and 9).

PE-PU diffusivity data (Fig. 6) show a good linear trend as a function of $(T - T_g)$. Figure 7 shows the PES-PU diffusion coefficient, which appear to be related to $T - T_g$ not so much in a regular way, probably for the more ordered structure, as said above.

A not clear trend is observed in the plots D vs. σ^2 (Figs. 8 and 9). This short analysis reveals that the kinetic terms of membrane permeability can be related in a more simple way to the polymer-free volume that is proportional to $(T - T_g)^{14}$ than to the gas diameter, or cross-section, of the diffusing molecules.¹⁵

From a physical point of view, this means that both the structure and the dynamics of the polymers play a fundamental role in the kinetic term of permeability, while the size of diffusing molecule, at least for the investigated gases, seems to have a minor role on the D values.

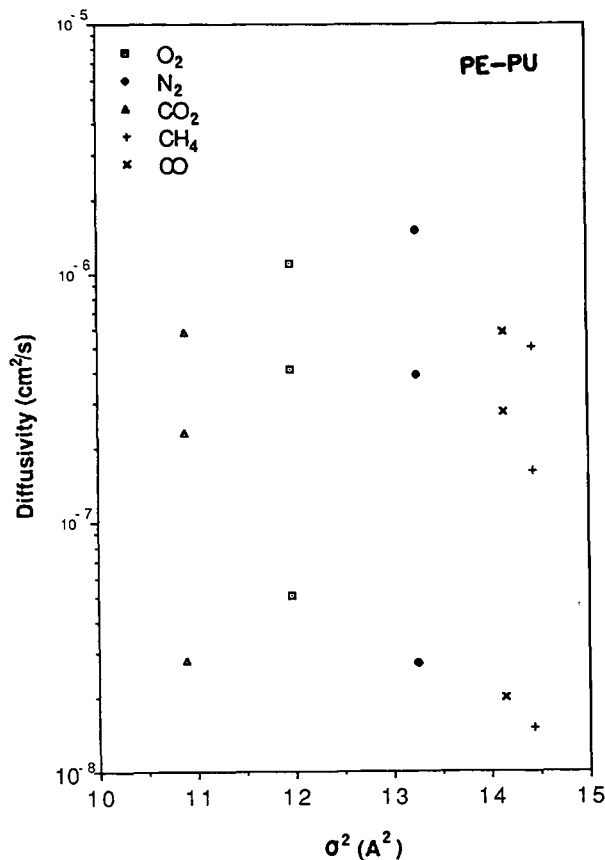


Figure 8 Diffusion coefficient of different gases through PE-PU membrane vs. the square of the diameter (σ^2) of the permeating gas.

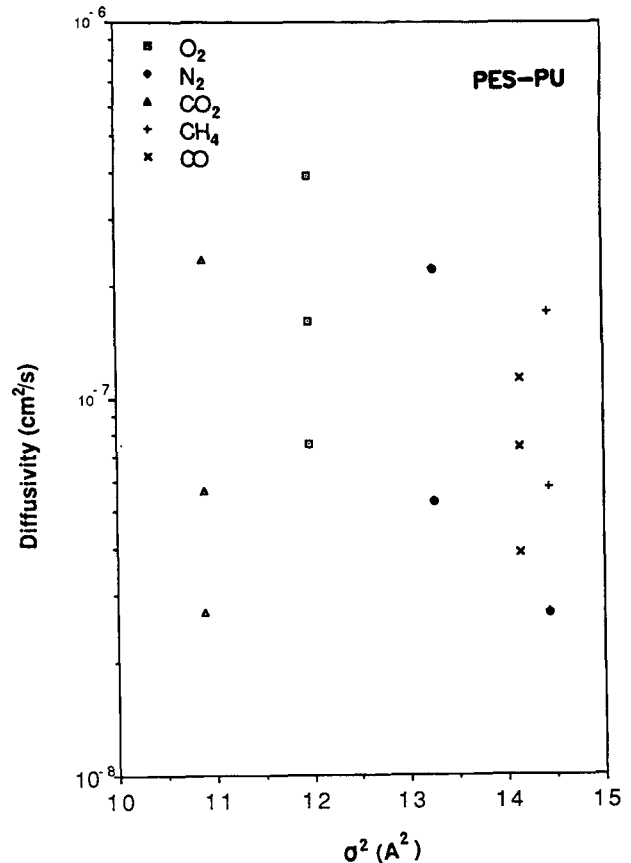


Figure 9 Diffusion coefficient of different gases through PES-PU membrane vs. the square of the diameter (σ^2) of the permeating gas.

Solubility

It has been shown previously⁵ that the solubility data of gases in polymer may be analyzed with a procedure formally similar to that one proposed by Prausnitz and Shair¹⁶ and based on regular solution theory. According to this approach, the experimental solubility coefficient (S_i) data of nonpolar gases fulfill the equation:

Table VI Fugacity in the Pseudoliquid State, Critical Temperatures and Pressure of Different Gases¹⁶

Gas	f_i^L	T_c (°C)	P_c (ATM)
N ₂	217	-147	33.5
CO	210	-140	34.5
O ₂	275	-118.4	50.1
CH ₄	160	-82.1	45.8
CO ₂	30	31	72.9

$$-\ln S_i = \ln A + \left[\ln f_i^L + \phi_p^2 \frac{V_i^L (\delta_i - \delta_p)^2}{RT} \right], \quad (2)$$

where A is a constant related to the density and the molecular weight of the polymer and whose value is determined by experimental data; f_i^L is the fugacity of the gas i (Table VI) in a hypothetical liquid state at a normal pressure, evaluated according to¹⁶; V_i^L is the partial molar volume of the gas dissolved, as an hypothetical liquid, into the polymer; δ_i and δ_p are the solubility parameters of the gas i and of the considered polymers (Tables VII and II); δ_p was calculated according to Fedors¹⁷; and ϕ_p is the volume fraction of the polymer in the solution, assumed equal to 1.

By plotting $-\ln S_i$ as a function of the term in square brackets of eq. (2) a linear relationship is obtained (Fig. 10). From the regression analysis, the slope of the line results equal to one and the value of the constant A equal to 1.6.

Notwithstanding the scattering of the data, probably due to the error propagation as discussed before, the solubility data are in general well described in terms of the difference between the solubility parameters of the gas and the polymers and of the fugacity of the hypothetical liquid solute.

From a physical point of view, the lower the fugacity of the hypothetical solute the greater the solubility. Moreover, the solubility increases by decreasing the difference in the cohesion energy density between the polymer and the diffusing gas.

CONCLUSION

The permeabilities of amorphous PE-PU and PES-PU to O₂, N₂, CO₂, CO, CH₄, and H₂O are strong functions of the chain length of the prepolymer used in the synthesis and are higher in the case of PE-PU.

This can be related to the different structure of the polymers, which is less flexible and more ster-

Table VII Solubility Parameters, Molar Volume, and Collision Diameter of Different Gases^{16,18,19}

Gas	δ_i (cal/cm ³) ^{1/2}	V_i^L (cm ³ /g mol)	σ (Å)
N ₂	2.58	32.4	3.64
CO	3.13	32.1	3.76
O ₂	4.0	33.0	3.46
CH ₄	5.68	52	3.8
CO ₂	6.0	55	3.3

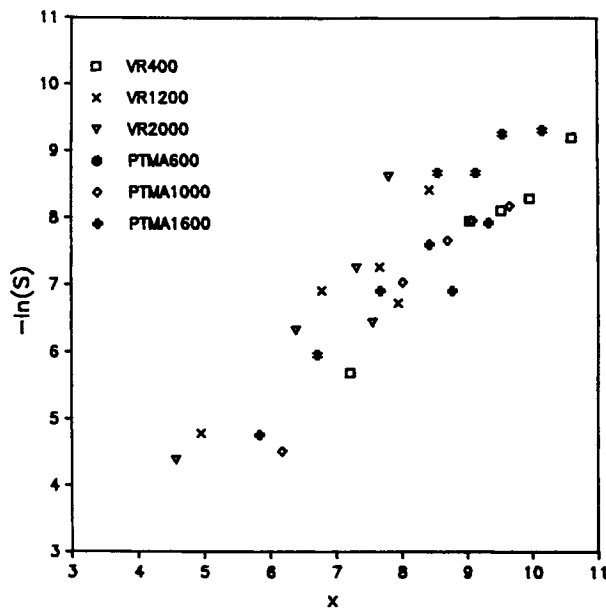


Figure 10 Solubility coefficient data of permeating gases, evaluated as $S = P/D$, vs. $x = \ln f_i^L + V_i^L (\delta - \delta_i)^2 / RT$ according to eq. (2).

eoregular in the case of PES-PU. The PU polyester show a higher T_g at equal M_c and a tendency to crystallize when M_c goes over 1,600 daltons. Permeabilities of the two PU families are similar only for the lowest molecular weight M_c . The functionality of the crosslinking agent does not influence the permeabilities.

Similarly, the kinetic term D of the permeability strongly depends on the network chain molecular weight, is of the same order for the two PU families in the low range of M_c , and is lower for PES-PU at higher M_c . The linear relation between $\log D$ and $T - T_g$ in the case of PE-PU shows that D is a linear function of the free volume, while in the case of PES-PU the relation does not appear to be so simple. The size of the diffusive gases has also some influence on D .

The thermodynamic term (S) of the transport results as function of the fugacity of the dissolved gas and of the difference on the solubility parameters between the dissolved gas and the polymer, which can be satisfactorily represented by eq. (2).

Comparison of the permeabilities allows us to obtain information on the selectivities of the different gases. Tables II, IV, and V show that good selectivities are reached in the case of the systems H₂O, CH₄, CO₂, and CH₄, while the cases of O₂ and N₂ are less favourable even if of some interest. The drying of natural gas and the CH₄ recovery from the

wells rich in CO₂ could be interesting industrial applications for these membranes.

This work was supported by Ministero della Pubblica Istruzione, C.N.R. Progetto Finalizzato Chimica Fine e Secondaria, and S.p.A. Eniricerche.

REFERENCES

1. S. Paul, *Surface Coatings*, Wiley, New York, 1985.
2. J. Buist and H. Gudgeon, *Advances in PU Technology*, Elsevier, London, 1968.
3. J. H. Saunders, *Polyurethanes, Chemistry and Technology*, Part I, Interscience Publisher, London, 1962, Chap. 3.
4. M. Pegoraro, A. Penati, and L. Zanderighi, *X VIII FATIPEC, Congress*, **3**, 203 (1986).
5. M. Pegoraro and A. Penati, *J. Membr. Sci.*, **27**, 203 (1986).
6. ASTM, *Annual Book of ASTM Standards*, D4274-83, method C, American Society for Testing and Materials.
7. J. Mitchell and D. M. Smith, *Aquametry*, Interscience, New York, 1948.
8. ASTM, *Annual Book of ASTM Standards*, E96-80, American Society for Testing and Materials, Easton, MD, 1987.
9. L. Zanderighi, F. Bianchi, R. Monga, and M. Pegoraro, *Chim. Industr.*, **72**, 146 (1990).
10. ASTM, *Annual Book of ASTM Standards*, D2575-70, American Society for Testing and Materials, Easton, MD, 1987.
11. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, Chap. B8.
12. G. Giannotta and T. Wyen, Thesis, Politecnico di Milano, 1985.
13. J. H. Saunders, *Polyurethanes, Chemistry and Technology*, Part I, Interscience Publishers, London, 1962, Chap. VI.
14. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
15. P. Meares, *Polymers: Structure and Bulk Properties*, Van Nostrand, London, 1965, p. 321.
16. J. M. Prausnitz and F. H. Shair, *A.I.Ch.E. J.*, **7**(4), 682, (1961).
17. R. F. Fedors, *Polym. Eng. Sci.*, **14**(2), 174 (1974).
18. *Handbook of Chemistry and Physics*, 67th ed., CRC Press, Boca Raton, FL, 1986-87.
19. D. W. Breck, *Zeolite Molecular Sieves*, John Wiley and Sons, New York, 1974.

Received February 21, 1990

Accepted November 30, 1990