

Gas Transport Properties of Siloxane Polyurethanes

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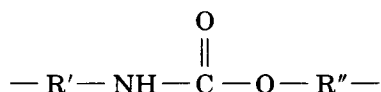
SYNOPSIS

Polyurethanes (PUs) were synthesized from toluenediisocyanates (TDIs) and a polymeric diol having polydimethylsiloxane and polyoxyethylene blocks of the ABA type, ended with OH groups. Prepolymers, prepared in toluene solution using ratios $[\text{NCO}]/[\text{OH}] \geq 2$, were crosslinked with triisopropanolamine (TIPA) (ratio $[\text{OH}]/[\text{NCO}] = 1.1$) (two-step process). PUs were also obtained with a one-step process using, contemporaneously, TDI, block copolymer, and, as crosslinking agent, TIPA or the glyceride of ϵ -hydroxyhexanoic acid. Polydimethylsiloxane (PDMSO) was prepared as a reference material. The course of the reaction between block copolymer and TDI was studied by differential scanning calorimetry in the absence and presence of benzoyl chloride (BzCl). Without BzCl, with ratios $[\text{NCO}]/[\text{OH}] > 2$, uncontrolled crosslinking side reactions occur. The properties of the PU films obtained with the two methods were studied both for the density of crosslinking and for gas transport properties. The two-step polymers are less crosslinked than the others and are characterized by higher diffusion coefficients and by higher permeability to gases. The permeability order is 10^{-9} ($\text{N cm}^3 \text{ cm}^{-1} \text{ cm}^{-1} \text{ cm Hg}^{-1} \text{ s}^{-1}$) for CH_4 , O_2 , CO , and N_2 and is 10 times higher for CO_2 . The selectivity for the couple O_2/N_2 is higher than that obtained with PDMSO films. Considerable selectivities are shown for the couples CO_2/N_2 and CO_2/CO . © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In the last few years we have studied the permeability of gases to various types of crosslinked polyurethane (PU) membranes.

PUs are characterized by the presence of urethane groups $-\text{NH}-\text{CO}-\text{O}-$ in the chain



where R' and R'' groups are, respectively, rigid aromatic components having low molecular weight and polymeric flexible diols (polyols).

Diols $\text{HO}-\text{R}''-\text{OH}$, R'' being an aliphatic polyether, polyester, or polycarbonate,¹⁻⁴ were used.

PUs are particularly suitable for generating polymers having very different chemical nature and also very different structure (partially crystalline, glassy amorphous, or elastomeric).

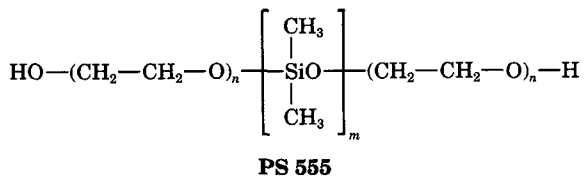
This article describes the synthesis of a family of PUs-polysiloxanes block polyether and the evaluation of their transport properties: permeability (P), diffusivity (D), and solubility (S) of various gases. The aim of this research was the identification of some correlation between the structure of PUs and their transport properties.

EXPERIMENTAL

Reagents

The reagents were toluenediisocyanate (TDI) as an 80 : 20 mixture of 2,4- and 2,6-toluenediisocyanate (Merck) and polymethylsiloxane (PS 555) ended with carbinols (Petrarch Inc. Systems).

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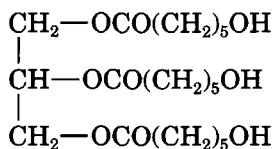


$m \sim 13; n \sim 17$

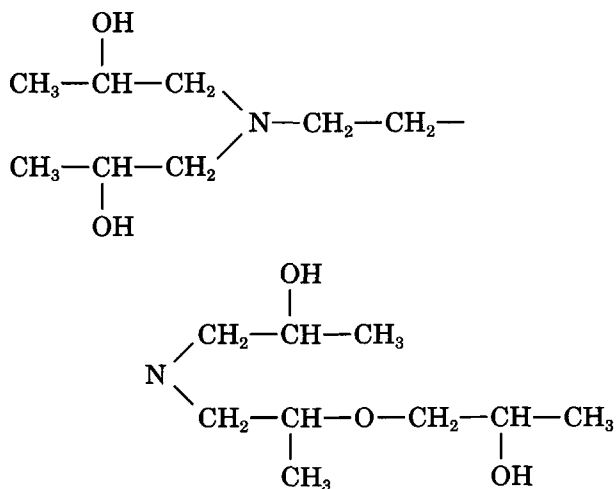
PS 555 is a block copolymer having an average numerical molecular weight of 2400 (M_n 2490 from GPC). Traces of polyethyleneglycol, diphenyl cresyl phosphate, and of an unidentified substance, probably basic, are present. There are two end-position hydroxyl groups for each molecule.

Crosslinking Agents

These agents were: C, product derived from glycerol and ϵ -hydroxyhexanoic acid (Janssen);



triisopropanolamine (TIPA, Aldrich), $\text{N}(\text{CH}_2-\text{CHOH}-\text{CH}_3)_3$; and pentapropoxylate ethylenediamine (EDA, laboratory product).



Additives

Benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$ (BzCl, Carlo Erba, RP) and stannous octanoate (Nuocure 28, URAI) were the additives.

Gases

CH_4 , CO , and CO_2 were 99% grade from S.I.O. s.p.a.; compressed air was used for O_2 and N_2 permeability and diffusivity evaluation.

Solvent

The solvent (toluene) was thoroughly dehydrated and kept in molecular sieves. The solvent and the anhydrous solutions of PS 555 and of the crosslinking agents were tested for water content with the Karl Fischer method.⁵

Preparation of PU and Membranes

PU films were prepared according two different procedures (Table I).

One-Step PU Preparation (PS/1)

All reagents were reacted together in a toluene solution at room temperature. To react TDI and PS 555 diol we began using a ratio R, between NCO groups and the OH groups, equal to 1 ($R = [\text{NCO}]/[\text{OH}]$). This ratio should give a linear high MW polymer. However no good film was obtained. Only by using $R > 3.5$ could compact films be prepared by pouring the solution uniformly on glass after starting the reaction, and subsequently allowing slow evaporation of the toluene.

As to the mechanical properties, films of better quality were obtained using a ratio $R = 1.5-3.5$, but adding to a 50% toluene solution of PS 555 and TDI one trifunctional crosslinking agent, OH terminated as the glyceride of the ϵ -hydroxyhexanoic acid or TIPA. The most suitable molar ratio between the OH_d groups of the diol and the OH_t of the crosslinking agent $[\text{OH}_d]/[\text{OH}_t]$ was found to be about 0.6. The glyceride, insoluble in toluene, was dissolved in PS 555; TIPA was dissolved in toluene. The reactions of the $-\text{NCO}$ groups with the hydroxy groups of PS 555 and with those of the triol occur at the same time; so the rate of TDI cyclization is reduced. In this way a better distribution of the crosslinking centers can be obtained when the triol is present.

Two-Step PU Preparation (PS/2)

PS 555 was dissolved in toluene (conc. 40%) and reacted with TDI at 60°C for 3 h in the presence of 0.1–0.2% of BzCl used to avoid the uncontrolled crosslinking reactions. The usual ratio² $R = 2.1$ proved insufficient to obtain suitable films in the

Table I Crosslinking Density and Other Physical Properties Versus Synthesis Conditions

Membrane	R	Crosslinker	[—OH _d]/[—OH _t]	V ₂	ρ (g cm ⁻³)	W ₀ /W _i	ν/V ₀ 10 ⁵ (mol cm ⁻³)
PS/1	1.4	C	0.31	0.57	1.16	0.92	25.0
PS/1	2.0	C	0.62	0.68	1.18	0.96	66.0
PS/1	2.2	C	0.62	0.87	1.10	0.99	80.0
PS/1	3.4	C	0.62	0.71	1.27	0.97	49.5
PS/1	2.2	T	0.62	0.51	1.07	0.96	24.4
PS/1	3.0	T	0.62	0.54	1.12	0.96	25.4
PS/2	3.0	T	0	0.15	1.13	0.83	—
PS/2	3.0	E	0	0.16	1.12	0.80	—

Properties for different PS/1 (one-step) and PS/2 (two-step) membranes obtained from TDI and PS 555. R = ([—NCO])/([—OH_d] + [—OH_t]) in PS/1 and R = (NCO)/(OH_d) in PS/2. C, triglyceride of the ε-hydroxyhexanoic acid; T, triisopropanolamine; E, penta-propoxylate ethylenediamine.

second step: R had to be raised to at least 3. The prepolymer had to be used as soon as possible due to the risk of crosslinking.

The final polymer was obtained using, as crosslinking agents, TIPA, EDA, or the glyceride of the hydroxyhexanoic acid. A ratio [—OH]/[—NCO] = 1.1 was used. The reaction started in a beaker at room temperature, under stirring, in the presence of the catalyst Nuocure 28 (0.125 mL of 20% toluene solution of Sn octanoate/mL of reacting solution in the case of TIPA).

Before the end of crosslinking, the 40% polymer solution was spread with a Gardner's knife on a glass plate heated at 40°C. After 12 h the plate was put in an oven under vacuum at 50°C to complete the solvent evaporation.

After immersion in water, the membranes (50-μm thick) were taken off the supporting glass.

The polydimethylsiloxane (PDMSO), used as a reference material, was synthesized starting from Rhone-Poulenc reagents, which were a polysiloxane terminated with vinyl groups at both chain ends (MW 10000) and a V50 dimethylsiloxane oligomer (MW 3000) containing Si—H groups (H = 0.32%). They were mixed in the presence of a Pt catalyst.⁶

Analysis of Products

Thermal Analysis

Differential scanning calorimetry (DSC) curves for the T_g determinations of the PUs obtained were carried out on a TA 3000 DSC Mettler instrument using 12–15 mg of the samples with a scanning rate of 10 K min⁻¹ in nitrogen atmosphere.

DSC curves for the ΔH measurements of the reactions between the different TDI types and PS 555 with and without BzCl were obtained on a DSC-2

Perkin-Elmer instrument in aluminum pans under nitrogen, both in dynamic tests (scanning rate = 5 K min⁻¹) and in isothermal tests at 328 K. Indium was used as the standard for calibrating the temperature axis and the enthalpy output.

Crosslinking Density

The elastic modulus at equilibrium and the swelling index were measured at room temperature on specimens swollen in toluene using the apparatus and the methodology shown in previous work.⁷ It was assumed that the rubber elasticity theory could be applied to the block siloxane PU system. According to the affine model⁷ we can write the relation:

$$\sigma V_2^{1/3} = \frac{\nu R}{V_0} T \left(\alpha - \frac{1}{\alpha^2} \right)$$

where σ is the stress related to the initial cross section of the unswollen specimen; V₂ is the volumetric fraction of the polymer (of dry volume V₀) present in the swollen system of volume V (V₂ = V₀/V); ν is the number of elastically effective chains; α is the draw ratio between the length L of the specimen, swollen under stress, and the length L₀ of the specimen swollen in absence of stress; R is the gas constant; T is the absolute temperature. Reporting σV₂^{1/3} versus α - 1/α² a linear plot was obtained; its slope is the coefficient (ν/V₀)RT from which the density (ν/V₀) of the elastically effective chains can be obtained. Measurement of V₂ was carried out on the specimen at the end of the mechanical tests, measuring the masses of the swollen (W_r) and of the dried (W₀) specimen, with the formula:

$$V_2 = \frac{V_0}{V} = \frac{\frac{W_0}{\rho}}{\frac{W_0}{\rho} + \frac{W_r - W_0}{\rho_s}}$$

where ρ_s is the density of the toluene and ρ is the density of the dried polymer.

Measures of Transport Properties of Gases

The permeability P and the diffusion coefficient D of the gases at 35° were measured with a modified Lissy apparatus.⁸ In this device the standard volume $V(t)$ of the permeated gas, collected in a semicell, is plotted versus time. The permeability is obtained from the slope of $V(t)$ when linear stationary conditions are reached; the diffusion coefficient is calculated from the time lag⁹ evaluated by extrapolating the $V(t)$ straight line to $V(t) = 0$.

In the case of the most permeable gas (CO_2) we measured $V(t)$ by the flux method.⁷ The standard error in measuring P and D is lower than $\pm 10\%$. The errors in the solubility coefficient S , are larger as its values are calculated by the ratio P/D .

The solubility parameters of the polymers were calculated with the group contribution method of Fedors¹⁰; those of the gases were taken from Prausnitz.¹¹

RESULTS AND DISCUSSION

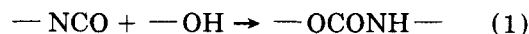
Reactivity of Reagents Used

The $\equiv\text{Si}-\text{OH}$ end group of the polysiloxane chains is very reactive and the formation of the bond $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ is highly favored. Several attempts to obtain a direct reaction between the isocyanic groups and the $-\text{OH}$ groups of the polysiloxane-diols have not succeeded in producing urethane bonds. This is confirmed by the literature.^{12,13} On the contrary it is possible to add $-\text{NCO}$ groups to the polysiloxane chains shielded with hydroxyethylene units, such as a PDMSO dicarbinol in blocks ABA as PS 555. The end hydroxy groups of this polyol react with the $-\text{NCO}$ groups of TDI to make urethane bonds. Using an industrial TDI and PS 555 in the range $2 \leq R \leq 3$ in toluene the reactions occur even at room temperature and are accompanied by crosslinking. This behavior is anomalous in comparison with that observed by us¹ in reacting polyether diols and the same TDI, when the reactions occurred in some hours at 60°C without crosslinking ($R = 2.1$). We ascribe this behavior to basic

substances that probably are present as impurities in PS 555; the addition of ethylene/oxide to polysiloxane diol is catalyzed by bases.

It is also well known that BzCl acts as an inhibitor of the crosslinking reactions, neutralizing the basic substances¹⁴ that catalyze the formation of allophanates or inhibiting the oligomerization of diisocyanates. We observed the inhibitory action of BzCl by performing DSC measures of the heat developed by the reactions between pure 2,6-TDI and anhydrous PS 555 in the presence and absence of BzCl for several ratios $[-\text{NCO}]/[-\text{OH}]$ with a scanning rate of 5°C/min in the range from 30 to 200°C (Fig. 1).

The heat developed by the reaction



appeared to be a nonlinear function of the molar ratio NCO/OH . ΔH should increase with R until $R = 1$ and subsequently remain steady for $R > 1$ because TDI should remain in excess. We observed asymptotic behavior at a ΔH value lower than the theoretical one¹⁵ (100 kJ/mol) which corresponds with $R < 1$. This fact may be attributed to the starting of the reaction, due to its high rate, before the beginning of the DSC experiment. Looking at Figure 1, as R increases the asymptotic trend is interrupted and a progressive growth of ΔH can be observed. This shows the existence of secondary reactions, the most likely of which are the trimerization and the formation of allophanates¹⁴ that produce crosslinking. The existence of secondary reactions is proved by the inhibiting effect of the BzCl (Fig. 1) because, in its presence, ΔH does not grow when $R > 2.2$.

Similar measures have been carried out for the system containing PS 555 and the isomer 2,4-TDI (Fig. 2). The latter is more reactive than the 2,6-isomer regarding the formation of urethane bonds according to the literature¹⁶: in fact ΔH is higher for $R \leq 1$. However it is less reactive in the secondary reactions.

Isothermal tests have been performed also in the case of the reaction between TDI (mixture 80 : 20) and PS 555.

From all the results the existence of secondary reactions is confirmed.

The formation of uncontrolled crosslinking and the inhibiting effect of BzCl were also studied with rough tests, carrying out the reaction at various ratios of R , at various solvent concentrations, in the absence and the presence of BzCl at various concentrations, operating in a beaker under continuous magnetic stirring (Table II). The conventional time

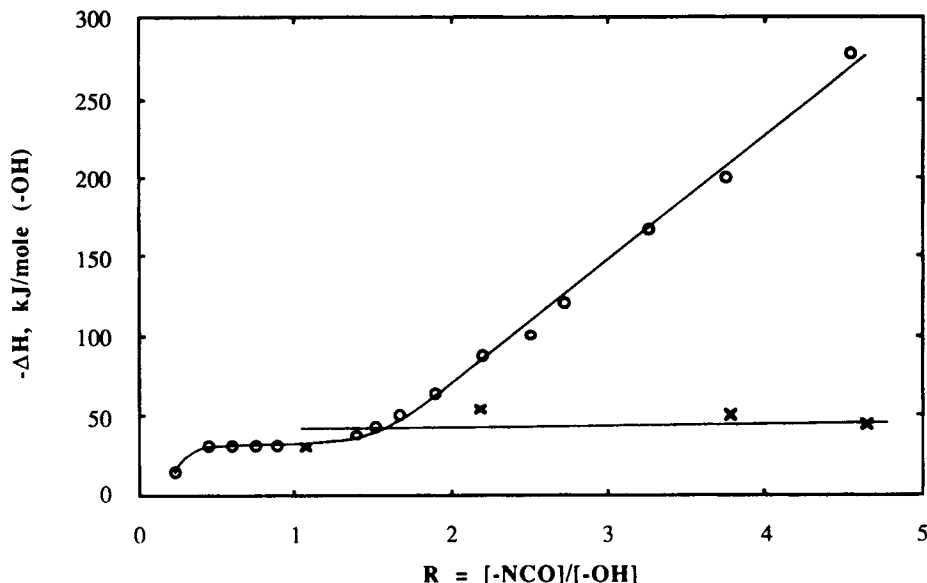


Figure 1 Heat of reaction between PS 555 and 2,6-TDI versus $[-\text{NCO}]/[-\text{OH}]$ ratio: (O) without BzCl; (X) with 0.2% BzCl.

of crosslinking is that at which the magnetic stirrer of the reactor stops due to viscous resistance. This time shortens as the concentrations of the solvent and of BzCl are lower and as R is higher. This empirical method is useful only for quick estimates for practical applications.

Measures of the $-\text{NCO}$ number in the presence of TDI and silicone oils not containing OH groups have proved that the secondary reactions do not involve the dimethylsiloxane block of PS 555.

In conclusion we point out that:

1. it is not possible to obtain a linear polymer of sufficiently high molecular weight by reacting our OH terminated block polymer directly with TDI even with $R = 1$, because in our conditions the reactivity of NCO is higher in secondary reactions than in the addition to OH;
2. secondary reactions are favored by high ratios of R and bring network formation;
3. the presence of BzCl reduces the secondary

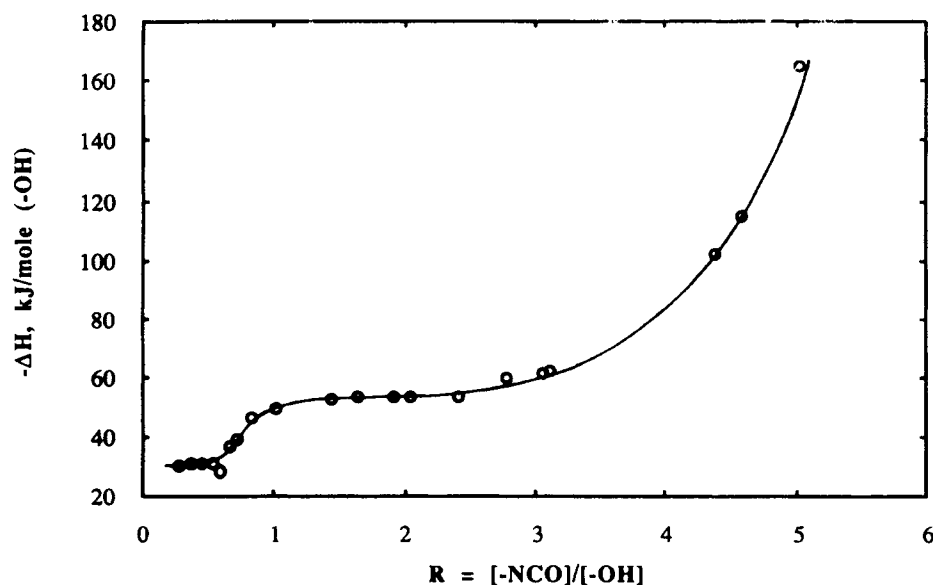


Figure 2 Heat of reaction between PS 555 and 2,4-TDI versus $[-\text{NCO}]/[-\text{OH}]$ ratio.

Table II Crosslinking Time and Delay Effect Due to BzCl in Rough Empirical Tests

[NCO]/[OH]	% Toluene	% BzCl ^a	Crosslinking Time
2.0	50	0.0	6.0 min
2.0	60	0.0	22.5 min
2.3	70	0.0	25.5 min
2.3	50	0.2	4 days
2.3	70	0.2	6 days
3.0	50	0.2	48 h
3.0	50	0.6	7 days
3.0	50	1.0	7 days

^a With respect to PS 555.

reaction rates and allows one to operate with lower ratios of R for obtaining films suitable for applications both in the case of PS/1 and PS/2 procedures.

Properties of Films

To satisfy the application requirements, films must show sufficient mechanical properties, must not be brittle and sticky, and must have a homogeneous thickness.

We found that films of good quality can be obtained working with both the one-step and two-step processes: in the latter case, even working with $R = 3$, the density of crosslinking was always lower than that obtained with the one-step process.

Table I shows the relation between synthesis conditions and some important physical properties. As a function of molar ratios R , of the type of crosslinking agent, and of the ratio $[-OH_d]/[-OH_t]$ we found: the volumetric fraction v_2 of the polymer in the swollen system submitted to tensile tests in toluene; the density ρ of the dry crosslinked polymer; the ratio between the residue W_0 of the crosslinked polymer remaining in the specimen after long contact times with toluene in the dynamometer (i.e., after the extraction of the soluble substances) and its initial mass W_i ; and, in the last row, the density of the chains that are elastically effective (ν/V_0), calculated according to eq. (1) (mol cm^{-3}).

All measures show that in the one-step process the crosslinking density depends on the crosslinking agent type and is higher when the glyceride C is used as a crosslinking agent; it is favored by high values of R . The low values of V_2 obtained in the case of the two-step system indicate the lower effectiveness of the crosslinking process when this method is used.

Thermal analysis of the films gives some important information on the structure of the polymers obtained with the one-step and two-step processes. PS 555 alone shows a T_g at about -120°C due to the PDMSO block and a melting temperature at about 20°C which can be attributed to polyoxyethylene blocks. In the case of pure polyoxyethylene¹⁷ an empirical correlation between its melting temperature T_m and its degree of polymerization P was found: $T_m = P(0.391 + 0.0236P)$. By introducing $P = 17$, a T_m value of 21.4°C , is found very close to the experimental one found by DSC for PS 555, which contains blocks of polyethyleneoxide (PEO). In the PUs obtained with both one-step and two-step processes we found a T_g in the range -120 to -130°C , attributable, by analogy, to the glass transition of PDMSO, but no melting temperature around room temperature. This suggests that no organized zone of interconnected PEO blocks is present in our PUs. As an explanation we propose that the interaction between the oxygen atoms of PEO and the H atoms of the $-\text{NH}$ groups of PU, previously revealed by us in PU-polyethers,¹⁸ can compete against the interactive forces among the PEO units and reduce the level of order of these chain units, preventing their crystallization.

In all PS/1 we always found a small endothermic peak in the range 150 – 190°C . According to the literature,¹⁹ this could correspond to the melting of the "hard" domains produced by the hydrogen bonds among $-\text{CONH}-$ groups of different chains. This peak disappears when a second DSC test was carried out on the same sample. Moreover this peak was absent even in the first thermal DSC run in the case of the two-step PUs, in agreement with the lower percentage of TDI utilized for these PUs that, as a consequence, show a lower number of hard domains.

Further, small endothermic peaks were found for both PS/1 and PS/2 in the range 70 – 90°C ; they also disappear in a second DSC run. Until now they could not be attributed: the melting of possible hard domains of lower order grade¹³ or the elimination of small amounts of water absorbed by the films after their preparations could be possible sources.

On the basis of the DSC curves and the composition data of the membranes (Tables I, III) the following conclusions can be drawn:

Both systems we examined are polyphasic: the existence of an elastomeric polysiloxane phase (about 25% in PS/1 and 30% in PS/2) is recognizable; moreover a mostly amorphous phase, although not well-defined, constituted of segments formed by $-\text{CH}_2\text{CH}_2\text{O}-$, TDI, and crosslinking units, is all

Table III Structural Characteristics and Transport Properties at 35°C of Membrane Obtained (PS/1; PS/2; PDMSO)

	PS/1; R = 2.2 C	PS/1; R = 3.4 C	PS/1; R = 2.2 TIPA	PS/1; R = 3.0 TIPA	PS/2; R = 3.0 TIPA	PS/2; R = 3.0 EDA	PDMSO
CO ₂							
P	27.4	10.7	28.5	11.5	34.0	32.5	240.0
D	0.3	0.4	0.7	0.6	1.5	1.5	
S	78.0	25.6	42.8	19.2	22.8	18.0	
CH ₄							
P	4.5	2.0	5.7	3.5	5.6	5.1	63.0
D	0.7	0.5	1.0	0.7	1.9	2.3	
S	6.2	3.5	5.8	5.0	2.9	2.2	
O ₂							
P	3.7	1.8	4.6	2.7	4.5	4.5	52.0
D	0.3	0.3	0.5	0.5	1.2	1.3	
S	10.9	5.2	9.8	5.0	3.6	3.5	
CO							
P	2.2	0.9	2.8	1.5	2.7	2.4	33.0
D	0.6	0.4	0.6	0.9	2.3	1.8	
S	3.9	2.1	4.7	1.6	1.1	1.4	
N ₂							
P	1.4	0.7	2.0	1.1	2.0	1.9	28.0
D	0.5	0.3	0.4	0.5	1.1	1.1	
S	3.0	2.3	4.5	2.2	1.8	1.7	
ν_e^a (mol/cm ³)	80×10^{-5}	49.5×10^{-5}	24.4×10^{-5}	25.4×10^{-5}	—	—	—
Dimethylsiloxane % (W)	25.6	22.3	26.4	24	30.2	29.3	100
TDI, % (W)	27.2	36.6	27.2	33.7	16.5	16.4	—
Crosslinker % (W)	8.9	7.7	5.9	5.3	8	10.3	—

The terms of P , D , and S values, regarding each gas, are: permeability coefficient, $P \cdot 10^9$ (Ncm³ cm⁻¹ cmHg⁻¹ s⁻¹); diffusion coefficient, $D \cdot 10^6$ (cm² s⁻¹); and solubility coefficient, $S \cdot 10^3$ (Ncm³ cmHg⁻¹ cm⁻³), respectively.

^a ν_e = crosslinking density.

together present. Finally, in PS/1 only a low percentage of crystallized hard phase is also present.

Gas Permeability, Diffusion Coefficient, and Solubility Coefficient

The polysiloxane-block polyethylether PUs are very complex polyphasic systems, as shown by the DSC analysis. Therefore, the molecular interpretation of their properties is not easy and a model in which the gas transport occurs in parallel between the different phases and the various types of domains, should be too simplistic.

Table III shows the values of permeability P , diffusivity D , and solubility coefficient S for the gases O₂, N₂, CH₄, CO, and CO₂ in the different PS/1 and PS/2 films. For comparison the permeability of PDMSO is also reported. The permeability of our PUs is lower by one order of magnitude. The permeability is usually higher in the case of the PS/2

which contains the smallest TDI concentration of all these PUs. Moreover the permeability of the PS/1 decreases with increasing percentage of TDI, which is the generator of the hard domains. Both these facts prove that the hard domains reduce the permeability.

It is well known that the permeability P of a polymer toward a permeating agent is the result of two factors: the coefficient of solubility S is the distribution coefficient between the polymer and the environment under equilibrium conditions; the diffusion coefficient is related to the transport rate of the permeating agent in the polymer. The first factor is controlled by the free energy change of the absorption process that, for gases, can be considered the sum of a condensation process (c) and of a solution process (s) of the gas in the polymer.²⁰ Therefore $\Delta G = \Delta G_c + \Delta G_s$. According to this model the solubility of CO₂ must be higher than that of the other gases studied because its ΔG_c and ΔH_c of conden-

sation is of prevailing importance in comparison with ΔG_s and ΔH_s , and because its ΔH_c is higher than that of all the other gases we tested.²⁰ The small solubility differences of the other gases (which have small ΔH_c) have to be ascribed to the not very different interactions between each absorbed gas and the absorbing polymer. This fact comes out clearly by representing in a qualitative way (Fig. 3) the S_i values of CH₄, O₂, CO, and N₂ at 35°C versus the interaction factor evaluated according to the regular solution theory:

$$\frac{V_i^L (\delta_p - \delta_i)^2}{RT}$$

This factor is related to the difference (to the square) between the solubility parameters of the polymer δ_p and of the condensed gas δ_i , as well as to its molar volume V_i^L , in the condensed state.²¹ This plot shows, in the range of the experimental errors, a small change of S_i . This demonstrates that there is no meaningful affinity of the examined gases in comparison with the PUs-siloxanes we prepared. In Figure 3, different ellipses show the domains of different gases; triangles out of the domains are related to the tetrafunctional crosslinker.

The diffusion coefficient D is the second parameter that influences the permeability. It depends on the gas diameter, on the fraction of free volume in the polymer,²² and on its distribution as a function of the "hole" diameter; D is moreover a function of

the polymer structure, and of the diffusing molecule size and shape.

The data in Table III show that the diffusion coefficients of all the gases are higher for PS/2 than for the one stage PS/1. This may be attributed to the higher free volume of PS/2. In fact PS/2 polymers are characterized (Table III) by a higher fraction of siloxane blocks that form the elastomeric phase, which have a very low glass transition temperature and therefore a higher total free volume.²³ According to Williams, Landel, and Ferry²³ a linear increase of free volume on increasing $T - T_g$ is possible.

Moreover PS/2 polymers have the lowest fraction of hard segments (%TDI) and are consequently less crosslinked than all the other PUs: they show a higher number of free chain ends and for this reason they have a larger free volume.²⁴

Table IV shows the selectivities defined as ratios of permeabilities between the pairs of gases O₂/N₂, CO₂/H₂, CO₂/CH₄, and CO₂/CO for the different PS/1 and PS/2. In comparison with the results for PDMSO, a clear improvement of the selectivity also accompanied by a permeability reduction, can be observed for all PS/1 and PS/2 systems.

CONCLUSIONS

The PU polymers synthesized in the presence of an excess of TDI are polyphasic systems containing one elastomeric phase made of PDMSO and one amor-

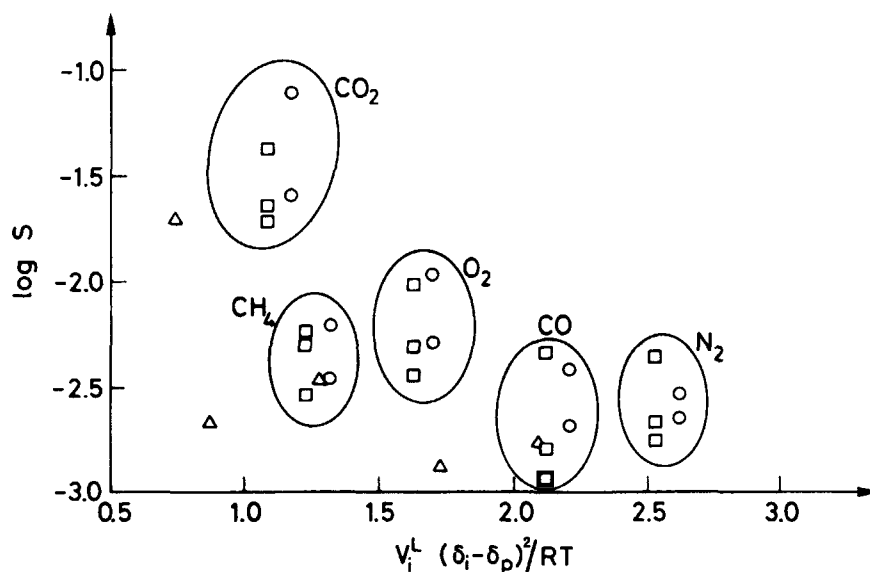


Figure 3 Solubility coefficient of different gases versus the affinity factor: (O) triglyceride of ϵ -hydroxyhexanoic acid as crosslinker; (□) TIPA as crosslinker; (Δ) pentapropoxylate ethylenediamine as crosslinker (tetrafunctional).

Table IV Selectivities of Different Membranes for Different Gas Couples

Polymer	O ₂ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄	CO ₂ /CO
PDMSO	1.9	8.6	3.8	7.3
PS/1; R = 2.2; C	2.6	19.6	6.1	12.6
PS/1; R = 2.2; TIPA	2.3	14.5	4.9	10.2
PS/1; R = 3.4; C	2.6	15.4	5.4	11.3
PS/1; R = 3.0; TIPA	2.5	10.5	3.3	7.7
PS/2; R = 3.0; TIPA	2.3	17.0	6.1	12.6
PS/2; R = 3.0; EDA	2.4	17.3	6.4	13.3

phous hard phase formed by NHCO groups associating with themselves or with PEO units more or less organized according to the lower or higher TDI percentage.

Only in the case of PS/1 is a crystalline phase also present.

In the PUs obtained with the two-step process the structures differ overall by the absence of more ordered hard zones, as shown by the disappearance of the melting point present in PS/1 over 150°C. The two-step PUs are less crosslinked and have generally higher permeabilities and higher diffusion coefficients than the one-step PUs.

The selectivity for the transport of the gases O₂ (in respect to N₂) and CO₂ (in respect to CO, N₂, and CH₄) is higher for the block siloxane-PUs described in this work than in the case of PDMSO alone.

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