Gas Permeability of Model Polyurethane Networks and Hybrid Organic–Inorganic Materials: Relations with Morphology

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ABSTRACT: Various polyurethane (PU) and hybrid organic–inorganic networks based on isocyanate chemistry were synthesized using a two-stage method. All the networks were amorphous. For PU membranes the morphology and the permeability coefficients of different gases (H_2, N_2, O_2) were a function of the polarity and the chain length of the soft segment and a function of the composition of the networks. The membranes based on the same soft segment chain length and on the same molar composition were structurally nanoheterogeneous systems for the less polar soft segments (α,ω-hydroxy-terminated hydrogenated polybutadiene and a fatty acid oligoester). They were homogeneous for a polycaprolactone type soft segment. The gas diffusion was appreciably hindered in the case of better miscibility between the soft chains and the hard crosslinks. Decreasing the soft segment length decreased the gas permeability coefficient of the network. As the chemical compositions were changed by increasing the soft segment content, an increase in permeability coefficients was observed. The morphology and transport properties of PU networks and hybrid organic–inorganic networks with low inorganic content were compared for the same soft segment content. The similarities observed between the two types of networks led us to conclude that the organic or inorganic nature of the crosslinking agent has no influence on the gas transport properties of these networks. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2579–2587, 1997

Key words: polyurethane networks; hybrid organic–inorganic networks; gas transport properties; morphology

INTRODUCTION

It is well known that gas permeation through a dense polymer according to the solution–diffusion process depends on the nature of the polymer : crystallinity degree,[1,2] chain packing, chain stiffness and segment mobility,[3,4] and ratio and size of free volumes.[5–7] Few studies focused on the role of the functionality and the size of the crosslinks in polymer networks.[8] Therefore, it seemed interesting to study and compare two networks based on the same chemistry but leading to different natures and sizes of the crosslinks. We chose to study polyurethane (PU) networks and hybrid organic–inorganic networks based on isocyanate chemistry. The first networks were interesting because their morphological and physicochemical properties could be varied over a wide range by changing the reagents' chemical structure, their characteristics, and their compatibility. Many

studies have been concerned with linear PUs[9–16] and the role of crystallinity on the transport properties; few studies have concerned PU networks.[8,17–19] It was shown recently[20] that, depending on the formulation, these networks could contain chemical clusters, making very interesting to study the consequence of this nanostructure formation on the transport properties of the networks.

The hybrid organic–inorganic network morphology is often described by the Wilkes et al. model[21] as a dispersion of inorganic particles in an organic thermoplastic or elastomeric matrix. The materials obtained by hydrolysis and condensation of alkoxysilane-terminated oligomers show a high connectivity between the organic and inorganic phases, and the first stage of the synthesis is identical to that of PU synthesis.

PU networks can be described as a dispersion of organic crosslinks and in some cases organic clusters in an organic phase; hybrid organic–inorganic networks with low inorganic content can be described as a dispersion of inorganic clusters in an organic phase. Thus, studying the two network types allow the comparison of the effect of the two crosslinks' nature on the transport properties of the membranes.

EXPERIMENTAL

Materials

The formulae, suppliers, and molecular weights of the reagents are listed in Table I.

Synthesis of PU Networks

The PU networks resulted from a two-stage synthesis. In the first stage the macrodiol reacts with an excess of diisocyanate at 80°C under a nitrogen atmosphere to form the isocyanate-terminated PU prepolymer. The amount of residual diisocyanate depends on the reactivity ratio of the two NCO functions of the diisocyanate and on the macrodiol to diisocyanate ratio. The ratios 1/3, 1/2, and 7/8 were studied that led to 40, 22, and 1.6 wt %, respectively, of measured residual diisocyanate.[20,22,23]

In the second stage, after adding 0.01 wt % of dibutyltin dilaurate, the NCO functions provided from the prepolymers and the residual diisocyanates react with a suitable amount of crosslinking alcohol in order to have a stoichiometric NCO to OH ratio of 1. Thus, the three studied formulations, expressed in macrodiol-diisocyanate-triol mole numbers, are 1-3-4/3, 1-2-2/3, and 7-8-2/3. After stirring, the mixtures are poured in polytetrafluoroethylene (PTFE) coated molds, cured at 100°C for 24 h under 100 bar pressure, and then allowed to cool slowly to room temperature.

On a morphological level, the final network can be schematically represented by a dispersion of hard crosslinks in a relatively soft PU matrix. The basic hard crosslink represented by the domain A (Fig. 1) is composed of a triol unit linked to three hard diisocyanate units. The 7-8-2/3 formulation, leading to a low percentage of residual diisocyanate, favors this type of crosslink. On the contrary, the presence of high residual diisocyanate ratios in the other two formulations favors larger hard domain formation represented in Figure 1 by the B or C clusters.

Synthesis of Hybrid Organic–Inorganic Networks

In this study the formulation expressed in macrodiol–diisocyanate-γ-amino propyltriethoxysilane (γ-APS) moles number is 1-2-2.

The organic–inorganic materials also result from a two-stage synthesis. The first stage consists of forming the isocyanate-terminated prepolymer with the same conditions as for the PU networks. The isocyanate to macrodiol molar ratio is in this case equal to 2.

After this stage, the prepolymer and the residual diisocyanate are end capped with the γ-APS. This reaction is carried out in a tetrahydrofuran solution (10% by weight) at room temperature for 1 h. Then the solvent is removed under a vacuum after 12 h.

The alkoxysilane-terminated species are then hydrolyzed and condensed using water and trifluoroacetic acid. The amount of water is calculated to obtain a total hydrolysis of the —$Si(OR)_3$ groups (e.g., 3 mol water for 1 mol γ-APS). In this study one acid to Si ratio was used: 10^{-3}. A previous study shows that this ratio has an influence on the ceramer morphology.[22,24]

Films are obtained by casting the mixture into a PTFE coated mold and by curing under a pressure of 100 bar. The cure cycle is 24 h at 100°C.
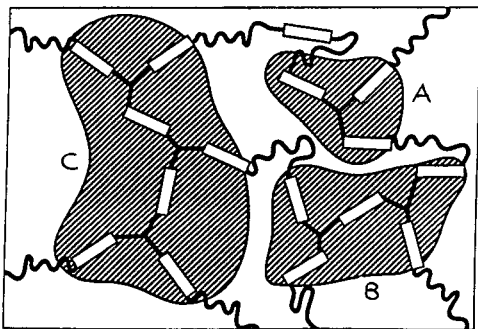
Methods

Permeation Measurements

The permeation cell consists of two compartments separated by the studied membrane (useful area: 3 cm^2). The cell is thermostated at 20°C. A prelim-

Table I   Characteristics of Reagents Used for Polyurethane or for Ceramers Synthesis

Reagent	Structure	Abbreviation	$\overline{M}_n$ (g mol^{-1})
α,ω-Hydroxy-terminated oligomer: hydrogenated polybutadiene $x = 34$, $y = 4$ (Nippon Soda)	HO—(CH$_2$—CH)$_x$(CH$_2$—CH$_2$—CH$_2$—CH$_2$)$_y$—OH $\quad\mid\quad$ C$_2$H$_5$	HPBD	2100
Polyester diol PRIPLAST 3197 (Unichema Int.)	Fatty acid oligoester	C36*	2000
Polycaprolactone (Interox)	H—[O—(CH$_2$)$_5$—C]$_x$O—(CH$_2$)$_2$—O—(CH$_2$)$_2$—O—[C—(CH$_2$)$_5$—O]$_y$H, O, O	PCL6 PCL20	550 2000
4,4'-Dicyclohexylmethane diisocyanate (Bayer)	O=C=N—⬡—CH$_2$—⬡—N=C=O	H$_{12}$MDI	262
Trimethylolpropane (Aldrich)	CH$_2$—OH, CH$_3$—CH$_2$—C—CH$_2$—OH, CH$_2$—OH	TMP	134
γ-Aminopropyltriethoxysilane (Union Carbide)	O—C$_2$H$_5$, NH$_2$—(CH$_2$)$_3$—Si—O—C$_2$H$_5$, O—C$_2$H$_5$	γ-APS	221

Figure 1 Schematic representation of the microstructure of a polyurethane network. Domain A represents a punctual crosslink and the domains B and C represent crosslink clusters that can be obtained in the case of a high residual diisocyanate content after the first stage of synthesis. (▭)The diisocyanate, (⅄) the triol, and (∿) the soft segment.

inary high vacuum desorption is realized to ensure that the static vacuum pressure changes in the downstream compartment are smaller than the pressure changes due to the gas diffusion. A 3×10^5 Pa gas pressure is then introduced in the upstream. The pressure variations in the downstream compartment are measured with a Datametrics pressure sensor. A steady-state line is obtained after a transitory state by plotting the measure pressure versus time.

The permeability coefficient P_e, expressed in Barrer units (1 Barrer = 10^{-10} cc$_{STP}$ cm cm^{-2} s^{-1} cm Hg^{-1}), is calculated from the slope of the steady-state line.

The diffusion coefficient D (cm^2 s^{-1}) is deduced from the time lag provided by the extrapolation of the steady-state line on the time axis, using the simplified Fick expression of the mass transport equation at infinite time.

Dynamic Mechanical Analysis

The films are tested in tension mode by means of dynamic mechanical spectroscopy using a Rheometrics RSA II solid analyzer at 10 Hz from -150 to 200°C in the temperature steps mode. The position of the α relaxation peak (T_α), the storage modulus E', and the loss factor tan δ are then obtained.

Microstructural Studies

The films are first analyzed by small angle X-ray scattering (SAXS). In the case of heterogeneous media, the nanometric size of the dispersed particles can be evaluated by the determination of the

Porod radius (R_p). The mean distance between these particles can also be obtained.

A study of the urethane functions has been developed, using a FTIR Nicolet MX1 apparatus in an attenuated total reflexion mode, to study the extent of H bonding in PU networks.

RESULTS AND DISCUSSION

First of all, it is important to note that all our networks are amorphous. Indeed, the crystalline zones are known to be impermeable to gases and their presence would highly modify the permeation data.[16–18]

PU Networks

Influence of Macrodiol Nature

Three types of soft segments with the same number average molar weight ($\overline{M_n} \approx 2000$) but different degrees of polarity have been studied: the hydrogenated polybutadiene (HPBD) is an apolar soft segment whereas the polycaprolactone type segment (PCL20) is polar. The C36* soft segment, a fatty acid oligoester, can be considered as intermediate.

The influence of the chain length of the soft segment has also been discussed considering two PCL type segments: PCL20 with $\overline{M_n} \approx 2000$ and PCL6 with $\overline{M_n} \approx 550$.

All the networks result from the same formulation: 1-3-4/3 [e.g., 1 mol macrodiol, 3 mol 4,4′-dicyclohexylmethane diisocyanate (H$_{12}$MDI) and 4/3 mol trimethylolpropane (TMP)], which corresponds to a residual diisocyanate content after the first stage of the synthesis of about 40%.

Viscoelasticity and SAXS results are discussed more extensively in another publication.[23]

The results of permeation data (H$_2$, O$_2$, N$_2$), T_α measurements, SAXS analysis, and IR spectroscopy are summarized in Table II. They are discussed here after taking into account the temperature at the maximum of the α relaxation peak and the microstructure of the networks.

Comparing the α relaxation position of our networks, we can see in Figure 2 that the permeation measurements proceed in the glassy state for only one network: the PCL6 based network that has the lower soft segment molar mass. The difference between the permeation measurements temperature ($T_o = 20$°C) and the temperature at the maxi-

**Table II   Influence of Macrodiol Type on Properties of Polyurethane Networks Having 1-3-4/3 Composition**

Soft Segment	HPBD	C36*	PCL20	PCL6
H_2, P_e (Barrers)	22	15	7	2.3
O_2				
P_e (Barrers)	4.6	5.5	1.5	0.3
D (10^7 cm^2 s^{-1})	2.6	2.2	1.2	0.1
N_2				
P_e (Barrers)	1.5	1.8	0.5	0.25
D (10^7 cm^2 s^{-1})	0.3	0.25	0.15	0.1
$T_0 - T_\alpha$	20	44	10	−70
SAXS observation	Heterogeneous	Heterogeneous	Homogeneous	Homogeneous
SAXS particle size (Å)	15	22		
Bonded NH percentage	88	not measured	96	not measured

P_e is the permeability coefficient, D is the diffusion coefficient, and $T_0 - T_\alpha$ is the difference between the permeation measurement temperature and the temperature at the maximum of the main α relaxation. The bonded NH percentage was determined by FTIR-ATR.

mum of the main relaxation peak (T_α) is −70°C for the PCL6 based network whereas it varies from 10 to 44°C for the other networks (Table II). Nevertheless, no discontinuity of the permeability coefficient and the diffusion coefficient is observed when comparing the rubbery PCL20 based network and the glassy PCL6 based network. On the contrary, the difference between the permeability coefficients of the HPBD based network and the PCL20 based network, two networks having al-
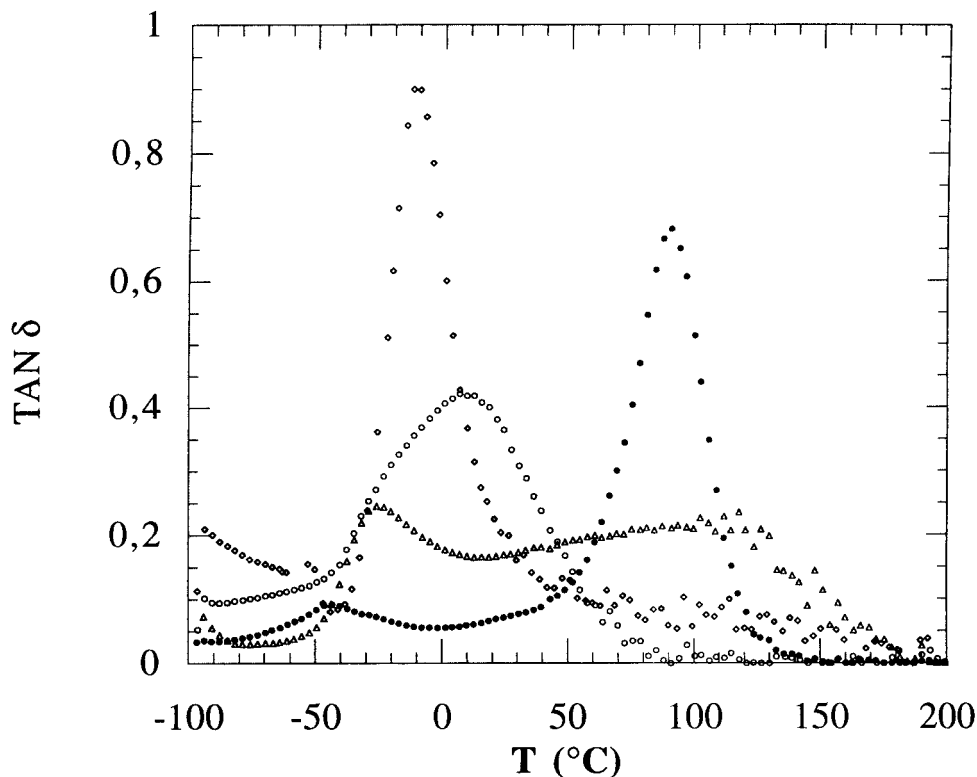
Figure 2   Evolution of tan δ versus the temperature for the PU networks having the 1-3-4/3 composition and based on different macrodiols: ($\diamond$) HPBD, ($\bigcirc$) PCL20, ($\triangle$) C36*, and ($\bullet$) PCL6.

most the same $T_o - T_\alpha$ value (10–20°C), is much higher.

Thus, for the same kind of soft segment, the state (rubbery or glassy) of the network at the permeation measurement temperature does not seem to be an important factor. The explanation can be that the diffusion of simple gases, with small kinetic diameters, only implies the oscillation of one or a small number of chain segments. This movement is sufficient to allow the process of activated jumps from hole to hole so that no real advantage is obtained when a larger chain length becomes mobile above the glass transition.[25]

The nature of the soft segment, the interactions that it can create in the network, and the microstructure of the networks are on the other hand very important parameters. Some information concerning the interactions between the soft segments and the crosslinks can be deduced first from the shape of the α relaxation peak and second from the comparison between the temperature of the α main relaxation of the network and that of the soft segment involved in the network. Indeed, a shift of T_{α_s} value emphasizes a copolymer effect and the presence of a simple loss peak, even a wide peak, emphasizes the presence of strong interactions in the network. It has been shown that replacing an apolar soft segment (e.g., HPBD) by a polar soft segment (e.g., PCL6) leads to an increase of the interactions in the network. This is also well traduced by the difference between the solubility parameter of the soft segment (21 MPa$^{1/2}$ for PCL20 and 17 MPa$^{1/2}$ for HPBD) and that calculated using Fedor's tables for a crosslink composed by three diisocyanate units reacted with the TMP segment (δ = 25 MPa$^{1/2}$). The most important difference is observed for the HPBD soft segment, indicating a low miscibility of the constituents of this network.

Because the microstructure of the network must reflect the degree of miscibility of the species, a SAXS study was performed. The PCL based PU networks appear homogeneous whereas a microphase separation is evidenced for HPBD and C36* based networks with a mean particle size around 10–15 Å and an interparticle distance of about 100 Å.

Furthermore, because the HPBD soft segment does not have any polar group along its chain, the hydrogen bonds must be more localized than in the case of the PCL soft segment that contains carbonyl groups. This is confirmed by FTIR-ATR spectra: the bonded NH absorption region centered at 3350 cm^{-1} is larger for the PCL20 based network than for the HPBD based network. And the extent of hydrogen bonding represented by the NH percentage is slightly higher in the PCL20 based network than in the HPBD based network (Table II).

Returning to the transport properties of the networks, we can see that the permeability coefficients and the diffusion coefficients are the highest for the network having the highest degree of segregation: the HPBD based network. The gases diffuse preferentially through the soft phase of the polymer, and for this network the soft phase is rich in saturated polyolefin with probably only a few H$_{12}$ MDI units due to chain extension during the first stage of the synthesis. There is a thermodynamic phase separation between the crosslinks and the soft segment due to their different polarity degrees, and the hydrogen bonds are principally localized in the crosslinks cluster. The transport is thus made easier in comparison to the PCL based network, for which the crosslinks and the hydrogen bonds are more uniformly distributed with the soft segment.

Influence of Composition

The influence of the formulation was studied on networks based on two different macrodiols, C36* and PCL6; the compositions studied were 7-8-2/3, 1-2-2/3, and 1-3-4/3. The results are presented in Table III.

The main difference between the two types of networks is the degree of miscibility between the crosslinks and the soft segment. In the case of C36* soft segment, a microphase separation is observed and the $T_o - T_\alpha$ values remain constant whatever the formulation and whatever the crosslink content. In the PCL6 based network, no microphase separation is observed and $T_o - T_\alpha$ increases as the crosslink content in the network decreases (e.g., 7-8-2/3 formulation) (Fig. 3). In spite of this difference in the degree of miscibility, the same trend is observed for the two network types with respect to the transport properties.

Indeed, whatever the nature of the soft segment and whatever the gas used, the permeability coefficients and the diffusion coefficients are higher in the 7-8-2/3 composition than in the 1-3-4/3 composition. Intermediate values are obtained for the 1-2-2/3 composition. Nevertheless, the permeability ratios for the extreme formulations 7-8-2/3 and 1-3-4/3 are relatively low: they
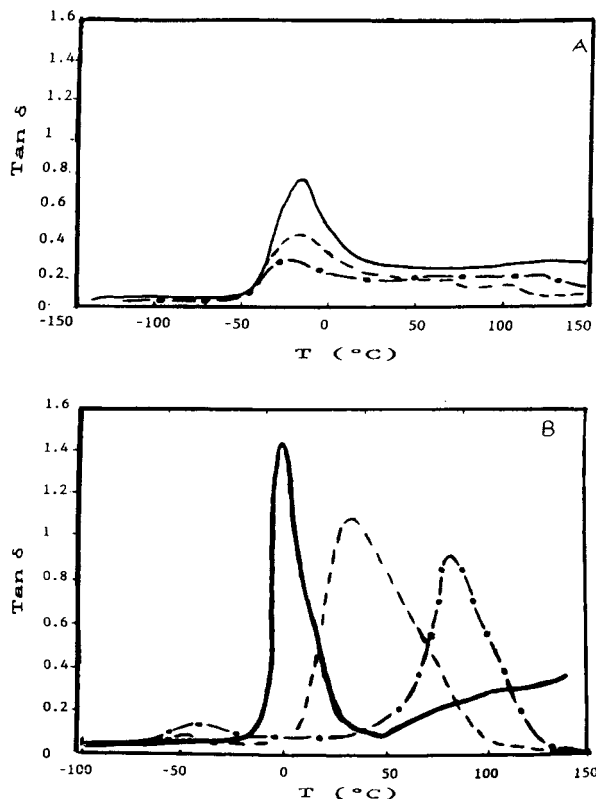
Table III   Influence of Composition on Properties of Polyurethane Networks Based on C$_{36}$* and PCL6

Soft Segment	C$_{36}$*			PCL6	
Molar Ratio	1-3-4/3	1-2-2/3	7-8-2/3	1-3-4/3	7-8-2/3
Residual diisocyanate content					
after 1st stage of synthesis	40	20	1.6	40	1.6
Soft segment (wt %)	62	75	83	62	83
H$_2$, P_e (Barrers)	15	21	23	2.3	4.4
O$_2$					
P_e (Barrers)	5.5	6.4	8	0.3	0.7
D (10^7 cm^2 s^{-1})	2.2	2.5	2.6	0.1	0.2
N$_2$					
P_e (Barrers)	1.8	2.1	2.3	0.25	0.45
D (10^7 cm^2 s^{-1})	0.25	0.3	0.3	0.1	0.15
$T_0 - T_\alpha$	44	44	44	−70	10

P_e is the permeability coefficient, D is the diffusion coefficient, and $T_0 - T_\alpha$ is the difference between the permeation measurement temperature and the temperature at the maximum of the main α relaxation.

do not exceed 2 for the two types of soft segment. It seems then that the permeability coefficient is above all related to the soft segment percentage in the network and not so much to the size of the

Figure 3 Evolution of tan δ versus the temperature for the (A) C36* based PU networks and (B) PCL6 based PU networks having the following compositions: (——) 7-8-2/3, (- - -) 1-2-2/3, and ($\cdot$-$\cdot$-$\cdot$) 1-3-4/3.

crosslinks. Furthermore, as shown previously, the nature of the soft segment determines the permeability level. Indeed, for the same formulation, the permeability coefficient is still higher for the less polar soft segment (Table III).

Hybrid Organic–Inorganic Networks

All of the networks have the same 1-2-2 composition (e.g., 1 mol macrodiol, 2 mol diisocyanate, and 2 mol γ-APS). The residual diisocyanate content after the first step of synthesis is about 20% and the soft segment content is 62% by weight.

Influence of Macrodiol Nature

The influence of the polarity of the macrodiol is investigated for an H$^+$ to Si ratio equal to 10^{-3}. As we can see in Table IV, the microstructural SAXS studies of the hybrid organic–inorganic networks show the same trend as for PU networks. Indeed the PCL6 based hybrid is homogeneous whereas the two other networks, based on less polar macrodiol, contain dispersed particles with a size of 15 Å. The morphologies of the PU networks and the hybrid networks are thus quite identical. Concerning the transport properties, we note that the permeability coefficients and the diffusion coefficients of the organic–inorganic networks are similar to that of the corresponding PU networks. From all these results it can be concluded that for a given morphology of the networks the transport properties do not depend on the organic or inorganic nature of the crosslinking agent.

Table IV   Influence of Nature of Soft Segment on Properties of Hybrid Organic–Inorganic Networks with 1-2-2 Composition

Soft Segment	HPBD	C_{36}*	PCL6
H_2, P_e (Barrers)	23	19	3.5
O_2			
P_e (Barrers)	5.3	5.9	0.6
D (10^7 cm^2 s^{-1})	4.7	4	0.1
N_2			
P_e (Barrers)	1.5	1.9	0.3
D (10^7 cm^2 s^{-1})	0.2	0.3	0.03
SAXS particle size (Å)	16	15	Homogeneous

The H^+ to Si ratio is equal to 10^{-3}. P_e is the permeability coefficient and D is the diffusion coefficient.

CONCLUSION

The gas transport studies on various PU networks have shown that the most important factor of the gas diffusion is the nature of the soft phase and the ensuing morphology. More precisely, the polarity of the macrodiol compared to that of the crosslinks appears to be a very important factor. With polar macrodiols (PCL type soft segment), the miscibility between soft chains and hard crosslinks is enhanced, the network is homogeneous, and a high number of hydrogen bonds can develop between the NH groups of the urethane units and the polar groups of the soft chains surrounding the crosslinks. In these conditions, the gas diffusion is appreciably hindered.

On the contrary, all the other factors studied in this work have a small influence on the transport properties. For a given network type, a slight decrease is observed as the soft segment chain length decreases and a change in the chemical composition by increasing the soft segment content leads to a small increase of the gas diffusion. This indicates that the gas transport properties seem more related to the soft segment content than to the size of the crosslinks.

The comparison between the PU and the ceramers based on the same soft segment shows that the two kinds of networks have the same morphology and that the organic or inorganic nature of the crosslinking agent has no influence on the gas transport properties of the networks.

This result can be explained by the fact that, if we assume a complete conversion of the hydrolyzed $Si(OR)_3$ species, the theoretical maximum massic silica content is about 8% for the network containing the smallest soft segment chain length (PCL6) and only about 4% for soft segments with $\overline{M_n} \approx 2000$ g mol^{-1}. This content, determined by the type of chemistry that we used, is low and the similarity observed between PU and hybrid organic–inorganic networks is then not surprising. To exactly know the behavior of the inorganic phase with respect to gas diffusion, we expect in future studies to use another chemistry to increase the inorganic content in the networks.

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