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# Gas Transport Properties of Sulfonated Copolyimides: Influence of Structural Parameters and Relative Humidity

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**Summary:** Structure-property relationships in terms of gas transport have been established for a large series of sulfonated copolyimides. At anhydrous state, a large range of permeability values can be obtained varying the nature of the non-sulfonated diamine, the sulfonated diamine content and the sulfonated block length. The diffusion coefficient is in all cases the dominant factor that explains the permeability level. The gas permeability coefficients decrease when the copolyimides are hydrated. A particular behaviour has been evidenced on some membranes for carbon dioxide.

## Introduction

Polyimides have been widely studied as gas separation membranes.[1-3] Indeed polymers having different main chains can be easily prepared and a lot of work has concerned the influence of functional groups substitutions in the diamine or dianhydride components on the gas transport properties.[3,4] Nevertheless, few studies have dealt with copolyimides and they have principally focused on gas transport properties at anhydrous state.[5]

The aim of this work is to discuss the gas transport properties at various hydration states of a particular kind of copolymers : ion-conductive copolyimides. These copolymers are prepared by introducing ionic groups onto the polymer backbone by means of a sulfonated monomer. The interest of this method is to control both

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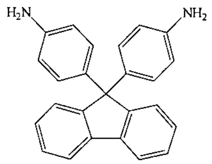
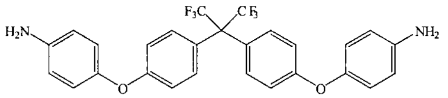
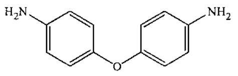
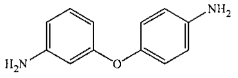
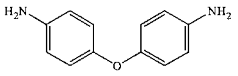
sulfonation degree and ionic group distribution and to allow the choice of the chemical structure of the non-sulfonated sequence. Varying these different parameters allows to study structure-properties relationships in terms of gas transport for a large series of hydrophobic/hydrophilic systems. Furthermore, from a practical point of view, these polymers could represent a good alternative to perfluorosulfonated ionomer (Nafion) especially for fuel cells applications and it is then interesting to compare their performance to those of Nafion.

# Experimental Part

## Membrane material

Sulfonated copolyimides have been synthesised using a naphtalenic anhydride (1,4,5,8-tetracarboxylic acid : NTDA) and two types of diamines: an already sulfonated one (2,2'-diamino 4,4' biphenyl sulfonic acid : BDSA) and a non-sulfonated one, the nature of this last being variable (Table 1).

Table 1. Structure of the different non-sulfonated diamines used for copolymer synthesis.

| Abbreviation | Name | structure |
|---|---|---|
| cardo | 9,9-bis(4- aminophényl ) fluorène |  |
| BAPHF | bis[4-(4- aminophénoxy ) phényl hexafluoropropane |  |
| ODA4,4'<br>ODA3,4' | 4,4' - oxydianiline<br>50/50<br>3,4 '-oxydianiline |  <br> |
| ODA4,4 | 4,4'- oxydianiline |  |

Statistical copolymers were obtained by a one step polycondensation. Segmented copolymers were obtained by a two stage one pot method according to the scheme presented in Figure 1. The first step involves the preparation of the sulfonated sequences: their average length x is adjusted by the molar ratio of the two monomers BDSA /NTDA. In a second step, the polycondensation is pursued by adding i) the amount of the non-sulfonated diamine that determines the molar percentage of the sulfonated diamine in the total diamine content: [SD] and i.i) the appropriate amount of NTDA in order to respect the total stoichiometry.

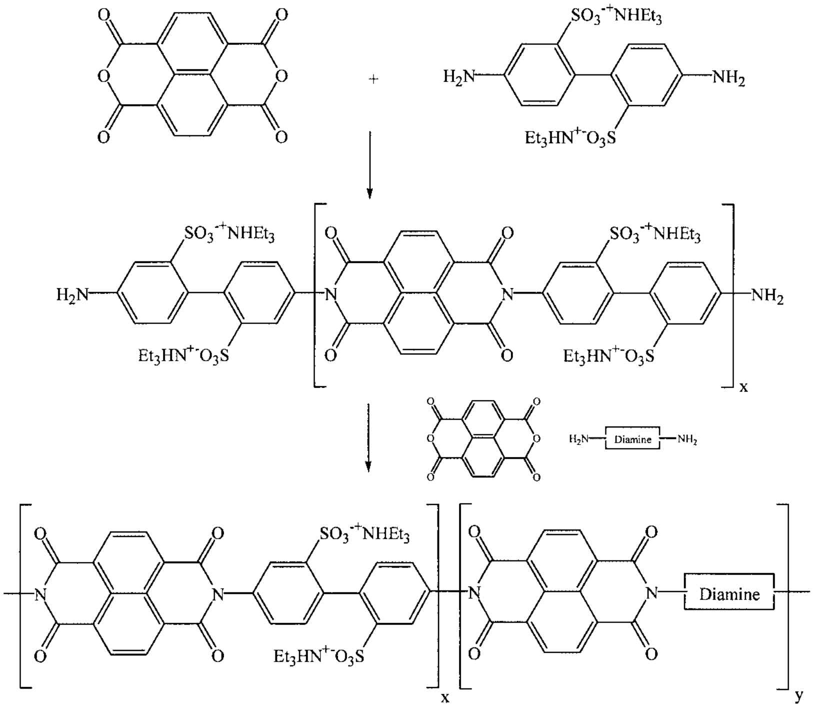


Figure 1. Scheme of the segmented copolymers synthesis.

One step and two step polycondensation are carried out in m cresol at 180°C, using benzoic acid as catalyst and copolyimides in triethylammonium sulfonate form are obtained.

The microstructure of this type of polymers has been previously studied by small angle neutron scattering and a phase separation between ionic and non-ionic phase has been evidenced on a nanometer scale.[6]

## Film preparation

All polymer films were cast at 120°C from m cresol solvent at approximately 8% wt% polymer onto a glass plate. The films were dried in a vacuum oven according to the following cycle : 2 hours at 50°C, 28 hours at 70°C and 10 hours at 90°C. They were unstuck from the glass plates support by immersion in methanol. Membranes with controlled thickness from 25 to 40 μm were obtained, they were acidified with 0.1M HCl solution overnight and then rinsed with water. They were finally dried 4 hours at 80°C in a vacuum oven.

## Permeability measurements

The permeation cell consisted in two compartments separated by the studied membrane. The cell was thermostated at 20 ± 1°C. A preliminary high vacuum desorption was realised to ensure that the static vacuum pressure changes in the downstream compartment were smaller than the pressure changes due to the gas diffusion.

i) For gas permeation at anhydrous state, a $3.10^5$ Pa gas pressure was introduced in the upstream. The pressure variations in the downstream compartment were measured with a datametrics pressure sensor. A steady-state line was obtained after a transitory state by plotting the measured pressure versus time. The permeability coefficient expressed in barrer units (1 barrer : $10^{-10}$ $cm_{STP}$ $cm.cm^{-2}$ $s^{-1}$ $cm_{Hg}{}^{-1}$) was calculated from the slope of the steady-state line.

The diffusion coefficient D ($cm^2.s^{-1}$) was deduced from the time lag provided by the extrapolation of the steady-state line on the time axis.

The solubility coefficient S ($cm^3cm^{-3}cm_{Hg}{}^{-1}$) was estimated according to the fundamental relation : Pe = D.S.

i.i.i) For gas permeation experiments on membranes at different relative humidities, the membrane was equilibrated at the desired water relative partial pressure by means of an evaporator before introducing in the upstream compartment the $3.10^5$ Pa gas pressure. The permeability coefficient was calculated from the slope of the straight line representative of the evolution of the pressure in the downstream compartment as a function of time. In that case, it was impossible to determine the diffusion coefficient.

## Results

### Transport properties at anhydrous state

The influence of three stuctural parameters were studied on the gas transport properties : the sulfonated groups content [SD], the length (x) of the sulfonated sequences and the nature of the non-sulfonated diamine.

i) *Sulfonated groups content :*

Concerning the first factor, a series of copolyimides containing different concentrations of sulfonic acid groups was prepared. The sulfonated block length (x) was kept constant and equal to 5. The non-sulfonated diamine was chosen in order to obtain soluble polymers in all the range of composition studied: a mixture of 4,4'oxydianiline and cardo diamine in molar proportion was used. The properties of the copolymers were also compared to those of the corresponding homopolymers.

The density was determined for the different copolymer compositions. The density of a polymer is a macroscopic measure of the number of factors such as average chain packing from the cast solvent, drying and annealing conditions. Using in all cases, m cresol as the solvent and the same casting, drying and annealing conditions, we felt that the film preparation effects would be the same for all samples and thus that density values should reflect the chain packing. As shown in Table 2, the density increases as the sulfonated groups content increases in the copolymer. The fractional free volume (FFV) was estimated by the group contribution method of Bondi [7] for the two homopolymers. It is much lower for the totally sulfonated polymer (FFV= 0.088) than for the non-sulfonated polyimide (FFV= 0.14).

Concerning the gas transport properties, the same kinds of evolution are observed whatever the gases used. The discussions will thus focus on one gas : carbon dioxide and the values of the transport parameters (the permeability coefficient Pe, the diffusion coefficient D and the solubility coefficient S) obtained for this gas are summarised in Table 2. The permeability coefficient of the totally sulfonated polyimide is about 50 fold lower than the non-sulfonated one. This result underlines, as the density and FFV values, the higher intersegmental packing of the totally sulfonated polymer. As expected, a decrease of the permeability is observed as the sulfonated groups content increases in the copolymer. This evolution is principally related to the diffusion coefficient. Indeed D highly decreases as the sulfonation rate increases whereas no great evolution of the solubility parameter S is observed as a function of the copolymer composition.

Table 2. Density and $CO_2$ transport properties of copolyimides as a function of their sulfonated diamine content.

| [SD] | d | Pe | D | S |
|---|---|---|---|---|
| (%) | $(g.cm^{-3})$ | (barrer) | $(10^{-8}\ cm^2.s^{-1})$ | $(cm^3_{STP}.cm^{-3}cm_{Hg}{}^{-1})$ |
| 0 | 1.299 | 147 | 2.7 | 0.55 |
| 10 | 1.336 | 122 | 1.9 | 0.64 |
| 20 | 1.356 | 86 | 1.2 | 0.72 |
| 30 | 1.398 | 70 | 1.0 | 0.7 |
| 40 | 1.415 | 56 | 0.9 | 0.62 |
| 50 | 1.434 | 24 | 0.4 | 0.6 |
| 70 | 1.45 | 17 | 0.3 | 0.57 |
| 85 | 1.481 | 5.7 | 0.1 | 0.57 |
| 100 | 1.511 | 2.6 | 0.07 | 0.37 |

ii) *Length of the sulfonated sequences :*

This parameter was investigated for a molar sulfonated diamine ratio [SD] equal to 30% and for two copolyimides series synthesised with cardo diamine on one hand and with BAPHF on another hand (Table 3). In both cases, the permeability decreases by a factor 1.6 as the length of the sulfonated and non-sulfonated sequences, respectively x-y, increases from 3-2 to 9-8. It can also be noticed that the permeability coefficients of the statistical copolymers are always higher than those of the segmented copolymers. The solubility coefficient does not vary as a function of the microstructure. It depends thus principally on the global composition of the copolymers and its constant value whatever the length of the sulfonated sequences evidences a constant free volume fraction in each copolymers series. This conclusion is also supported by the density values that remain constant whatever the length of the sulfonated sequences. On the other hand, the diffusion is very sensitive to the length of the copolymer sequences. Its decrease can be explained by a more tortuous gas path as the sulfonated sequence length increases.

iii) *Nature of the non-sulfonated diamine :*

This parameter was investigated for 30% [SD] value, for 3 different non-sulfonated diamines and for x-y values equal to 5-4. An influence is observed on both solubility and diffusion but the diffusion coefficient remains also in that case the dominant factor that explains the variation of the permeability. Indeed, the lowest permeability coefficients are obtained with a mixture of ODA 4,4' and ODA 3,4' in a molar proportion. As bulkier groups such as trifluoromethyl groups are introduced in the diamine, the intersegmental packing is restricted leading to higher permeability coefficients. The highest permeability coefficients are obtained for the cardo diamine, which presents the most bulky side group and rigid structure.

Table 3. Transport properties for different sulfonated copolyimides and different sequence lengths.

| diamine | d | x-y | Pe | D | S |
|---|---|---|---|---|---|
| | ($g.cm^{-3}$) | | (barrer) | ($10^{-8}$ $cm^2.s^{-1}$) | ($cm^3_{STP}.cm^3cmHg^{-1}$) |
| cardo | 1.348 | Stat. | 265 | 3.9 | 0.68 |
| | 1.345 | 3-2 | 259 | 4 | 0.65 |
| | 1.347 | 5-4 | 164 | 2.8 | 0.59 |
| | 1.342 | 9-8 | 162 | 2.5 | 0.65 |
| BAPHF | 1.420 | Stat. | 33 | 0.87 | 0.38 |
| | 1.431 | 3-2 | 28 | 0.74 | 0.38 |
| | 1.411 | 5-4 | 23 | 0.64 | 0.36 |
| | 1.427 | 9-8 | 16 | 0.45 | 0.36 |
| ODA4,4'/ODA 3,4' | / | 5-4 | 5.2 | 0.1 | 0.52 |

In conclusion, the sulfonated copolyimides series we have studied allow us to cover a large range of permeability values. The permeability coefficient is very sensitive to the sulfonated groups content as the totally sulfonated polyimide is a very low diffusive material. For a given [SD] value, the structure of the non-sulfonated diamine governs the permeability level by means of both diffusion and solubility parameters. Furthermore, increasing the length of the sulfonated sequence leads to a more tortuous gas path and as a consequence to a decrease of the gas flow. It is thus possible, by an appropriate choice of these different factors, to prepare membranes with required permeability values.

## Gas transport properties at various relative humidities

The gas fluxes were measured at 20°C on membranes equilibrated at different water partial pressures. Indeed for fuel cells application, it is important to know these values since wet state corresponds to the working conditions.

Figure 2 presents the evolution of $H_2$ permeability as a function of hydration states in the case of polyimides based on cardo and ODA4,4' diamines mixture, for [SD] values equal to 0, 40 and 100%.

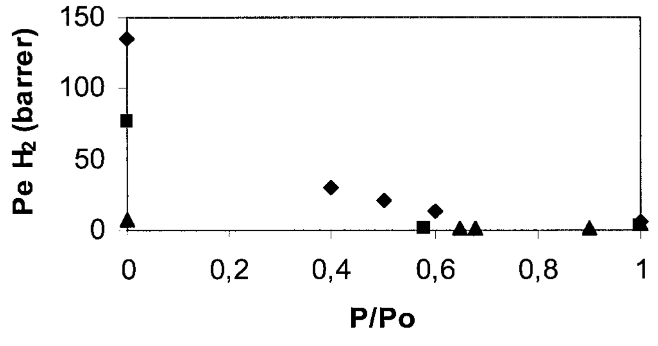


Figure 2. evolution of hydrogen permeability as a function of the hydration state for ( ◆ ) the non-sulfonated polyimide, ( ■ ) the copolymer with [SD] = 40% and (▲ ) the totally sulfonated polyimide.

The first observation is that the permeability coefficient decreases for hydration level increasing up to 50 % R.H. while a smaller evolution is observed between 50 and 100% RH. The flux depressing effect of water at low pressures has already been observed on polyimides by Chen et al [8] using $CO_2/H_2O$ mixed penetrant feeds. These data show an antiplasticization effect of water in these matrices.

The second observation is that the flux decrease is higher for high contents of the non-sulfonated phase. As shown above, this phase is mainly responsible of the gas transport (leading to a lower intersegmental packing of the copolymer) and it is supposed to be the "hydrophobic" phase in the phase separation characteristic of these copolymers. However, the water solubility in the non-sulfonated polyimide can not be considered as negligible. For example, at a partial pressure equal to 0.5, the water uptake is equal to 6.2%, 16.3% and to 28.3% for respectively the non-sulfonated polyimide, the copolyimide and the totally sulfonated polyimide. Thus, as the water partial pressure increases, the water molecules tend to occupy sites contained in both “hydrophobic” and “hydrophilic” phases of the copolymer. There is not a drastic hydrophobic/hydrophilic separation compared to perfluoro-sulfonique membranes as the Nafion membrane. In this last, it was concluded from different studies [9,10] that the gas transport takes place mainly in the non-ionic phase (a point which is confirmed by our study) but it was maintained upon hydration due to the high hydrophobic character of the perfluoro-organic phase. Consequently, we can conclude in the case of copolyimides, that the gas flow decreases upon hydration due to the fact that the non-sulfonated phase is able of sorbing water. A detailed analysis of water sorption isotherms and water/polymer interactions as a function of the copolymer composition is actually under study in order to bring additional information concerning the behaviour of these matrices.

The third observation results from the comparison of gas permeability evolution between the anhydrous and saturated (P/Po=1) states for different copolyimides and different gases (Table 4) : the decrease of gas flux going from anhydrous to wet state is as much important as the anhydrous permeability coefficient is high. The most important point is that, at wet state, and especially for $H_2$ and $O_2$ all the membranes exhibit almost the same gas permeability coefficients. Moreover, the ratios f between the anhydrous and saturated values were calculated for respectively $H_2$

(from 4 to 45), $O_2$ (from 1 to 15), and $CO_2$ (from 1/4 to 3). It appears that these ratios are less and less important when going from $H_2$ to $O_2$ and to $CO_2$. For a given copolyimide, one can simplify writing $f_{H2} \approx 4f_{O2}$ and $f_{O2} \approx 4f_{CO2}$. A particular effect occurs when $f_{O2}$ is below 4 : the corresponding value for $f_{CO2}$ is below 1, leading to an increase of the $CO_2$ permeability when going from the anhydrous to the wet state. Two cases are thus observed in Table 4.

Table 4. Evolution of the gas permeability coefficient between anhydrous state and wet state for different copolyimides and different gases.

| Non-sulfonated diamine | [SD] | $PeH_2$ (barrer) | | $PeO_2$ (barrer) | | $PeCO_2$ (barrer) | |
|---|---|---|---|---|---|---|---|
| | | R.H.=0 | R.H.=100 | R.H.=0 | R.H.=100 | R.H.=0 | R.H.=100 |
| CARDO/ODA | 30 | 89 | 5.6 | 11 | 1.6 | 70 | 55 |
| | 40 | 76 | 3.7 | / | / | 56 | 43 |
| | 50 | 42 | 4.3 | 3.3 | 1.7 | 24 | 50 |
| CARDO | 30 | 166 | 3.7 | 24 | 1.6 | 164 | 51 |
| BAPHF | 30 | 43 | 4.1 | 4.6 | 0.95 | 23 | 11 |
| ODA3,4’ | 30 | 14 | 2.5 | 0.83 | 0.84 | 5.2 | 23 |

## Conclusion

A large series of sulfonated copolyimides has been studied in order to establish relations between structural parameters and gas transport properties at various hydration rates.

At anhydrous state, the gas transport takes place principally in the non-ionic phase. It is thus possible to cover a large range of permeability values varying i) the nature of the non-sulfonated diamine and particularly the steric hindrance it induces in the polymer ii) the sulfonated diamine content and the sulfonated block length since the totally sulfonated polyimide is a very low diffusive material. The diffusion coefficient is in all cases the dominant factor that explains the permeability level at anhydrous state.

The gas permeability coefficients decrease when the copolyimides are hydrated. The magnitude of this decrease depends on the nature of the gas but also on the non-sulfonated diamine content in the copolymer. Indeed the non-sulfonated phase, that assumes mainly the gas transport, is able to contain a non negligible amount of water at hydrated state. These water molecules act as an antiplasticizer and they have an hindering effect on gas transport.

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