



## Permeability of block copolymers to vapors and liquids

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### Abstract

Permeability of block copolymers is an important feature for a broad range of applications including packaging, bio-materials (e.g. for controlled release or encapsulating membranes), barrier materials, high performance impermeable breathable clothing and membrane separation processes. This paper reviews the literature on permeability of block copolymers to pure or mixed vapors and liquids for the past 40 years. Different types of block copolymers are considered, starting with the most investigated polyurethanes and polyurethaneureas followed by polyimides, polyamides and miscellaneous types of block copolymers (e.g. block copolymers containing siloxane segments, hydrocarbon block copolymers and related materials). Block copolymers offer a great structure versatility which is highly interesting for a fundamental analysis of permeation through polymeric materials. A special attention has been paid to the key permeability properties and their correlation to the chemical structure of block copolymers. Systematic structure/property relationships have been emphasized to promote the future design of block copolymers with improved permeability properties. Far from being limited to fundamental investigations, this literature review points out the originality of block copolymers, which combine a great structure versatility with several high potential industrial prospects. Many patents on block copolymers indeed reflect a strong industrial interest in applications based on their (selective) permeability. A sharp increase in the related patents for the past 10 years certainly shows the strong potential of block copolymers to take up several current challenges in the medical, chemical and petrochemical fields. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Permeability; Block copolymers; Structure–property relationships; Membranes

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## 1. Introduction

Since the 1960s and even more during the past two decades, permeability of block copolymers has been the subject of a great number of investigations that revealed very interesting properties and offered new insights into mass transfer through polymeric materials.

Block copolymers represent a very wide range of materials with great variety in macromolecular architectures. Polyurethanes (PU) are very good examples for block copolymers. They can be obtained from several types of reagents (e.g. polyether, polyester or polycarbonate oligomers, aromatic or aliphatic diisocyanates and chain extenders, etc.), therefore leading to polymeric materials that can display very different properties. One of the key features of block copolymers is their *versatile structure* that makes them particularly interesting materials for *fundamental investigations*. Systematic studies of block copolymers with closely related structures can clearly allow a better understanding of permeability in terms of *structure/property relationships* [1–22]. Such relationships enable to identify the key parameters governing the mass transfer and open the way for new tailor-made polymeric materials with specified properties.

Far from being limited to fundamental investigations, the literature of the past 10 years also shows that block copolymers have a *very high industrial potential* especially for the removal of organics from water [14,20,23–27] or air [28] and the separation of purely organic mixtures by membrane separation processes. Potential applications include the purification of new fuel octane enhancers [12,13,21,29] and

**Nomenclature***Abbreviations*

ABE	acetone–butanol–ethanol
1,4-BD	1,4-butane diol
BPDA	3,3',4,4'-biphenyl tetracarboxylic dianhydride
BTDA	3,3',4,4'-benzophenone tetracarboxylic dianhydride
BTX	benzene, toluene, xylene
DABA	3,5-diamino benzoic acid
DMPA	dimethylol propionic acid
EDA	1,2-ethylene diamine
ETBE	ethyl- <i>tert</i> -butyl ether
6FDA	4,4'-hexafluoroisopropylidene-bis(phthalic anhydride)
HB	hydrogen bonding
HBI	hydrogen bonding index
HMDI	1,6-hexamethylene diisocyanate
H12MDI	4,4'-methylene-bis(cyclohexyl isocyanate)
IPDI	isophorone diisocyanate
JFAED	Jeffamine ( $\alpha$ - $\omega$ -diamino copolyether oligomer)
LFER	linear free energy relationship
LVE	liquid vapor equilibrium
MDA	4,4'-methylene dianiline
MDEA	methyldiethanol amine
MDI	4,4'-methylene-bis(phenyl isocyanate)
MOCA	4,4'-methylene-bis( <i>o</i> -chloro-aniline)
MPD	<i>m</i> -phenylene diamine
MTBE	methyl- <i>tert</i> -butyl ether
ODA	4,4'-oxy dianiline
ODPA	3,3',4,4'-oxydiphthalic anhydride
PAUI	polyamideurethaneimide
PB	poly(butadiene)
PBA	poly(butylene adipate)
PCL	poly(caprolactone)
PDMO	poly(decamethylene oxide)
PDMS	poly(dimethyl siloxane)
PE	poly(ethylene)
PEA	poly(ethylene adipate)
PEBA	poly(ether- <i>block</i> -amide)
PEO	poly(ethylene oxide)
PFDA	2-(perfluorohexyl)ethyl-3,5-diamino-benzoate
PHMO	poly(hexamethylene oxide)
PHMS	poly(hexamethylene sebacate)
PMDA	pyromellitic dianhydride

POMO	poly(octamethylene oxide)
PPO	poly(propylene oxide)
PTMO	poly(tetramethylene oxide)
PU	poly(urethane)
PUU	poly(urethane–urea)
P2VP	poly(2-vinylpyridine)
SBS	styrene/butadiene/styrene
SPR	surface plasmon resonance
2,4-TDI	2,4-toluene diisocyanate
2,6-TDI	2,6-toluene diisocyanate
TIPA	triisopropanol amine
TMAACl	trimellitic anhydride acid chloride
TMP	1,1,1-trimethylol propane
TMPI	3-trimethylammonium-(1,2-propane diol) iodide
VOC	volatile organic compound
X	soft block
Y	hard block

### *Symbols*

$a_i$	activity of component $i$ (dimensionless)
$C_i$	weight fraction of component $i$ in the feed mixture (dimensionless)
$C_i'$	weight fraction of component $i$ in the permeated mixture (dimensionless)
$C_i^S$	weight fraction of component $i$ in the sorbed phase (dimensionless)
$D$	diffusion coefficient ( $\text{m}^2/\text{s}$ )
$G$	total swelling (wt%)
$G_i$	partial swelling of component $i$ (wt%)
$J$	normalized flux ( $\text{kg } \mu\text{m}/\text{h m}^2$ )
$J_i$	partial normalized flux of component $i$ ( $\text{kg } \mu\text{m}/\text{h m}^2$ )
$M_c$	molar mass between cross-links (g/mol)
$P$	pressure (Pa)
$r$	correlation coefficient (dimensionless)
$t$	time (s)
$T_g$	Glass transition temperature ( $^{\circ}\text{C}$ )
$v_i$	Molar volume of component $i$ (l/mol)
$W_{\text{HB}}$	weight fraction of hard blocks in the block copolymer (dimensionless)
$W_{\text{SB}}$	weight fraction of soft blocks in the block copolymer (dimensionless)

### *Greek symbols*

$\alpha$	selectivity factor (dimensionless)
$\beta$	enrichment factor (dimensionless)

$\chi$	Flory–Huggins interaction parameter (dimensionless)
$\delta$	film thickness ( $\mu\text{m}$ )
$\delta_i$	solubility parameter of component $i$ ( $\text{J}^{0.5} \text{cm}^{-1.5}$ )
$\phi_i$	volume fraction of component $i$ (dimensionless)
$\rho_i$	density of component $i$ (g/ml)
$\tau$	sorption half-time (s)

the separation of aromatics from alkanes [6,30–38] related to the removal of aromatics from gasoline for the protection of environment, that still remain important issues for the petrochemical industry.

Following former general reviews on permselective polymeric membranes [39–42], this review focuses on permeation of vapors and liquids through block copolymers, that can interest a wide range of applications including packaging, biomaterials (e.g. for controlled release or encapsulating membranes), barrier materials and membrane separation processes.

In a first part, a brief introduction to permeation through polymeric materials will be made, defining the basic parameters characterizing mass transfer in such systems. Second, permeability of block copolymers to vapors and liquids will be analyzed for different types of copolymers in a systematic way, starting with PU and polyurethaneureas (PUU) that have been the most investigated. Rather recent works have also shown very interesting properties for special polyimide block copolymers that will be analyzed in the third part. Permeability through polyamide block copolymers will be the subject of the fourth part. Although they are still relatively scarce, works on permeability of block copolymers containing siloxane segments have revealed new approaches to polydimethylsiloxane (PDMS) hybrid materials, with unique properties that will be reviewed in the fifth part. Another part will be devoted to hydrocarbon block copolymers and related materials, pointing out the special role played by morphology in these particular systems.

Our analysis of about 300 references covered the period of time starting from the 1960s to the end of the year 2000. A special attention was paid to the key permeability properties of block copolymers and their correlation to their chemical structure, on the basis of structure/property relationships already described in the literature or obtained from our own analysis of reported experimental data, in order to help and promote the future design of polymer materials with improved permeability properties.

## 2. Introduction to permeation through polymeric materials

Permeation of vapors and liquids through polymeric materials can occur in a wide range of systems (e.g. bulk materials, films, microspheres, etc.) as soon as a *chemical potential gradient* is present to induce mass transfer [43]. The rational study of permeation through non-porous materials usually involves fixed and well-known material geometries for which mass transfer equations can be derived easily. Therefore, for the sake of simplicity, the great majority of permeation studies use polymeric films that correspond to the plane geometry leading to the simplest mass transfer equations [44].

Permeation of vapors or liquids through non-porous polymeric films is driven by a chemical potential gradient across the membrane, that is usually maintained by ensuring immediate sorption and rapid

desorption of the permeated species at the downstream side of the membrane [45,46]. A sweeping gas or a very low downstream side pressure (i.e. much less than the vapor pressure of the permeated species) can be used for that purpose in membrane systems that are called vapor permeation [47] or pervaporation [48–50] for the permeation of vapors and liquids, respectively. When the permeated species are desorbed by a circulating liquid, the membrane process is called perstraction [51].

### 2.1. The sorption–diffusion model

Assuming good hydrodynamic conditions to prevent any mass transfer limitation in the upstream boundary layer (also known as concentration polarization [52,53]), permeation through non-porous polymeric films is usually described by the solution-diffusion model [54,55] that considers three successive steps for mass transfer (Fig. 1):

- The dissolution (or sorption) of molecules at the membrane upstream side in contact with the vapor or liquid
- The diffusion step driven by the chemical potential across the membrane
- The desorption of the permeated species at the membrane downstream side, that is usually considered as a non-limiting step.

Changing the membrane macromolecular structure or the nature of the permeating species can influence the species partitioning at the upstream side (i.e. the thermodynamics of polymer swelling) and also the diffusion within the polymer matrix and, therefore, can affect the overall mass transport features.

The polymer swelling determines the concentration of the sorbed species at the membrane upstream interface and fixes the chemical potential gradient (i.e. the driving force for mass transfer) across the membrane. When dealing with permeation of a feed mixture, it also ensures a first enrichment, the composition of the sorbed mixture being usually different from that of the feed mixture.

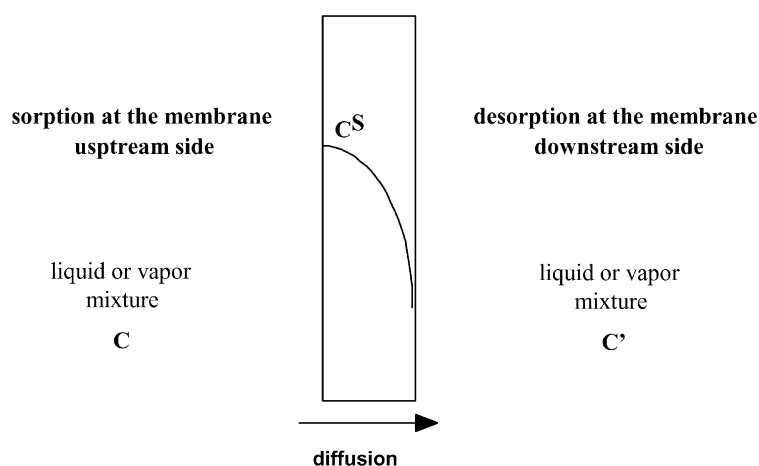


Fig. 1. Permeation through non-porous polymeric materials according to the solution-diffusion model.  $C$ ,  $C^S$  and  $C'$  are the compositions of the feed, absorbed and permeated mixture, respectively, conventionally expressed as the mass fractions of the preferentially permeated species.

Diffusion through the dense membrane is the limiting step. It can strongly affect the overall permeation features, especially when the different permeated species have very different molecular sizes.

Therefore, according to the solution-diffusion model, it is usually considered that a good understanding of permeation through non-porous polymeric materials requires both sorption and diffusion be analyzed separately [56]. Basic aspects of sorption and diffusion are briefly reminded thereafter, defining key parameters that will be used thoroughly in the rest of this work.

## 2.2. Sorption in polymeric materials

According to the thermodynamics of irreversible processes [57], the sorption step constitutes a *thermodynamic equilibrium* that determines the composition of the sorbed species at the membrane upstream interface. Moreover, it is usually well admitted that the equilibrium corresponding to the *dynamic* permeation process (e.g. pervaporation, vapor permeation) is the same as that occurring during *static* swelling of the polymeric membrane in the same mixture. Therefore, different types of sorption experiments enable to determine the composition and activities of the sorbed species at the membrane/feed interface. Very rarely subject to controversy [58], the validity of this crucial hypothesis for mass transfer analysis has been confirmed by many experimental data [54].

### 2.2.1. Sorption of pure liquids or vapors

The sorption of *pure* liquids or vapors in polymeric materials are usually characterized by the swelling  $G$  (wt%) that can be calculated from the mass uptake,  $m - m_0$ , of the membrane at equilibrium and the mass of the dry polymer  $m_0$ :

$$G \text{ (wt\%)} = \frac{m - m_0}{m_0} \times 100 \quad (1)$$

From the swelling  $G$ , the volume fraction of sorbed species  $\phi_s$  in the polymer membrane can be derived provided the density values for both sorbed species and polymer material be known:

$$\phi_s = \frac{1}{1 + \frac{100}{G} \frac{\rho_s}{\rho_p}} \quad (2)$$

A sorption isotherm characterizes the swelling of a polymeric material at a given temperature and for a given range of penetrant activities (e.g. curve  $G$  versus activity or, most commonly,  $\phi$  versus activity). Sorption isotherms are important data which reflect the affinity of a given penetrant for a polymer material and many theoretical or semi-empirical attempts have been made for their modeling.

A complete review of the different sorption models is far beyond the scope of this work. However, two classic theories deserve special comments because they have been used very widely for modeling sorption of pure species in block copolymers and (sometimes) allow a first estimate of polymer/penetrant affinity on the basis of a single parameter.

First, the Flory–Huggins theory was the first lattice model to describe thermodynamics of polymer–solvent equilibria [59,60]. Based on very drastic assumptions that should theoretically limit its use to apolar systems [61], the Flory–Huggins theory is based on a statistical calculation of the different configurations obtained for binary polymer/solvent systems using a simple lattice model. By neglecting the solvent molar volume as compared to the polymer molar volume, the Flory–Huggins theory

describes sorption isotherms in binary systems using a single semi-empirical parameter called the interaction parameter  $\chi$ :

$$\ln a_s = \ln \phi_s + (1 - \phi_s) + \chi(1 - \phi_s)^2 \quad (3)$$

Based on the Scatchard–Hildebrand theory or regular solution theory [62] and, therefore, on very restrictive assumptions that should also restrict its use to apolar systems, the value of the interaction parameter  $\chi$  can be estimated from the solubility parameters for the solvent and polymer

$$\chi = 0.34 + \frac{v_s}{RT} (\delta_s - \delta_p)^2 \quad (4)$$

where  $v_s$  is the solvent molar volume.

The value of the interaction parameter  $\chi$  is a reflection of the intensity of polymer/solvent interaction. As clearly shown by Eq. (4), the *smaller* the  $\chi$  value, the *greater* the polymer/solvent interaction. The interaction parameter  $\chi$  had been first considered as a *constant* parameter by the initial Flory–Huggins theory. Worthy of mention, especially when referring to block copolymers that are mainly polar materials, the interaction parameter  $\chi$  has been shown to vary greatly with concentration particularly for polar polymer solvent systems [63–65], as also clearly mentioned by Flory as early as in the 1950s [61].

Second, the Flory–Rehner theory [66] considers sorption equilibria in cross-linked polymers by adding an elastic contribution to the initial Flory–Huggins equation

$$\ln a_s = \ln \phi_s + (1 - \phi_s) + \chi(1 - \phi_s)^2 + \frac{\rho_p v_s (1 - \phi_s)^{1/3}}{M_c} \quad (5)$$

where  $M_c$  is the molar mass between cross-links. Block copolymers are mainly chemically or physically cross-linked materials for which the Flory–Rehner theory has been applied widely, even if some restrictions have been pointed out, as will be discussed later because it provides an interesting insight into the physical chemistry of solvent sorption in block copolymer materials.

### 2.2.2. Sorption of binary mixtures of liquids or vapors

The sorption of binary liquid or vapor mixtures in polymeric materials (i.e. ternary systems) is characterized by the *total* swelling  $G$  (wt%) defined as for the sorption of pure species (Eq. (1)). However, the sorption of binary mixtures is *usually selective*, meaning that the composition of the sorbed mixture differs from that of the feed mixture. Therefore, it is interesting to define partial swelling values  $G_i$  (wt%) related to each sorbed species  $i$  by

$$G_i \text{ (wt\%)} = \frac{m_i - m_0}{m_0} \times 100 = C_i^S G \text{ (wt\%)} \quad (6)$$

where  $C_i^S$  is the mass fraction of species  $i$  in the sorbed mixture. These partial swelling values can be determined by desorbing the swollen polymer sample by careful experimental procedures such as those described by Jonquière et al. [67] and Tanbonliong and Prausnitz [68].

Often related to absorption or membrane separation processes, thermodynamics of ternary systems involving a polymer phase is fairly complex and currently remains a challenging and active research field [56,68–71], far beyond the initial extension of the Flory–Huggins theory to ternary systems [72].

### 2.3. Diffusion through polymeric materials

Diffusion of vapors or liquids through polymeric materials is a complex process whose quantitative



analysis is not trivial and still remains subject to debate [73,74]. Moreover, as already very clearly stated by Meares in 1976 [46], the complexities of a general treatment of multicomponent diffusion in polymeric films remain very severe [75–82]. Therefore, for the sake of clarity, our next presentation will be limited to the diffusion of *pure* vapors or liquids through polymeric materials and is aimed at introducing the basic concepts and terminology that will be used latter in this work.

### 2.3.1. Determination of average diffusion coefficients

Diffusion coefficients of small molecules through polymeric materials are usually derived from gravimetric measurements although other methods have also been reported [83,84].

Mass uptake of a polymer film of thickness  $\delta$  is usually obtained as a function of time during the *transient regime* of vapor or liquid sorption at constant solvent activity  $a_s$ . Analysis of the experimental data is based on solving the Fick's second equation according to several methods that have been reviewed by Crank [44] and recently nicely briefly summarized by Balik [73]. As way of very typical examples, an average value for the penetrant diffusion coefficient,  $D$ , can be obtained from a plot giving the ratio of the swollen polymer mass at time  $t$  and  $t = \infty$  (corresponding to sorption equilibrium),  $M_t/M_\infty$ , as a function of the square root of time  $t^{1/2}$  (Fig. 2) following:

- Method 1: from the initial slope  $s_0$ :  
when  $t \rightarrow 0$

$$\frac{M_t}{M_\infty} = \frac{4}{\delta} \left( \frac{D}{\pi} \right)^{1/2} t^{1/2} \quad (7)$$

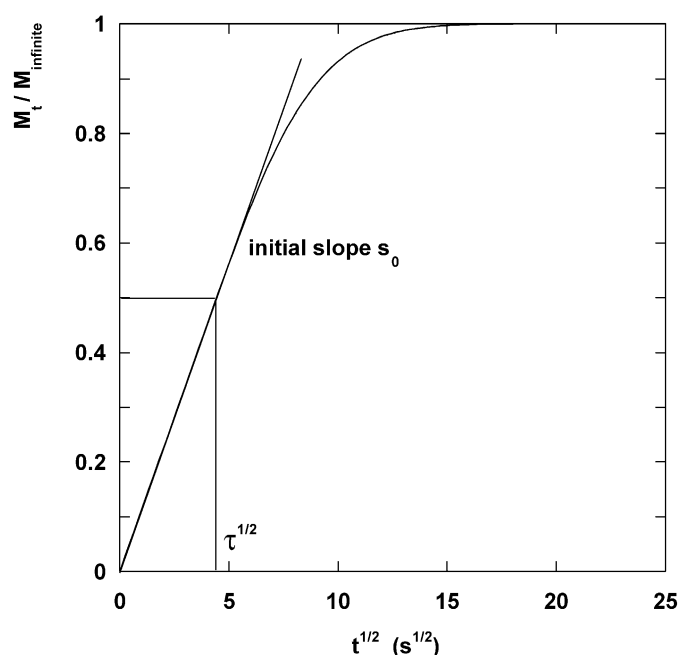


Fig. 2. Determination of average diffusion coefficient from a transient sorption experiment: key parameters  $s_0$  and  $\tau$ . (Sorption curve simulated for  $D = 10^{-12} \text{ m}^2/\text{s}$  and a film thickness  $\delta = 20 \text{ }\mu\text{m}$ ).

therefore

$$D = \frac{\pi}{16}(\delta s_0)^2 \quad (8)$$

- Method 2: from the sorption half-time  $\tau$ :

$$D = \frac{0.0492}{\tau} \delta^2 \quad (9)$$

$\tau$  being the time corresponding to  $M_t/M_\infty = 0.5$  (i.e. sorption of 50% of the maximum mass uptake obtained at equilibrium) and  $\delta$  the thickness of the film.

The former methods provide an *average* value for the diffusion coefficient and are recommended for systems with very low sorption levels (e.g. sorption of permanent gases in aromatic glassy polymers). When sorption becomes important, it induces plasticizing of the polymeric material and the variation of diffusion coefficients with penetrant concentration can no more be neglected.

### 2.3.2. Concentration dependent diffusion coefficients

Two types of laws have been proposed to describe the concentration dependence of the diffusion coefficient of a unique penetrant through polymeric materials.

The first laws are purely *empirical* and have been applied to systems that do not involve strong specific interactions (i.e. apolar systems). Proposed by Aitken and Barrer in 1955 [85], the most ancient law suggested a linear increase with the penetrant concentration in the polymer material  $C_s$  according to:

$$D = D_0(1 + kC_s) \quad (10)$$

The Barrer's law can account for diffusion of paraffins in rubber [85] and is in fact a first order approximation of the Long's model that will be discussed later. Greenlaw et al. [75] reported another empirical law that applied very well to the *n*-hexane diffusion through polyethylene:

$$D = K_d C_s \quad (11)$$

Very rarely used, the former empirical laws are limited to poorly swollen materials and do not reflect the variation, often very important, that is observed for most polymer/solvent systems above the glass transition temperature.

The second type of laws have been derived from *theoretical* considerations based on *free volume* theories [86–88] whose main aspects have been briefly reviewed by Meares [89]. Derived on the basis of a statistical calculation and assuming the additivity of free volume contributions for polymer and solvent [90], the Long's model certainly provides the most used equation to describe the concentration dependence of diffusion coefficient [45,91–93]:

$$D = D_0 \exp(\gamma C_s) \quad (12)$$

where  $D_0$  is the diffusion coefficient at infinite dilution (also called intrinsic diffusivity) and  $\gamma$  the plasticizing constant. The latter parameter characterizes the solvent ability to plasticize the polymer and increase its own diffusion through the swollen material. Involving two parameters only, the Long's model is relatively simple. It has been shown to apply even for systems with strong variations in

diffusion coefficient, for which the former empirical models systematically failed [91,92]. More recently, Vrentas and Duda [88] proposed another approach to free volume theory. Contrary to the former free volume theories, the Vrentas and Duda model is *predictive*, therefore allowing the diffusion modeling on the single basis of physical parameters. However, the high number of physical parameters required for estimating diffusion coefficients [94] seems to have so far limited its application to a small number of well-defined systems. Therefore, the simplicity of the Long's model is most often preferred in the literature on diffusion through polymeric materials.

#### 2.4. Permeability, flux and selectivity

Different terminologies have been reported to characterize mass transfer through polymeric films [95–97].

For the permeation of *permanent gases* through glassy polymers, the permeability coefficient  $P$  is usually estimated from the gas flux and the driving force gradient for mass transfer [97]:

$$P = \frac{\text{Flux}}{\text{Driving force gradient}} = \frac{\text{Flux}}{\Delta p / \delta} \quad (13)$$

According to the solution-diffusion model, the permeability coefficient can also be considered as the product of the penetrant diffusion and solubility coefficients:

$$P = DS \quad (14)$$

Many units can be found in the literature for permeability coefficients and useful conversion tables have been reported [95]. However, the most common unit certainly remains the Barrers (i.e.  $10^{-10} \text{ cm}^3$  (STP)  $\text{cm}/(\text{cm}^2 \text{ s cm Hg})$ ) that gives very convenient values for the permeation of permanent gases through most polymers [97]. The sorption of permanent gases in glassy polymers being usually very low, the permeability coefficient is *usually constant* and *characteristic* for the gas–polymer system.

Permeation of *liquids or vapors* through polymeric materials usually involves much higher sorption coefficients than for permanent gases, leading to much more complex systems for which *plasticizing effects* generally occur. For these particular systems, the permeability coefficient is no more a characteristic for the penetrant–polymer system because it varies strongly with different parameters such as the penetrant concentration in the feed. In that case, it is a common practice to characterize mass transfer by the permeation flux defined as:

$$\text{Flux (kg/h m}^2\text{)} = \frac{\text{amount of permeant}}{(\text{membrane area})(\text{time})} \quad (15)$$

The permeation flux is most generally inversely proportional to the thickness of the dense permeable film [98]. Therefore, to allow a comparison of the properties of films with close but not constant thicknesses, a *normalized flux* can be calculated for a reference thickness of the dense film (usually  $1 \mu\text{m}$ ):

$$J \text{ (kg } \mu\text{m/h m}^2\text{)} = \frac{(\text{amount of permeant})(\text{film thickness})}{(\text{membrane area})(\text{time})} \quad (16)$$

To characterize the permeation of binary feed mixtures, the *total flux* is calculated as for the permeation of pure species (Eq. (15) or (16)). Mass transfer through polymeric materials is usually selective,

meaning that the composition of the permeated mixture usually differs from that of the feed mixture. Therefore, the *normalized partial permeation fluxes* are also estimated from the composition of the permeated mixture:

$$J_i \text{ (kg } \mu\text{m/h m}^2\text{)} = \frac{\text{(amount of species i)(film thickness)}}{\text{(membrane area)(time)}} = C'_i J \quad (17)$$

where  $C'_i$  is the mass fraction of species  $i$  in the permeated mixture.

Different ways of characterizing *permeation selectivity* have been reported in the literature, with the common feature of being always referred to the *preferentially* permeated species [96]:

- The simplest way consists of plotting the composition of the permeated mixture  $C'$  as a function of that of the feed mixture  $C$ . One obtains a *square diagram* in a similar way as what is commonly used to represent liquid vapor equilibria (LVE) in distillation. This representation presents several advantages. The first one is to allow an easy assessment of the membrane performance in terms of enrichment of the permeated mixture. The second advantage is to enable a direct comparison with what would be obtained from a simple evaporation of the feed mixture (single distillation stage) when the LVE curve is also displayed on the same diagram.
- Another very common definition of selectivity in gas, liquid or vapor permeation is given by the *selectivity parameter* (also known as the separation factor)  $\alpha$ , that was initially defined by analogy with the relative volatility used in distillation:

$$\alpha = \frac{C'_A/C'_B}{C_A/C_B} = \frac{C'}{1-C'} \frac{1-C}{C} \quad (18)$$

Values for the selectivity parameter  $\alpha$  are extremely sensitive to the composition of the feed mixture, especially in the low range of concentrations of the preferentially permeated species. As way of example to illustrate this point, for a composition of the permeated mixture in the preferentially transferred species equal to 0.9 (i.e.  $C' = 0.9$ ), values for the selectivity parameter  $\alpha$  of 171, 441 and 1791 are obtained for feed mixture compositions  $C$  of 0.05, 0.02 and 0.005, respectively. Therefore, the value of selectivity parameter  $\alpha$  is absolutely meaningless without the corresponding composition of the feed mixture. Moreover, it is very difficult to compare the performances of different films tested under different experimental conditions using the selectivity parameter  $\alpha$ .

- Permeation selectivity is also commonly defined by the *enrichment factor*  $\beta$ :

$$\beta = \frac{C'}{C} \quad (19)$$

The enrichment factor  $\beta$  is also very sensitive to the feed mixture composition, although less than the selectivity parameter  $\alpha$ . However, the enrichment factor  $\beta$  is an interesting *key factor for dimensioning* membrane-based separation processes. As a way of example, for tangential pervaporation with constant feed rate, the module productivity is proportional to the product  $(\beta - 1)J$  [96,99]. Therefore, despite its inherent limitation, the enrichment factor  $\beta$  is certainly preferable to the most used selectivity parameter  $\alpha$ .

In the rest of this work, the permeation features of a great number of systems will be discussed in terms of flux and selectivity. To allow an easy comparison of mass transfer selectivities obtained in very

different experimental conditions and for the reasons exposed formerly, we will systematically give our preference to the first way of representing selectivity by reporting both  $C$  and  $C'$  values.

### 3. Permeability of block copolymers to vapors and liquids

#### 3.1. Polyurethanes and polyurethaneureas

##### 3.1.1. Permeability to pure vapors or liquids

**3.1.1.1. Water.** Water is certainly the first species to have been considered for sorption, diffusion and permeation studies on PU and PUU. Most investigations were undertaken to understand the basic relationships between the polymer structure and water sorption or permeability, in order to control the hydrophilic character by a proper macromolecular design.

###### 3.1.1.1.1. Influence of the chemical nature of the soft block

**3.1.1.1.1.1. Simple soft blocks.** In 1969, Schneider et al. [1] already reported the very strong influence of the soft block chemical nature on water sorption and permeability for four PU X/MDI/1,4-BD with different types of soft segments X (polyethers: PEO2000, PTMO2000, PPO2000; polyester: PBA2000) and the reactant stoichiometry (1/3.2/2). For the soft segments PTMO2000, PPO2000 and PBA2000, extremely low water sorption were obtained at 21 °C (typically  $G < 3$  wt%). As expected from these very low sorption values, these PU were poorly permeable to water (normalized water fluxes less than 1.5 kg  $\mu\text{m}^2$  h at 21 °C). The soft segment PEO2000, well known for its very hydrophilic character, induced a very different behavior with a much higher water sorption ( $G = 113$  wt%) and permeability (normalized water flux  $J = 165$  kg  $\mu\text{m}^2$  h) at the same operating temperature. The same conclusions was also drawn by Hsieh et al. who again obtained very low water sorption and permeability at ambient temperature for very closely related PU X/MDI/1,4-BD with the soft blocks PTMO2000, PBA2000 and PCL2000 and the stoichiometry (1/3/2) [100] or (1/2/1) [4]. For these PU, water permeability was shown to increase in the following order of the soft segments X = PBA < PCL < PTMO. An ester group being capable of a much stronger interaction with water than an ether group, the strong decrease in water permeability (almost –100%) observed with the polyesterurethanes PBA2000/MDI/1,4-BD and PCL2000/MDI/AP may be related to the combined action of an increased glass transition temperature and an accumulation of methylene groups in the soft block structure. Kanapitsas et al. reported very close values for water sorption (typically  $G < 3$  wt%) at 40 °C in related materials based on PPO2000 or PBA2000, aromatic or aliphatic diisocyanates and 1,4-butanediol [101]. In 1974, Barrie and Nunn working on commercial PU synthesized with no chain extender, PTMO/1,4-TDI (polyetherurethane, Du Pont de Nemours and Co.) and PEA/PBA/MDI (polyesterurethane with mixed soft segments, General Tyre and Rubber Co.), also determined water sorption coefficients of less than a few weight percent within the range of temperature 36–60 °C [102]. The water diffusion coefficient at infinite dilution and the water permeability were slightly higher (+70% at 36 °C) for the polyetherurethane as compared to the polyesterurethane. This increase in water permeation through the polyetherurethane was ascribed to a decrease in polymer rigidity as reflected by a significant decrease in the polymer glass transition temperature (almost –20 °C less than that of the polyesterurethane).

The influence of *functional groups* incorporated within the polymer soft blocks was also reported by Antonucci et al. who were interested in fluorinated PU as potential protective materials for stone

monuments [103]. Even if the polymer structures were not fully described in the former paper, the results clearly showed that increasing the fluorine content of perfluoropolyether soft segments from 27 to 41 wt% induced a water vapor sorption decrease of 50% for a water activity of 0.5 at 30 °C. In the same conditions, the water permeability dropped by a factor 3.75.

The strong influence of the soft block structure on water sorption or permeation was also shown for polyurethaneureas that were obtained using a diamine (rather than diol) chain extender (ethylene diamine [104] or hydrazine [105]) and soft blocks PEO and PPO of molecular weights close to 1000. For the PUU PEO1000/H12MDI/EDA and PPO1025/H12MDI/EDA, Chen et al. reported swelling data for liquid water at 25 °C of 106 and 3.6 wt%, respectively [104]. Related PUU with more rigid hard blocks (MDI/hydrazine) were investigated by Petrik et al. [105]. Compared with the properties of the former PUU, a much smaller value was found for the PEO-based PUU PEO1040/MDI/hydrazine ( $G = 36$  wt%) whereas a very close swelling ( $G = 2.9$  wt%) was obtained for the polymer PPO1040/MDI/hydrazine. Worthy of mention, the hard block contents of all the former polymers were almost identical (between 32 and 35 wt%). Therefore, the strong decrease in polymer hydrophilicity observed for PEO/MDI/hydrazine had to be ascribed to the hard block chemical structure.

*3.1.1.1.2. Mixed soft blocks.* All the former studies have clearly shown the very different behaviors of the soft blocks PEO, PPO, PTMO, PEA, PCL and PBA. All these soft blocks but PEO, and to a slightest extent PEA, displayed a strong hydrophobic character responsible for very low water sorption and permeability. Highly contrasting with the former soft blocks, the highly hydrophilic PEO led to block copolymers with much higher water affinity. As could be expected from these strongly antagonistic features, several research groups then attempted to control the water permeability by combining the influence of hydrophilic and hydrophobic soft blocks in *mixed soft segment* PU and PUU.

Chen et al. first applied the former strategy to develop new membranes for potential application in reverse osmosis [104]. Their results on sorption of liquid water at ambient temperature in various PUU PEO1000/PPO1025/H12MDI/EDA with mixed soft segments with different contents in PEO and PPO and a constant hard block content (almost 32 wt%), revealed a *quasi-exponential* dependence of the sorption coefficient on the polymer PEO content  $W_{\text{PEO}}$  (expressed as the PEO mass fraction in the PUU). The water permeability at ambient temperature followed a more complex trend, first remaining fairly low for polymer PEO content less than 0.2, second increasing very sharply (+450%) with the polymer PEO content, then reaching an almost constant value for a higher enrichment in PEO corresponding to  $W_{\text{PEO}}$  values higher than 0.25. Very recently, Green et al. [106] reported the results of an interesting study on the hydration of PU closely related to the polymers investigated by Chen et al. [104]. The PU PEO2000/PPO2000/H12MDI/1,4-BD were made of two times longer soft block precursors, corresponding to a hard block content of 15 wt%. Applying surface plasmon resonance (SPR) to characterize the dynamics of polymer hydration, Green et al. showed that the angle shift measured by SPR varied linearly with the polymer swelling. Based on a simple calculation made from the compositions reported for the different PU and from data taken from an original plot, Fig. 3 shows that the SPR angle shift, and therefore the water sorption coefficient even if the original paper did not report the corresponding values, increases *exponentially* with the polymer PEO content. This trend is obviously in very good agreement with what was found from the sorption data reported by Chen et al. for related PUU. Investigating other related PUU PEO1450/PTMO2000/H12MDI/EDA with mixed PEO/PTMO soft blocks and a hard block content of 18 wt%, Yilgör and Yilgör recently described the same type of variations for water sorption and permeability as a function of the polymer PEO content. For these polymers also, the water sorption increased quasi-exponentially whereas the water permeability obeyed

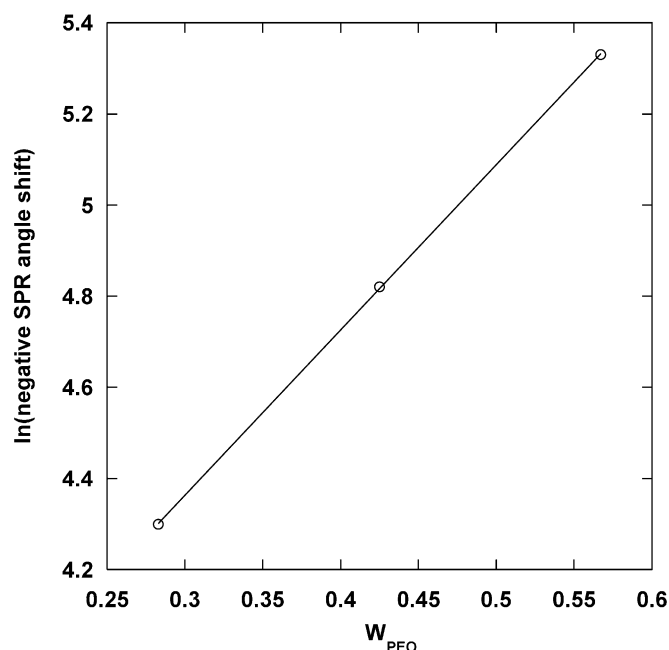


Fig. 3. Water sorption as characterized by SPR angle shift as a function of the polymer PEO content for three polyurethanes PEO2000/PPO2000/H12MDI/1,4-BD with mixed soft segments (from the SPR data and polymer compositions reported by Green et al. [106]).

a more complex sigmoid-type trend [19]. Analyzing the properties of very closely related PU (PEO1450/PTMO2000/H12MDI/1,4-BD) with a much higher hard block content ( $W_{HB} \approx 0.6$ ), Schneider et al. reported interesting results on liquid water sorption at 30 °C [107]. From their original tabulated data, Fig. 4 clearly shows that the water sorption varied *linearly* (rather than exponentially) with the polymer PEO content. This rather unexpected trend might be related to the particularly strong rigidity of these polymers containing almost 60 wt% of hard blocks.

Other interesting *mixed soft segments* to have been reported for tailoring the hydrophilic character of PU or PUU are triblocks PPO–PEO–PPO [7,105,108] and PEO–PPO–PEO [109]. Even if the related works focused on water sorption rather than permeability, they clearly brought an interesting insight into the interaction of water with complex macromolecular architectures involving polyblock soft segments, and provided first elements from which the polymer permeability could be anticipated.

As a basis for their future work on PU and PUU based on triblock soft segments, Petrik et al. first investigated water sorption by the soft segment precursors which were copolymers with a central segment of PEO and terminal blocks of PPO [63]. These authors clearly showed that water sorption in triblocks PPO–PEO–PPO did not simply result from additive contributions of the PEO and PPO segments. The water sorption coefficients found for the triblock copolymers were generally smaller than what would have been expected from an ideal behavior. Moreover, an analysis made on the basis of the Zimm and Lundberg theory [110,111] revealed that water clustering occurred in the triblocks PPO–PEO–PPO, to an extent increasing with the PPO content. For the derived PU PPO–PEO–PPO/MDI [7, 108] and PUU PPO–PEO–PPO/MDI/hydrazine [7,105], Petrik et al. also reported the highly non-ideal water sorption behavior that could not be predicted from the water sorption data corresponding to the

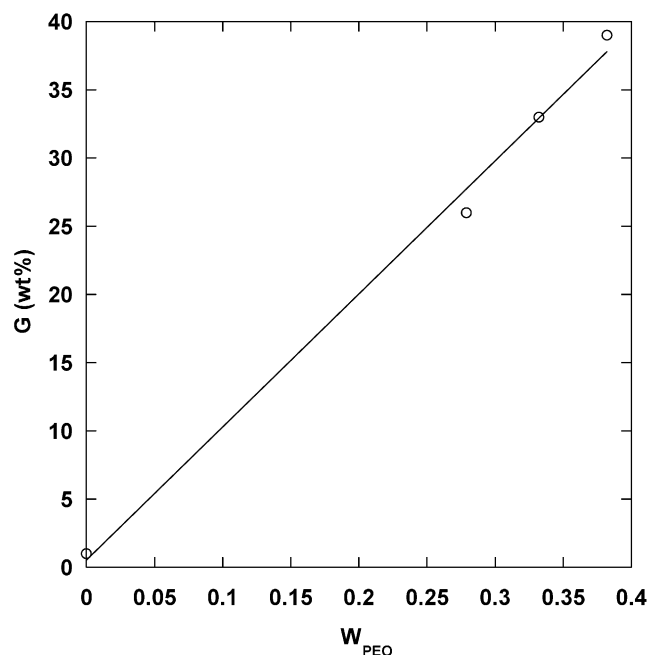


Fig. 4. Influence of the polymer PEO content on the water sorption coefficient at 30 °C for Polyurethanes PEO1450/PTMO2000/H12MDI/1,4-BD with mixed soft segments and a constant hard block content  $W_{HB} \approx 0.6$  (from the data reported by Schneider et al. [107]).

pure PEO and PPO oligomers. Moreover, water sorption in these complex polymer materials did not only depend on the PEO content but also on the total soft block length. That particular trend was ascribed to a shielding effect of the soft blocks by the hard blocks that could prevail for the shortest soft blocks. Analyzing the influence of mixed soft segments made of triblocks with a central segment of PPO and terminal segments of PEO (corresponding to the inverse configuration as compared to the triblocks used by Petrik et al. [7,105,108]) in PU PEO–PPO–PEO/MDI/1,4-BD, Schneider et al. also mentioned that the water sorption coefficient did not vary proportionally with the polymer PEO content [109]. In fact, for a constant hard segment content ( $W_{HB} \approx 40$  wt%), the ratio of moles of water absorbed to the number of ethylene oxide units decreased when the triblock PPO content increased, reflecting a strong detrimental effect of the PPO segment on the water sorption. A study of water sorption as a function of temperature also revealed that the PEO/PPO incompatibility could have an influence on water sorption. Obtaining homogeneous soft blocks by increasing temperature indeed induced a decrease in water sorption, the water repelling behavior of the PPO segment being more acute in these less segregated systems.

*3.1.1.1.2. Influence of the polymer soft block content ( $W_{SB}$ ).* Most of the published works on water sorption or permeation in PU with different soft block contents focused on polyetherurethanes. From a systematic analysis of the data reported in the literature, it seems an *exponential* variation in water sorption or permeability with the polymer soft block content generally characterizes these particular materials, with a strong increase for hydrophilic soft segments (e.g. PEO) and an opposite trend for hydrophobic soft blocks (e.g. PTMO and PPO). Related references on water permeation through polyesterurethanes are extremely scarce in the literature. Unlike polyetherurethanes, the polyesterurethanes



led to a *linear* (rather than exponential) variation in water sorption or permeability with the polymer soft block content.

Thereafter, the properties of PU with different soft segment contents are analyzed in details, starting with the most investigated polyetherurethane materials.

*3.1.1.1.2.1. Polyetherurethanes.* Typically, two methods have been privileged to vary the soft block content of PU and PUU in a systematic way:

- First method: Synthesis keeping the same hard block and using soft block precursors with different molecular weights (e.g. PEO with molecular weights between 500 and 2000)
- Second method: Synthesis using the same soft block and different reactant stoichiometries to allow a variation in hard and soft segment content.

Following the first method of varying the polymer soft block content, Petrik et al. reported liquid water sorption at 23 °C for five different polyetherurethanes obtained from MDI and PEO with molecular weights in the range 300–1600 [108]. For these rather simple materials that were obtained without any chain extender, the authors mentioned an inverse dependence of the swelling on the polymer hard block content (i.e.  $G \propto 1/W_{HB}$ ). However, a close examination of their data reveals an *exponential increase* in water sorption as a function of the polymer soft block content  $W_{SB}$  (Fig. 5). Extending their former work to related polyetherurethaneureas PEO(300 → 1600)/MDI/hydrazine with a constant stoichiometry (1/2/1), Petrik et al. then investigated water vapor sorption for a wide range of activities ( $a(\text{H}_2\text{O}) = 0.08 \rightarrow 0.97$ ) [105]. An analysis of their data at different water activities also shows that water sorption increases exponentially with the polymer soft block content for all the PUU materials but one

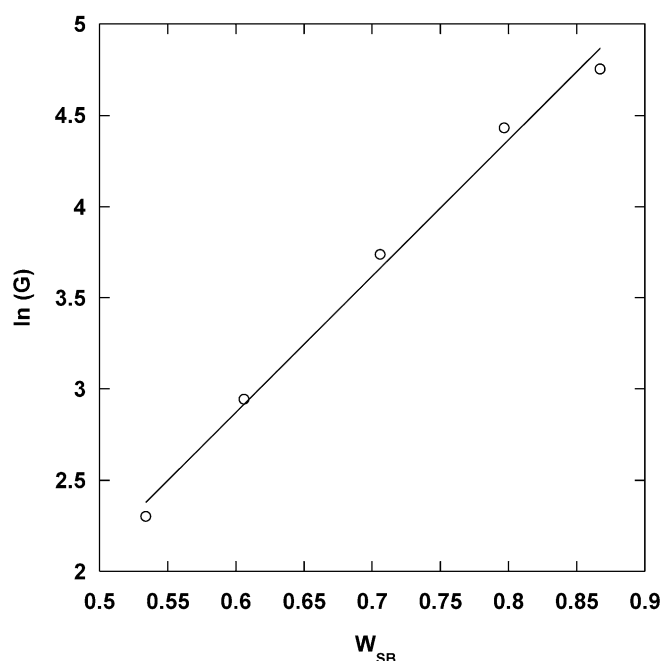


Fig. 5. Influence of the polymer soft block content on the liquid water sorption at 23 °C for polyetherurethanes with *hydrophilic* soft segments PEO (300 → 1600)/MDI with *hydrophobic* soft segments (from the data reported by Petrik et al. [108]).

corresponding to the most rigid polymer ( $W_{SB} = 0.353$ ). For this particularly rigid material, a strong relative decrease in water sorption (e.g. almost 50 and 40% for water activity of 0.54 and 0.75, respectively) is observed compared as what would be obtained from the exponential laws. However, the corresponding *absolute* decrease remains very low (typically less than 2 wt% for  $G$  values), water sorption in this particular material being very poor ( $G < 5.5$  wt%) over the whole activity range. In the same order of idea, Di Landro et al. investigated the properties of cross-linked polyetherurethanes synthesized from PPO telechelic oligomers with molecular weights of 400, 1200 and 2000 [112]. Unlike the polymers with highly *hydrophilic* PEO soft segments described by Petrik et al. the cross-linked PU PPO(400 → 2000)/1,4-TDI/TIPA (triisopropanol amine) contained *hydrophobic* soft segments. Even though the total water uptake in these polymer materials was of the same order of magnitude as that reported for the former PUU PEO(300 → 1600)/MDI/hydrazine (typically  $G < 6$  wt%), the water sorption behavior of these polyetherurethanes was remarkably different. Drawn from original tabulated data and calculated polymer soft block contents, Fig. 6 shows the *exponential decrease* in swelling as a function of the polymer soft block content. An interesting detailed analysis by FTIR spectrometry proved that the interaction between water and the urethane groups was the determining factor for water sorption in these polymers with hydrophobic soft blocks. Therefore, in that case where the soft blocks can be considered as water repellent, the hard blocks promote water sorption by allowing strong specific interactions between the penetrant and the polymer materials. To the best of our knowledge, data on solvent diffusion coefficients for block copolymers with increasing soft block sizes are extremely scarce in the literature. From the results reported by Di Landro et al. for the diffusion of water vapor through the polyetherurethanes PPO(400 → 2000)/1,4-TDI/TIPA (triisopropanol amine) [112], it is extremely

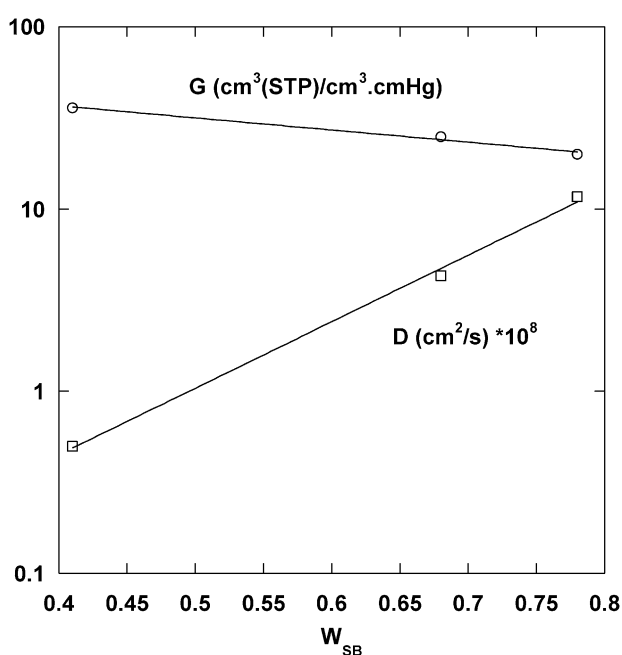


Fig. 6. Influence of the polymer soft block content on the water sorption and diffusion at 22 °C for polyetherurethanes PPO(400 → 2000)/1,4-TDI/TIPA with *hydrophobic* soft segments (from the data and polymer compositions reported by Di Landro et al. [112]).

interesting to note the *strong exponential increase* in the water diffusion coefficient with the polymer soft block content (Fig. 6). The water permeability (not shown on Fig. 6 owing to very different scales) also *increased* exponentially with the polymer soft block content, proving that diffusion prevailed over sorption to determine the overall water mass transfer behavior from the two former antagonistic trends.

The second method of varying the polymer soft block content (i.e. by keeping the soft block length constant and changing the reactant stoichiometry) was also chosen by a few researchers interested in correlating water sorption or permeation with the polyetherurethane structure.

From the data tabulated by Schneider et al. for the liquid water sorption at 30 °C in three polyetherurethaneureas PEO1450/H12MDI/1,4-BD with an hydrophilic soft block and different reactant stoichiometries, it can also be shown that the water sorption coefficient *increased exponentially* with the polymer soft block content ( $\ln(G \text{ wt}\%) = 1.30 + 5.22W_{\text{SB}}$  with a correlation coefficient  $r = 0.9957$ ). Despite a slight scattering in the experimental data, a strong *quasi-exponential decrease* in water permeability with the polymer soft block content, can be found for three polyetherurethanes PTMO2000/MDI/1,4-BD containing an hydrophobic PTMO soft segment [4] (Fig. 7). Here again, the polyetherurethanes led to an *exponential variation* in water sorption or permeability with  $W_{\text{SB}}$ , with a strong increase for hydrophilic soft segments and an opposite trend for hydrophobic soft blocks.

3.1.1.1.2.2. *Polyesterurethanes*. References on water permeation through polyesterurethanes with different polymer soft block contents are really scarce in the literature. Nevertheless, they are particularly valuable because they allow a first assessment on the differences induced by a polyester segment as compared with a polyether soft block.

Hsieh et al. reported water permeability data obtained with polyesterurethanes made from polyester

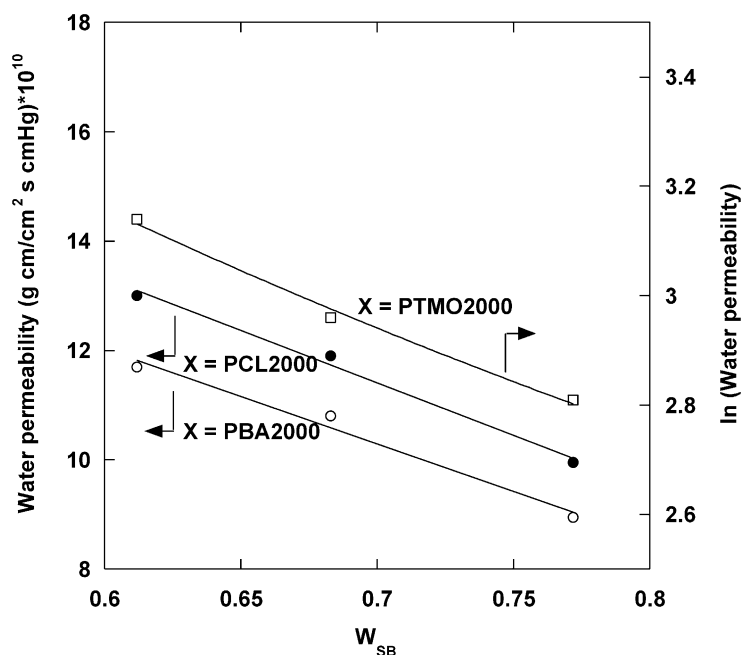


Fig. 7. Influence of the polymer soft block content on the water permeability at 25 °C for PU X/MDI/1,4-BD with hydrophobic soft segments X (polyether PTMO2000, and polyester PCL2000 and PBA2000) and different reactant stoichiometries ((1/2/1, 1/3/2, 1/4/3) (from the data tabulated by Hsieh et al. [4]).

soft segments PCL2000 or PBA2000, MDI and 1,4-BD in various proportions [4]. When plotted as a function of the polymer soft block content (Fig. 7), these data clearly show a *linear decrease* in the water permeability for these polymers with hydrophobic polyester soft blocks. Pissis et al. also mentioned the linear variation of the water sorption coefficient at 20 °C for other very closely related polyesterurethanes made from the polyester soft segment PEA2000, MDI and 1,4-BD using various reactant stoichiometries [113]. However, we believe the very low values obtained for the water sorption coefficients ( $G < 2$  wt%) and the slight scattering of the experimental data which can be expected for these difficult experiments should not allow any definite conclusion about the latter systems.

*3.1.1.1.3. Influence of the chemical nature of the hard block.* So far, the systematic investigation of the influence of the hard block chemical structure on water sorption or permeation has been reported very rarely.

Analyzing hydration of different PU and PUU made of mixed soft segments PEO/PTMO or PEO/PPO, H12MDI and either 1,4-BD or EDA, Green et al. showed by SPR that substitution of 1,4-BD for EDA led to a systematic decrease in the SPR angle shift of about  $-30\%$ , that would correspond to the same decrease in water sorption [106]. In the same order of idea, Kanapitsas et al. reported the results of their analysis of water sorption and diffusion for PU obtained from different diisocyanates (MDI or different isomers of H12MDI), 1,4-BD and polyether (PPO2000) or polyester (PBA2000) soft segments [101]. For all these polymers, the water sorption was very low (typically  $G < 3\%$ ) and the small differences observed for the different polymers could reasonably not be ascribed to any change in the hard block chemical structure. In the same way, the diffusion coefficients did not vary significantly with the hard block composition.

Another interesting study was that of Hsieh et al. on PU or PUU with hard blocks incorporating acid or amine *functional groups* from dimethylolpropionic acid (DMPA) or methyldiethanol amine (MDEA) chain extenders, respectively [100]. As a general trend, these functional groups led to a systematic increase in the polymer crystallinity and glass transition temperature that was partly ascribed to stronger intermolecular interactions between the soft (i.e. PTMO2000, PCL2000 or PBA2000) and hard (i.e. MDI/1,4-BD/DMPA or MDI/1,4-BD/MDEA) blocks. The net result was a sharp decrease in water permeability with the polymer functional group content. Moreover, the influence of amine groups was stronger than that of acid groups, most likely owing to stronger interactions of acid groups with water inducing higher water permeability.

*3.1.1.2. Pure organic species.* Permeation of pure organic species through PU and PUU has mainly been investigated in two different ways. As for the former studies on water permeation, the first way makes a systematic analysis of permeation of organic species using block copolymers with well defined variable structures, to understand the relationships between the material structure and its permeability. The second way extends the former analysis to systems differing in the chemical structure of the diffusive organic species, taking advantage of the versatility of the block copolymer–penetrant systems.

#### *3.1.1.2.1. Influence of polymer structural parameters*

*3.1.1.2.1.1. Influence of the soft or hard block content.* The influence of the polymer hard (or soft) block content on sorption or diffusion of pure organic species was mainly reported by Sreenivasan for polyetherurethanes PTMO1990/H12MDI/1,4-BD with various reactant stoichiometries [114–116]. In 1990, Sreenivasan clearly showed that toluene sorption at 25 °C in these polyetherurethanes could be

described by a rather complex law as a function of the polymer hard block content [114]:

$$G (\text{wt}\%) = A \frac{1 - W_{\text{HB}}}{\exp(W_{\text{HB}}) - 1} \quad (20)$$

Sreenivasan suggested an interesting potential application of that complex law which was the determination of the PU hard block content from a simple sorption measurement [114]. In fact for these systems, similarly as what had been obtained previously for water sorption in several polyetherurethanes, the polymer swelling in toluene can also be shown to vary exponentially with the polymer soft block content with a fairly good correlation coefficient ( $r = 0.998$ ):

$$\ln G (\text{wt}\%) = 1.464 + 5.037W_{\text{HB}} \quad (21)$$

Analyzing the data reported by Sreenivasan et al. for the sorption of six pure lipids in the same polyetherurethane [115], we also found a systematic exponential increase of the lipid sorption coefficient with the polymer soft block content, despite a slight scattering of the experimental data for the lipids with the lowest swelling values (e.g. triolein and cholesteryl acetate). As already mentioned, data on solvent diffusion coefficients through polymers with varying hard (or soft) block contents are extremely scarce in the literature and those reported by Sreenivasan et al. for the diffusion of six pure lipids in the former polyetherurethanes are therefore very valuable [115]. Fig. 8 shows the exponential variation of the diffusion coefficients of four lipids (stearic acid, cholesterol, cholesteryl acetate and triolein, taken as way of examples to avoid overlapping between different curves) as a function of the polymer soft block content. To the best of our knowledge, Figs. 6 and 8 both first describe the same type of exponential variation in the diffusion coefficients of water or organic species, respectively, for polyetherurethanes

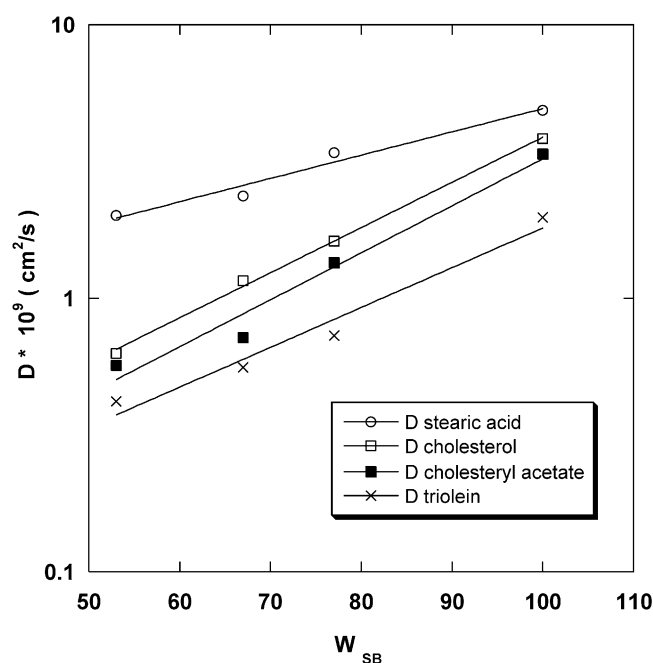


Fig. 8. Influence of the polymer soft block content on the diffusion coefficients of four lipids for permeation through polyetherurethanes PTMO1990/H12MDI/1,4-BD at 37 °C (from the data tabulated by Sreenivasan et al. [115]).

with different soft block contents. In another related paper, Sreenivasan extended his first study to the analysis of the influence of temperature on the lipid diffusion for the former systems [116]. The activation energies obtained for the lipid diffusion coefficients were strongly dependent on the polymer hard block content. The penetrant activation energy increased by a factor 2 for a hard block content increase from 23 to 66% for steric acid and cholesterol, whereas the increase was slightly lower (factor 1.65) for cholesteryl acetate and triolein in the same conditions.

Following a first paper that had shown the very interesting properties of polyetherurethanes as compared with PDMS for the removal of organic vapors from dry or humidified nitrogen by the vapor permeation membrane separation process [28], two contributions by Ponangi et al. tried to elucidate the key polymer structural parameters for the sorption [117] and diffusion [22] of organic species in commercial PTMO-based polyetherurethanes with various hard block contents. First, Ponangi and Pintauro showed that the sorption of three organic penetrants (i.e. benzene, hexane, tetrachloroethylene) was confined into the soft block domains [117]. After the systematic failure of the Flory–Huggins theory to account for the different sorption isotherms, Ponangi et al. made an interesting sorption analysis based on the Flory–Rhener model and nicely succeeded in relating the Flory–Rhener parameters to different polymer morphological parameters. The interaction parameter  $\chi$  was shown to increase linearly with the hydrogen bonding index (HBI) that is commonly used to assess PU phase separation by FTIR spectrometry. Moreover, the molar mass between cross-links  $M_c$  was quantitatively correlated to the HBI, the long spacing distance between the hard domains measured by small-angle X-ray scattering, and the polymer hard block volume fraction  $\phi_{HB}$ , based on a semi-empirical power-law. This very detailed sorption analysis then provided the basis for the related study of diffusion of benzene and tetrachloroethylene through the same polyetherurethanes recently reported by Ponangi et al. [22]. Using a free volume model modified from that of Fujita's to account for the hard block impermeability, the authors described the diffusion coefficients of both penetrants over a wide range of temperatures (30–60 °C) and penetrant concentrations. Even more interesting, the free volume parameters (i.e.  $A_d$ ,  $B_d$  and  $\beta$ ) were also correlated to the polymer morphology as reflected by the HBI.

*3.1.1.2.1.2. Influence of other polymer structural parameters.* In 1998, Desai et al. investigated the permeation of benzene, toluene and xylene through polyetherurethanes PTMO2000/2,6-TDI/TMP(1,1,1-trimethylolpropane) with *increasing degrees of cross-linking* [118]. The BTX sorption in these PU was very low (typically  $G < 2.5$  wt%). Using values for interaction parameters  $\chi$  estimated from the solubility parameters  $\delta_s$  and  $\delta_p$ , the Flory–Rhener theory led to values for molar mass between cross-links  $M_c$  which, unlike what would be theoretically expected, were fairly dependent on the penetrant. These values also strongly differed from those calculated from the molar composition of the polyetherurethanes, sometimes by one order of magnitude, clearly revealing the limitations of the Flory–Rhener theory for these particular systems. Average diffusion coefficients obtained from the initial slope  $s_0$  of the sorption curve in the transient regime were found to *increase* with the polymer cross-linking degree for benzene, toluene and xylene. The reason for that anomalous trend is not obvious but could be related to a slight deviation from the Fickian behavior (estimated in the usual way [44] by coefficients  $n$  in the range 0.58–0.69). However, such an increase in diffusion coefficients with cross-linking degree, though surprising, has also been reported for the permeation of binary mixtures for other PU [119] and also for modified polybutadiene membranes [120]. BTX permeabilities calculated from  $S$  and  $D$  values did not reveal any particular trend with the polymer or solvent structure.

Unlike a former related study by Kanapitsas et al. which had not shown any particular *influence of the hard block conformation* on water permeation for H12MDI isomers-based PU [101], Elabd et al.

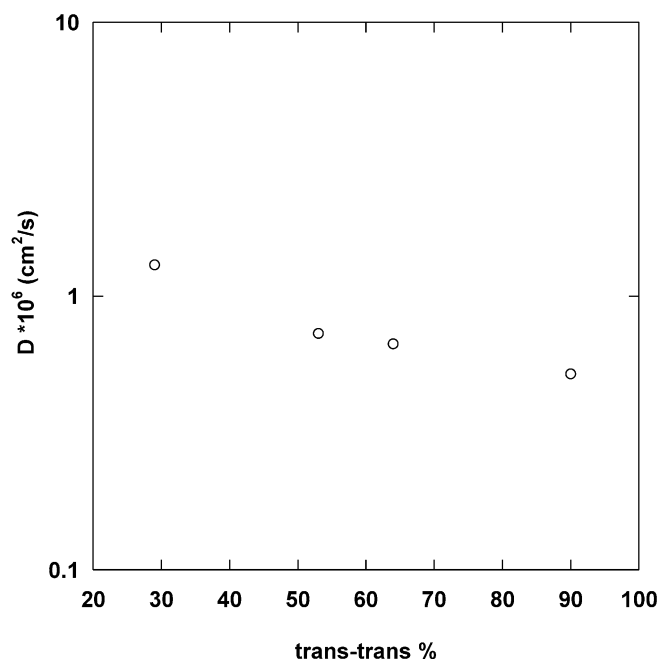


Fig. 9. Influence of the *trans–trans* percentage in H12MDI isomers on the acetonitrile diffusion coefficient for permeation through polyetherurethanes obtained from PTMO2000, different isomers of H12MDI and 1,4-BD as chain extender (reproduced with permission from Elabd et al. [121], copyright © 2002 Elsevier Science).

reported a slight decrease in the acetonitrile diffusion coefficient with the H12MDI *trans–trans* content for PU obtained from PTMO2000, different isomers of H12MDI and 1,4-BD as chain extender (Fig. 9) [121]. A DSC analysis showed a corresponding significant increase in the  $T_g$  of the polymer hard blocks with the H12MDI *trans–trans* percentage, whereas a constant soft block  $T_g$  was found for all the PU investigated. Therefore, it seems this slight decrease in acetonitrile diffusion coefficient could be ascribed to the more rigid character of the hard blocks with the highest H12MDI *trans–trans* contents, an additional FTIR study having also shown the interaction of acetonitrile with the polymer hard blocks for these particular systems.

*3.1.1.2.1.3. Influence of the polymer morphology.* A few other works also revealed the influence of polymer morphology on pure organic solvent permeation by introducing controlled changes in the material microstructure through various experimental conditions.

In 1993, Sreenivasan suggested diffusion of organic species through PU could be used as a probe to assess stretching-induced morphological changes in those block copolymers [122]. A systematic study of pure toluene diffusion through a polyetherurethane was undertaken after stretching to different degrees of elongation and relaxation of the polymer material. For elongations less than 100%, the toluene diffusion coefficient was unaffected by stretching. However, for elongations higher than a critical value of about 200%, the toluene diffusion coefficient sharply increased (+60%) to reach a constant value beyond 400% elongation. That increase in toluene diffusion was ascribed to polymer morphological changes induced by stretching, as shown by a wide-angle X-ray scattering analysis (i.e. dissociation of hydrogen bonds and decrease in the phase separation for degrees of elongation higher than the critical value of 200%).

Another way of affecting PU morphology is polymer swelling in very strong solvents leading to extreme sorption coefficient values, which then involve cooperative effects of the hard block domains. A good example is the work of Goydan et al. who reported particular mass uptake curves during the transient sorption regime of *o*-dichlorobenzene for extremely swollen membranes made of a commercial PU ( $G$  of about 230 wt%) [123]. Obtained for different film thicknesses, these curves presented two stages for the sorption process: a Fickian behavior for moderate solvent sorption, followed by a much slower solvent uptake for the highest swelling values. The second stage was ascribed to relaxation processes involving extensive changes in the hard block domains, therefore restricting the polymer mass uptake. Analyzing the sorption transient regime for several organic solvents (e.g. *n*-butanol, 1,4-dichlorobutane, toluene or chlorobenzene) at different temperatures for the commercial PU Vibrathane B600 (Uniroyal) (PPO/2,4-TDI/MOCA (4,4'-methylene-bis-(*o*-chloro-aniline))), Aminabhavi and Aithal also reported that, whereas the former solvents led to Fickian curves at low temperatures, they induced a two-stage sorption with relaxation phenomena at higher temperatures (typically between 70 and 90 °C) [124]. For that range of temperatures, very high swellings were obtained (usually  $G > 120$  wt%) and the sorption equilibrium could not be obtained even after a very long exposure, owing to the very slow relaxation of the PU material.

Another original way of controlling the polymer morphology was reported by Yokoyama and Furukawa who analyzed the properties of PU obtained from uni, bi and trimodal soft blocks PPO (with a constant number average molecular weight  $M_n = 1000$ ) that were prepared from blends of PPO ( $M_n = 200 \rightarrow 4000$ ), and hard blocks made from 2,4-TDI and 1,4-BD [8]. Systematic measurements of benzene sorption at 50 °C revealed that the soft block polydispersity ( $I = M_w/M_n$ ) had a strong influence on the PU swelling that doubled for an increase in polydispersity from 1 to 4. That effect was ascribed to the stronger contribution of the long chain soft blocks as compared with the shortest soft segments, which was also related to the  $T_g$  decrease observed with the broadening of the molecular weight distribution of the PPO soft blocks.

All the former examples clearly showed how a complex change in *polymer morphology* (induced by extensive stretching, strongly increasing temperature or solvent power, or using highly polydisperse soft blocks) can affect solvent sorption and permeation through PU block copolymers, far beyond their chemical composition.

**3.1.1.2.2. Influence of penetrant structural parameters.** The systematic analysis of sorption and diffusion of various solvents through PU has been the subject for several interesting investigations, which were reviewed by Aithal et al. up to the year 1990 with the merit of compiling a great number of permeation data in extensive tables [125]. More than being limited to a simple report of mass transfer data for block copolymer systems, a few of the published works attempted to elucidate the key parameters in terms of solvent molecular size, steric hindrance, branching effects or specific interactions. The different structure–property relationships then provided useful guidelines to forecast the permeability of related organic species through PU materials.

In 1969, Hopfenberg et al. reported the first systematic analysis of permeation of different alcohols through a polyesterurethane PBA2000/MDI/1,4-BD [126]. Using a set of linear alcohols (MeOH  $\rightarrow$  *n*-heptanol) and the four butanol isomers, this pioneer study clearly aimed at understanding the relationships between the alcohol molecular structure and its permeation features based on the solution-diffusion model. Linear and branched alcohols revealed very different behaviors which could not be unified by single relationships. For the set of linear alcohols, the swelling obtained for the pure liquids (i.e. at unit activity) increased with the alcohol molecular weight and were correlated qualitatively to the



difference in solubility parameters of the solvent and polymer. At the same time, the average diffusion coefficients decreased monotonically with an increase in alcohol chain length. The rather complex trend observed for permeability resulted from the antagonistic effects of the alcohol chain length on solubility and diffusivity. For the four butanol isomers, the polymer swelling depended on the alcohol degree of branching and increased in the order *tert*-BuOH < *sec*-BuOH < *iso*-BuOH < *n*-BuOH. Such a variation was ascribed to the sterical hindrance that would limit the hydrogen bonding interaction between the penetrant and the PU elastomer. An analysis of the butanol sorption in terms of solubility parameters failed, the solubility parameter being quasi-insensitive to the structural variation of the four butanol isomers. Moreover, the average diffusion coefficients and the permeability followed rather complex trends that could not be easily related to the molecular structure of the different alcohols. Also investigating the permeability of different alcohols (i.e. MeOH, EtOH, 1-PrOH, 2-PrOH, 1-BuOH, 2-methyl-1-propanol, 1-PentOH and 1-OctOH) through a commercial PU elastomer whose structure was unspecified, Hung and Autian mentioned that the swelling could not be simply related to the alcohol hydrophobic character [127]. However, quantitative structure–property relationships were obtained for the average diffusion coefficients for the linear alcohols. The diffusion coefficients were found to decrease linearly with the number of carbon atoms and also with the alcohol molar volume. For the linear alcohols, the activation energies obtained from diffusion experiments at different temperatures in the range 24–50 °C increased with the alcohol molecular weight (from 9.16 kcal/mol for MeOH to 12.1 kcal/mol for 1-OctOH). The average diffusion coefficients obtained for the branched alcohols (e.g. 2-PrOH, 2-methyl-1-propanol) were systematically lower than what would have been expected from the relationship obtained with the linear alcohols, reflecting the limitations of the first approaches for describing the behavior of sterically hindered molecules. In the same order of idea, Aithal and Aminabhavi reported a great deal of experimental data on sorption, diffusion and permeability of almost the same series of alcohols (i.e. MeOH, EtOH, 1-PrOH, 2-PrOH, 1-BuOH, 2-methyl-1-propanol, *iso*-PentOH) for the commercial PU Vibrathane B600 (Uniroyal) (PPO/2,4-TDI/MOCA) [128]. Even if the data were not correlated quantitatively to the alcohol molecular structure in that paper, they also clearly indicated the penalizing effect of molecular branching on the alcohol diffusivity and permeability. From experiments made at three different temperatures in the range 25–60 °C, the Arrhenius activation parameters  $E_D$  and  $E_P$  for diffusion and permeation, respectively, were also calculated. In good agreement with the free volume theories, both of these parameters increased with the alcohol molecular weight, therefore extending the conclusions formerly drawn by Hung and Autian for other related systems [127].

Systematic studies of sorption, diffusion and permeation using the commercial PU Vibrathane B600 (Uniroyal) were also reported by Aminabhavi et al. for series of organic solvents (i.e. aromatic solvents [129], aliphatic esters [130] and halogenated solvents [131]). Moreover, all of the experimental data were compiled and thoroughly discussed in the review by Aithal et al. [125]. Therefore, only the key results will be analyzed thereafter, stressing out the main observations about qualitative or quantitative structure/property relationships. For apolar aromatic solvents (i.e. benzene, toluene, *p*-xylene, mesitylene), the molar swelling  $G_m$  (expressed in mmoles of sorbed species/g of dry polymer membrane) decreased linearly with the solvent molecular weight [125,129]. However, such a QSPR could not be extended to aromatics bearing ether, nitro or halogenated groups [125]. The average diffusion coefficients of the former apolar aromatics also decreased with the solvent molecular weight, thus leading to a global decrease in permeability. The esters chosen by the same team using the same PU material included acetate esters obtained from simple linear alcohols (i.e. MeOH, EtOH, *n*-PrOH,

*n*-BuOH) and the branched *iso*-pentanol, and more complex esters (i.e. methyl acetoacetate, ethyl acetoacetate and methyl salicylate) for which no clear effect of molecular structure on permeation properties was observed [130]. However, for the former five esters, the *molar* swelling and diffusion coefficients decreased systematically from methyl acetate to *iso*-pentyl acetate, corresponding to a significant decrease in permeability (almost –70 and –80% for *n*-butyl acetate and *iso*-pentyl acetate, respectively, as compared to methyl acetate at 25 °C). Extending their former analysis to a series of halogenated solvents (1,2-dichloroethane, 1,2-dibromoethane, bromoform, trichloroethylene, carbon tetrachloride, 1,3-dibromopropane, tetrachloroethylene, 1,1,2,2-tetrachloroethane and 1,4-dichlorobutane), Aminabhavi and coworkers found high to extremely high sorption values, reflecting the very strong sensitivity of the polyetherurethane Vibrathane B600 to halogenated solvents [131]. As way of examples, sorption coefficients for 1,1,2,2-tetrachloroethane and bromoform reached extremely high values of 520 and 560%, respectively, at 25 °C. A systematic analysis of sorption based on the Flory–Rehner theory led to unrealistic values for the interaction parameter  $\chi$  (i.e. a negative value of –2.15 was even obtained for trichloroethylene) whereas the value for the molar mass between cross-links  $M_c$  strongly depended upon the nature of the halogenated solvent. Typically,  $M_c$  values varied in the range 300–5050, the extreme values being obtained for tetrachloroethylene and 1,1,2,2-tetrachloroethane. A detailed analysis of the sorption transient regime also showed a systematic deviation from the Fickian behavior. Such a deviation was ascribed to the contribution of the hard segments to the sorption phenomenon, inducing special relaxation effects and affecting the polymer ability to sorb organic species. Most likely owing to the particular role of the hard segments in these highly swollen systems, no correlation was found between the size and permeation features (i.e. sorption, diffusion coefficients, and permeability) of the different halogenated solvents. In the same order of idea, Schneider et al. investigated the swelling of the commercial PU Estane 2714 (Goodrich) (PTMO1000/MDI/1,4-BD with a soft block content  $W_{SB} = 0.52$ ) in non-hydrogen bonding solvents of increasing polarity [132]. Their main purpose was to use solvents capable of interacting with the soft segments and also with the PU hard blocks, depending on the solvent power of the penetrant (i.e. *n*-heptane, 1-chloroheptane, 1,7-dichloroheptane, 1,6-dichlorohexane, 1,5-dichloroheptane and *o*-dichlorobenzene). The sorption was strongly dependent on the solvent polarity. The *n*-heptane led to the lowest sorption coefficient ( $G = 6.5\%$ ) at 20 °C. Substituting heptane terminal hydrogen atoms for chlorine atoms gave a very significant increase in sorption (i.e.  $G = 41\%$  for 1-chloroheptane, and  $G = 78\%$  for 1,7-dichloroheptane at the same temperature). Moreover, the PU swelling in 1,6-dichlorohexane was 2.7 times higher than that observed in 1,7-dichloroheptane, to be compared to the swelling induced by the C6 aromatic species *o*-dichlorobenzene which exceeded 200%. Similarly as what would be described later for other related systems by Aminabhavi and coworkers [131], the values of molar mass between cross-links  $M_c$  calculated from the Flory–Rehner theory were strongly dependent on the nature of the halogenated solvent. Worthy of mention, they were found to increase very sharply with the solvent power of the interacting species (i.e.  $M_c = 250, 1120$  and  $3860$ , for *n*-heptane, 1,7-dichloroheptane and 1,6-dichlorohexane, respectively). To take into account the imperfectly segregated microstructure of the PU material, the model was modified to allow 30% mixing of hard blocks with the soft segments. The modified model enabled to calculate fairly realistic  $M_c$  values which were much less dependent on the nature of the interacting solvent for all the solvents inducing a moderate swelling (i.e.  $M_c$  in the range 840–1350, to be compared with the molecular weight of the PPO precursor  $M_{PPO} = 1000$ ). However, the solvents (e.g. 1,6-dichlorohexane and *o*-dichlorobenzene) that were responsible for the highest sorption values ( $G > 200\%$ ) still led to unrealistic  $M_c$  values ( $M_c > 3000$ , corresponding to almost three

times the molecular weight of the PTMO precursor). Such an obvious discrepancy was ascribed to the interaction of these highly solvating species with the PU hard segments. An analysis of the sorption transient regime also confirmed the very particular behavior of these extremely swollen systems with various anomalies that might be related to the solvent induced relaxation of the PU hard segments.

Based on a thermogravimetric analysis of sorption and diffusion of 12 miscellaneous solvents including alcohols, esters, aliphatic and aromatic species at various temperatures (in the range 30–50 °C) for a commercial PU (code number MP950 from Molded Products Co.) whose structure was unspecified, Hung reported new quantitative structure–property relationships which contributed to a further understanding of mass transfer through PU membranes [133]. The *molar swelling*  $G_m$  was found to decrease linearly with the solvent molecular weight for 10 (i.e. 80%) of the solvents investigated. However, the behavior of *n*-hexane (strong negative deviation) and that of chloro-benzene (strong positive deviation) were not accounted for by the former structure–property relationship. Moreover, the average diffusion coefficient was, in general, an inverse function of the solvent molar volume. However, two distinct relationships  $D$  versus  $V_m$  were obtained depending on the solvent molecular structure. The alcohols formed a first group with a slower diffusion rate as compared to the second group. The second group was composed of benzene, toluene, chloro-benzene, acetone, methyl acetate and ethyl acetate and revealed a specific relationship  $D$  versus  $V_m$ , despite a significant scattering of the experimental data which decreased with increasing temperature. Worthy of mention, although they have very close molar volumes, *n*-hexane diffused much faster than 1-hexanol and the ratio  $D_{n\text{-hexane}}/D_{1\text{-hexanol}}$  decreased with increasing temperature (from about 4 to 1.4 for temperatures in the range 30–50 °C). Another interesting analysis of mass transfer in terms of linear free energy relationships also revealed that the sorption and diffusion coefficients were correlated (i.e.  $\log D = a \log G_m + b$ ), with again a discrimination between HB-donor solvents and the less interactive solvents. All of these observations confirmed the role of H-bonding interactions in the mass transfer through PU materials that contain many H-bonding acceptor sites.

### 3.1.2. Permeability to vapor or liquid mixtures

The permeation of mixtures of vapors or liquids through polymeric materials is usually selective, meaning that the composition of the permeated species differs from that of the starting mixture. This very interesting effect of *selective permeability* could still lead to new applications for the separation of hydro-organic mixtures or purely organic mixtures.

**3.1.2.1. Hydro-organic mixtures.** Membrane separation processes have already offered new interesting alternatives to conventional separation processes (e.g. ternary distillation) for the treatment of hydro-organic mixtures [49,50,96]. Taking advantage of specific interactions between the polymeric membrane and the species to be extracted, pervaporation is particularly well suited to the treatment of azeotropic mixtures from which a minor component is to be removed [134]. The main industrial application of pervaporation concerns the dehydration of solvents that form azeotropic mixtures with water, using *hydrophilic* membranes (e.g. commercial polyvinyl alcohol membranes). A key example is the production of pure ethanol for the pharmaceutical industry by hybrid processes distillation/pervaporation [135] with important energy savings (from 30 to 60% as compared to the conventional azeotropic distillation) [136–139]. More recently, membrane separation processes have also been proposed for the removal of volatile organic compounds (VOCs) from water, air or gases, using *hydrophobic* membranes (e.g. commercial PDMS membranes) [47,140,141]. PDMS and related

membranes are usually very efficient for the recovery of weakly polar aprotic VOC with very high flux and selectivity, especially for halogenated solvents.

For a systematic analysis of selective permeability, PU and PUU present great advantages. The wide range of chemical structures available with such block copolymers indeed enables to *vary the balance of hydrophilic/hydrophobic character* by a proper choice of the soft and hard blocks. Depending on their chemical composition, PU and PUU can be either water or organic selective, covering a broad range of potential applications for the separation of hydro-organic mixtures.

*3.1.2.1.1. Water selective polyurethanes and polyurethaneureas.* Highly hydrophilic membranes are usually required for an efficient dehydration of organic solvents. PU and PUU are generally not hydrophilic enough to meet the requirements for this kind of applications. Therefore, the corresponding literature is very scarce but it revealed sometimes very special features that would have been rather difficult to anticipate.

A good example was reported by Huang et al. for the separation of ethanol aqueous mixtures using PU with poly(butadiene) hydrophobic soft blocks [119,142,143]. The water and ethanol permeability of asymmetric membranes made of PU PB/H12MDI/1,4-BD with various hard block contents were measured using a side-by-side diffusion testing apparatus [142]. In this experimental set-up, the membrane separated two cells containing pure water and ethanol, respectively, corresponding to time-dependent boundary conditions that makes a rigorous analysis of the mass transfer very difficult [44]. Nevertheless, as could be expected from their hydrophobic soft blocks, the membranes showed a higher permeability for ethanol than for water, with a permeability ratio that decreased as the polymer content in hydrophobic soft blocks decreased. Moreover, the water and ethanol fluxes were found to increase with the polymer hard block content, similarly as what had been described for water sorption or permeation through PU with hydrophobic soft segments [4,112]. Considering the hydrophobic character of the polybutadiene soft blocks and what had been obtained from the former diffusion analysis [142], the properties of the same membranes for the pervaporation of ethanol aqueous mixtures ( $C_{\text{EtOH}} = 90 \text{ wt\%}$ ) were rather unexpected [119]. The pervaporation experiments indeed revealed that the PU membranes were water selective (rather than ethanol selective). This inversion of pervaporation selectivity, as compared with the ideal selectivity obtained from the permeabilities of pure ethanol and water, was ascribed to the hydrophilization of the hydrophobic soft blocks by the sorption of ethanol. Such a hydrophilization would facilitate water sorption and diffusion through the PU membranes, in a similar way as what had been described by Ruckenstein and Sun for the anomalous sorption and pervaporation of hydro-organic mixtures by poly(vinyl acetal) membranes [144]. However, we believe a more rigorous analysis of this phenomenon would require the corresponding sorption data which were not available. Moreover, in the same conditions, the pervaporation flux increased quasi-exponentially with the polymer hard block content (that we calculated from the polymer chemical composition) whereas the selectivity remained quasi-constant. Cross-linking of the polybutadiene soft blocks with increasing amounts of divinylbenzene had almost no influence on the pervaporation selectivity whereas an optimum was obtained for the total flux value. An analysis by FTIR revealed that the soft block cross-linking hindered the hard block aggregation, therefore giving a looser polymer network for the low DVB contents, which might be the reason for the optimum of the pervaporation flux [119].

De Pinho et al. also described the properties of various complex PU and PUU with hydrophobic polyether soft blocks for the separation of ethanol–water mixtures [145]. The polymers were synthesized from bi (or tri)-functional isocyanate-terminated prepolymers, which were first obtained by reacting 2,4-TDI with a PPO diol ( $M_n = 400$ ) (functionality  $f = 2$ ) or 1,1,1-tri(hydroxymethyl) propane

( $f = 3$ ). The prepolymers were then either cross-linked by simple water addition or chain-extended with a polyester diol ( $M_n = 2000$ ). Asymmetric membranes were obtained in various casting conditions and systematically tested for the pervaporation of ethanol aqueous mixtures. The chemical composition of the different polymers was not fully described, therefore limiting a systematic analysis in terms of structure/property relationship. However, most of the membranes were very poorly permeable even at a temperature as high as 70 °C. Unlike what could have been expected a priori from their hydrophobic soft segments, the PU and PUU were strongly selective towards water ( $C'_{H_2O} = 92\text{--}98\%$  for a water content in the feed mixture of about 30 wt%). The very high number of HB-acceptors (i.e. urethane or urea groups), that was obtained for these polymeric networks containing very short soft segments, is most likely responsible for the water selective transfer. In good agreement with the former assumption, increasing the number of HB-acceptors by using trifunctional prepolymers further improved the selectivity towards water, as compared to that obtained with bifunctional prepolymers. Moreover, copolymerization with a high molecular weight polyester diol had a positive effect on the pervaporation flux that still remained fairly low ( $< 0.5 \text{ kg/h m}^2$ ).

In a related order of idea, Schauer et al. discussed about the use of short PPO diols in PU formulations for membrane applications [146]. To improve the very poor mechanical properties of PU made from high molecular weight soft blocks PPO4800 and PB3000, a short PPO diol ( $M_n = 420$ ) was incorporated in mixed soft segments PPO4800/PPO420 or PB3000/PPO420. If the mixed soft segments contained 10–20 wt% of PPO420, the PU were strong elastomers that could withstand the pervaporation conditions. When the soft segment content in PPO420 was higher than 50 wt%, glassy PU membranes were obtained. The membranes were evaluated for the separation of hydro-organic mixtures (i.e. H<sub>2</sub>O/EtOH and H<sub>2</sub>O/dioxane) by pervaporation at 25 °C. The membrane properties strongly depended upon the physical state of the PU, and therefore upon the mixed soft segment content in PPO420. As a way of example, for the separation of an ethanol aqueous mixture containing about 50 wt% water at 25 °C, the glassy PU PPO4800/PPO420(10/90 wt%)/2,4-TDI was extremely poorly permeable ( $J < 30 \text{ g/h m}^2$ , for an unspecified membrane thickness) and fairly selective towards the smallest penetrant (i.e. corresponding to a pervaporate enrichment in water:  $C'_{H_2O} \approx 90 \text{ wt}\%$ ). Such properties are typical for diffusion-controlled pervaporation using glassy hard materials. The elastomer PU PPO4800/PPO420 (80/20 wt%)/2,4-TDI displayed a completely opposite behavior with a much higher permeability ( $J \approx 200 \text{ g/h m}^2$ , for the same unspecified membrane thickness) and an inversion of selectivity, the membrane becoming mildly selective towards ethanol ( $C'_{EtOH} = 64 \text{ wt}\%$ , nevertheless less than what would be obtained from a single distillation stage  $C_{EtOH}^{LVE} = 80 \text{ wt}\%$  calculated from LVE data reported in Ref. [147]).

Ahsan et al. also described the separation of ethanol aqueous mixtures using cationic PU with hydrophobic PPO soft blocks (PPO1025/MDI/1,4-BD + TMPI (3-trimethylammonium-(1,2-propane diol) iodide)) [148]. The influence of the ionic content in the hard blocks was systematically assessed for the sorption and pervaporation of ethanol aqueous mixtures over the whole range of compositions at 25 °C. When the ionic content in the hard blocks increased from 0 to 50%, it was observed a sharp increase in pure water swelling (1.2 → 17.6 wt%) and a significant decrease in pure ethanol sorption (30 → 18 wt%), reflecting the increasing hydrophilic character of the cationic PU. The swelling behavior of these cationic polymers in various ethanol aqueous mixtures was fairly complex and varied in between these two extremes. In pervaporation, increasing the ionic content in the hard blocks led to an increase in *both* flux and selectivity, similarly as what had been pointed out already by Ping et al. [149] for the pervaporation of water/ethanol mixtures using different ionic polymers

derived from PE-*graft*-Poly(acrylic acid). That unusual trend was particularly interesting because it overcame the duality flux/selectivity which generally imposes a flux increase be obtained in detriment of selectivity in pervaporation. For a high ionic content (typically 50 %) and despite the hydrophobic character of their soft blocks, the PU membranes were highly selective towards water. As a way of example, a water feed content of 25 wt% led to pervaporate samples containing more than 95 wt% water and a total permeability of about  $7.2 \text{ kg } \mu\text{m/h m}^2$ .

*3.1.2.1.2. Alcohol selective polyurethanes and polyurethaneureas.* PDMS membranes, which are commercially available [140,150], are very efficient for the recovery of VOC from water or air by membrane separation processes. However, the extraction of protic organic species (e.g. alcohols) cannot be easily achieved by PDMS membranes because this highly hydrophobic material generally displays a poor affinity towards such highly polar species [24]. Because they are much more versatile materials which can be tailor-made to find a good balance of hydrophilic/hydrophobic character by a proper choice of their building blocks, PU and PUU could offer new alternatives to PDMS for the recovery of protic species from aqueous solutions.

Based on the former strategy, several papers have reported the properties of new PU with *hydrophobic* soft blocks for the extraction of alcohols from water by membrane separation processes. The hydrophobic soft blocks were made of polyethers (e.g. PPO, PTMO, more complex poly(alkylene oxides), etc.), polyester (e.g. PCL) or mixed soft segments. Almost half of the corresponding literature reported on the recovery of ethanol from aqueous mixtures [5,146,151,152], the remaining papers having been devoted to other challenging separations (e.g. extraction of butanols [24] or phenols [20,27,153,154]). (*Note:* Owing to their very particular features, PU or PUU with PDMS soft segments are not accounted for in this part and will be the subject of a specific sub-chapter on block copolymers containing PDMS segments.)

*3.1.2.1.2.1. Polyurethanes for the recovery of ethanol.* Ethanol is a low molecular weight alcohol with high polarity. Its extraction from dilute aqueous solutions (e.g. fermentation broth) is certainly one of the most challenging problems encountered by membrane separation processes [140,155]. Extending their former work on PU and PUU with very short hydrophobic soft blocks that were selective towards water during the pervaporation of ethanol aqueous mixtures [145], De Pinho et al. reported the properties of new PUU with much longer hydrophobic segments in order to increase the polymer hydrophobicity [5,151]. PUU cross-linked networks were obtained by reacting water with polyether triisocyanate prepolymers of increasing molecular weights ( $M_n = 3000, 4000, 6000$ ). Most likely owing to a confidentiality agreement, the chemical structure of the commercial polyether prepolymers was not fully described. The selectivity of the corresponding membranes did not depend upon the polymer structure for the pervaporation of ethanol aqueous mixture (EtOH: 50 wt%) at temperatures varying between 30 and 60 °C. Whatever the temperature, the selectivity remained constant and very low (pervaporate ethanol content: 58 wt%). However, the pervaporation fluxes increased sharply with the molecular weight of the prepolymer precursor. As a way of example, at 30 °C, the pervaporation flux increased by a factor 2.5 for a prepolymer molecular weight increasing from 3000 to 6000. More surprisingly, the ethanol activation energy did not vary with the molar mass between cross-links ( $E_a \approx 8 \text{ kcal/mol}$ ). The former study was then extended to the sorption of aqueous solutions of different alcohols (i.e. *n*-propanol, *n*-butanol and *n*-pentanol) with the same alcohol content (i.e. 2 wt%), revealing an increased affinity of these membranes in the order: ethanol < *n*-propanol < *n*-butanol < *n*-pentanol [151]. However, we believe a better analysis would certainly require systematic experiments carried out at the same alcohol activity (rather than concentration owing to the strong dependence of the alcohol activity

coefficient on its molecular structure). The use of *mixed soft segments* has also been proposed for a better control of the hydrophilic/hydrophobic balance for the extraction of ethanol from aqueous mixtures. As discussed thoroughly in a former part (Section 3.1.2.1.1 Water selective PU and PUU), Schauer et al. nicely showed how mixed soft segments could be used to design PU that were selective towards either water or ethanol [146]. As a way of example, the elastomer PU PPO4800/PPO420/2,4-TDI containing 20 wt% PPO420 in the mixed soft segment displayed a moderate flux ( $J \approx 200 \text{ g/h m}^2$ , for an unspecified membrane thickness) and a rather low selectivity towards ethanol ( $C'_{\text{EtOH}} = 64 \text{ wt\%}$  for a feed mixture containing 50 wt% ethanol) at 25 °C. Zhao and De Pinho also described PUU networks with mixed soft segments PPO1000/PB2800 [152]. The cross-linked materials were obtained from the reaction of a commercial tri-isocyanate prepolymer PPO1000/2,4-TDI (Hoechst), a polybutadiene diol PB2800 and water. The influence of the polymer PB content was analyzed for the pervaporation of ethanol aqueous mixtures at 25 °C. For aqueous mixtures containing 10 wt% of ethanol, increasing the polymer content in polybutadiene from 44 to 68 wt% led to a significant increase in ethanol selectivity ( $C'_{\text{EtOH}} = 17$  and 29 wt%, respectively) in detriment of the pervaporation flux that dropped by a factor of about 5. However, the pervaporation of a dilute ethanol aqueous solution ( $C_{\text{EtOH}} = 1 \text{ wt\%}$ , as more relevant to the recovery of ethanol from fermentation broths) showed much decreased membrane performances with slightly lower pervaporation fluxes (not exceeding  $200 \text{ g/h m}^2$  for a membrane thickness of 50  $\mu\text{m}$ ) and very low selectivities (pervaporate ethanol content less than 5.5 wt%).

**3.1.2.1.2.2. Polyurethanes for the recovery of butanols.** The selective extraction of the butanol isomers from water is also another challenging interesting separation. This has many potential applications, the most important of which is probably the continuous removal of the alcohol produced by the acetone–butanol–ethanol (ABE) fermentation. This fermentation process could lead to the sustainable production of alternative fuels if it were not strongly penalized by the fermentation inhibition which occurs at relatively low alcohol concentration (typically about 5 wt%, depending on the fermentation process) [156,157]. Pervaporation has been considered as a promising technique for the recovery of butanols from fermentation broths [156–158]. Moreover, Groot et al. have shown that a very significant increase in productivity (+65–70%) was obtained when pervaporation was coupled with a fermentor for the continuous extraction of the inhibitory products using PDMS membranes [159,160]. Bøddeker et al. compared PDMS with a polyetherurethane (unspecified composition) and a poly-ether-block-amide (PEBAX<sup>®</sup> 40, trade name of Elf Atochem now Atofina) for the recovery of the butanol isomers from dilute aqueous solutions ( $C_{\text{alcohol}} = 1 \text{ wt\%}$ ) [24]. The pervaporation flux was strongly dependent on the type of membrane with a fair advantage for the PEBAX<sup>®</sup> 40 (total flux usually higher than  $0.2 \text{ kg/h m}^2$  for a membrane thickness of 50  $\mu\text{m}$  at 50 °C) (Table 1). Compared to PDMS, the polyetherurethane led to total fluxes that were higher for *n*-BuOH and *iso*-BuOH (+26 and +12%, respectively) and significantly decreased for *sec*-BuOH and *tert*-BuOH (–30 and –12%, respectively). In the same conditions, the selectivity increased in the following order: PU < PEBA < PDMS with rather poor selectivities for the polyetherurethane membrane ( $C'_{\text{alcohol}} < 10 \text{ wt\%}$ ). The highest values of the productivity factor  $J(\beta - 1)$  were systematically obtained with the PEBA membrane, reflecting the best compromise obtained with this particular polymer whatever the butanol isomer. For a given polymer, the productivity factor increased with the alcohol polarity (i.e. in the order: *tert*-BuOH < *sec*-BuOH < *iso*-BuOH < *n*-BuOH) whereas the selectivity followed an opposite trend.

**3.1.2.1.2.3. Polyurethanes for the recovery of phenols.** PU membranes have also been reported for the extraction of phenols from water, separation that is required for the protection of environment in several industrial processes (e.g. production of phenolic resins, etc.) [20,27,153,154]. Rzeszutek and Chow

Table 1

Total flux, selectivity and productivity factor for the extraction of the four butanol isomers from dilute aqueous solutions ( $C_{\text{alcohol}} = 1 \text{ wt\%}$ ) by pervaporation at 50 °C using different membranes (thickness = 50  $\mu\text{m}$ )

Alcohol	Membrane	$J$ (g/h m <sup>2</sup> )	$C'_{\text{alcohol}}$ (wt%)	$J(\beta - 1)$ (g/h m <sup>2</sup> )
<i>n</i> -BuOH	PEBA	278	20	5282
	PDMS	70	37	2520
	PU	88	9	704
<i>iso</i> -BuOH	PEBA	242	19	4356
	PDMS	73	29	2044
	PU	82	8	574
<i>sec</i> -BuOH	PEBA	216	10	1944
	PDMS	64	22	1344
	PU	45	3	90
<i>tert</i> -BuOH	PEBA	199	6	995
	PDMS	60	14	780
	PU	53	2	53

From the data reported by Bøddeker et al. [24].

described the extraction of a wide set of phenolic compounds by simple sorption in two commercial PU membranes (Stevens Elastomerics/Urethane Products, Northampton, MA) [154]. The PU differed in the chemical nature of their soft blocks (i.e. polyether and polyester) and their exact compositions were not specified. Even if the corresponding permeabilities were not reported, the authors clearly showed that these polymeric membranes could be used for the selective removal of phenolic contaminants from waste water. Moreover, the polyetherurethane membrane showed a higher affinity towards phenolic species than the polyesterurethane membrane. As a way of example, at 25 °C, the polyetherurethane was typically two times more efficient than the polyesterurethane for the recovery of the bromo(or chloro)phenol isomers from dilute aqueous solutions ( $C_{\text{phenol}} = 2 \times 10^{-4} \text{ M}$ ). A very nice systematic investigation of a wide set of PU with evolutive structures was also reported by Hoshi et al. in a series of three papers on the separation of dilute phenol aqueous solutions by pervaporation [20,27,153]. In the first paper, the properties of a cross-linked PU PTMO2900/HMDI were analyzed for the sorption, diffusion and permeation of aqueous solutions containing up to 7 wt% phenol at 60 °C [153]. The polymer swelling increased dramatically with the phenol concentration from almost 1 wt% for pure water to more than 200 wt% for the highest phenol concentration of the feed mixture. At the same time, the phenol content of the sorbed liquid mixture increased up to almost 80 wt%. In the same conditions, the pervaporation flux reached a maximum value of 930 g/h m<sup>2</sup> (for an unspecified membrane thickness) whereas the phenol content in pervaporate increased up to 65 wt%, corresponding to a high permselectivity. Nevertheless, the pervaporation selectivity was always less than the sorption selectivity. Such a difference was ascribed to a diffusion differential effect, the lowest diffusion coefficient of phenol playing against its selective mass transfer. As expected from the Long's model ( $D = D_0 \exp(\gamma C_s)$ ), the difference in diffusion coefficients decreased as the phenol content in the feed mixture increased, minimizing the influence of the diffusion selectivity on the pervaporation selectivity for phenol concentrations higher than 3 wt%. The influence of the soft blocks and hard blocks was then reported in a second paper by Hoshi et al. [27]. PU PTMO1000/Y with different hard blocks Y were obtained from



various diisocyanates (i.e. HMDI, 2,4-TDI, MDI, IPDI (isophoronediiisocyanate) and H12MDI). The results obtained from the sorption and pervaporation of 1 wt% phenol aqueous solutions at 60 °C showed very little influence of the *hard block chemical nature* on the permeation properties. The same conclusion had also been made by Ohst et al. for the separation of toluene/cyclohexane mixtures through PU which were obtained from various diisocyanates [6]. However, in the same conditions, the *chemical nature of the soft block* had a strong influence on the permselectivity while it did not affect the pervaporation flux significantly. As a way of example, the pervaporation flux of the polyetherurethane PTMO1000/HMDI was slightly inferior (−13%) to that of the polyesterurethane PCL1000/HMDI. Nevertheless, the selectivity provided by the polyether soft block ( $C'_{\text{phenol}} = 27$  wt%) was much higher than that obtained with the polyester soft block ( $C'_{\text{phenol}} = 15$  wt%). This observation is in good agreement with the former conclusions of Rzeszutek and Chow who had reported the better affinity of a polyetherurethane as compared to a polyesterurethane for the extraction of various phenolic species from water [154]. The influence of the *polymer soft block content* on the pervaporation flux depended upon the chemical nature of the soft block. An analysis, made on the basis of soft block content values calculated from the polymer compositions reported by Hoshi et al. [27], showed that the total flux increased quasi-exponentially for the polyetherurethanes whereas a linear increase was obtained for the polyesterurethanes as a function of the soft block content  $W_{\text{SB}}$  (Fig. 10). Note that we had also found the same type of exponential or linear variations for different systems involving polyetherurethanes or polyesterurethanes, respectively, and pure water (Section 3.1.1.1.2) or pure organic species (Section 3.1.1.2.1). The originality of Fig. 10 is to show the same type of laws for the pervaporation of hydro-organic mixtures rather than pure compounds. The soft block content had also a strong influence on the

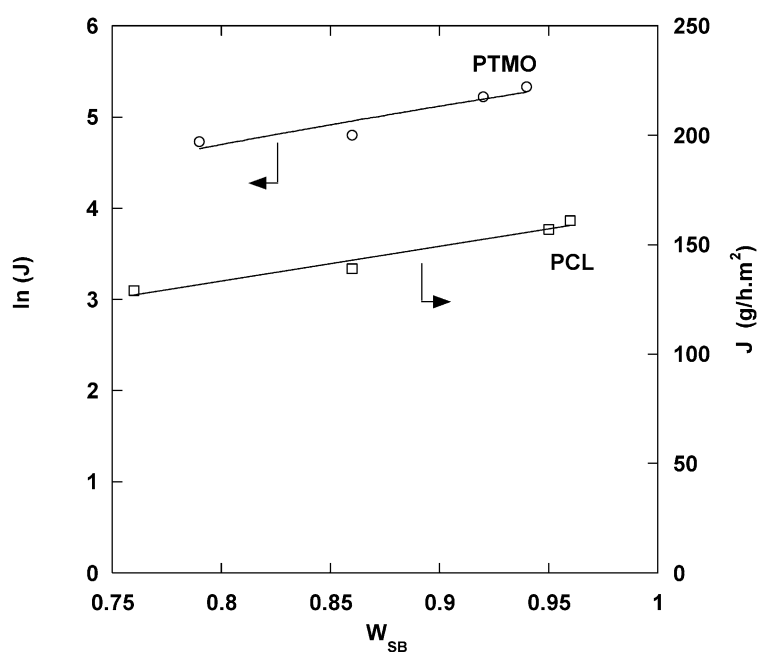


Fig. 10. Influence of the polymer soft block content on the total flux for the pervaporation of 1 wt% phenol aqueous mixture at 60 °C using polyetherurethanes PTMO/HMDI and polyesterurethanes PCL/HMDI (from the permeation data and polymer compositions reported by Hoshi et al. [27]).

pervaporation selectivity that increased with  $W_{SB}$ . As way of examples, for the pervaporation of 1 wt% phenol aqueous solutions at 60 °C, the polyetherurethanes PTMO1000/HMDI ( $W_{SB} = 0.86$ ) and PTMO2900/HMDI ( $W_{SB} = 0.94$ ) led to pervaporate phenol contents  $C'_{phenol}$  of 27 and 44 wt%, respectively. In the same conditions, the polyesterurethanes PCL1000/HMDI ( $W_{SB} = 0.86$ ) and PCL3000/HMDI ( $W_{SB} = 0.95$ ) gave  $C'_{phenol}$  values of 15 and 21 wt%, respectively. Therefore, the pervaporation selectivity was less sensitive to the soft block molecular weight of polyesterurethanes than that of polyetherurethanes. The third paper in the corresponding series by Hoshi et al. reported on the effect of the number of methylene groups in poly(alkylene oxide) soft blocks X on the properties of the corresponding PU X/HMDI [20]. The poly(alkylene oxides) investigated were PEO, PTMO, PHMO (poly(hexamethylene oxide)), POMO (poly(octamethylene oxide)) and PDMO (poly(decamethylene oxide)) corresponding to the number of methylene groups of 2, 4, 6, 8 and 10, respectively. The molecular weight of the different soft blocks was kept nearly constant (ca.  $M_n = 4500$ ). The sorption and pervaporation experiments were carried out in the same conditions as in the former works (i.e. with 1 wt% phenol aqueous mixture at 60 °C). The total sorption was very high ( $G \approx 90$  wt%) and independent of the number of methylene groups in the poly(alkylene oxide) soft block. The phenol content in the sorbed mixture increased from 42 to 71 wt% as the number of methylene groups increased from 2 to 10. This trend was expected from an improved hydrophobicity of the soft blocks enriched in methylene groups. In the same conditions, the pervaporate phenol content slightly increased from 25 to 36 wt%. The pervaporation selectivity was much less (almost –50%) than the sorption selectivity, reflecting the crucial role of diffusion selectivity that was favorable to the water (rather than phenol) mass transfer. The total pervaporation flux ( $J \approx 225$  g/h m<sup>2</sup> for an unspecified membrane thickness in the range 60–90 μm) did not vary significantly with the hydrophobicity of the PU soft block and resulted from a compromise between a slight increase in the phenol partial flux and a corresponding decrease in the water partial flux.

*3.1.2.2. Purely organic mixtures.* Owing to a limited withstanding of PU or PUU materials in strongly polar organic mixtures, the great majority of the works on permeation of purely organic mixtures through these block copolymers focused on the *separation of aromatics from alkanes*. A key example is the separation of benzene/cyclohexane mixtures which remains one of the most challenging separation problems for the petrochemical industry. Cyclohexane is obtained by catalytic hydrogenation of benzene which has to be eventually removed for pure cyclohexane recovery. The problem is that benzene and cyclohexane form close boiling point mixtures over the entire composition range, with a LVE leading to a quasi-nil enrichment in benzene or cyclohexane in the vapor phase. As very well described in a recent review of Garcia Villaluenga and Tabe-Mohammadi [161], membrane separation processes (e.g. pervaporation, vapor permeation or perstraction) could be very good alternatives to conventional separation processes (mainly azeotropic or extractive distillation) which are highly energy-intensive for this kind of separation. As early as in the 1970s, the Bayer Company had already understood the very high potential offered by PU materials for this kind of separation [162]. Even if the formulations were highly complex and no clear relationships between the membrane structure and properties could be drawn, the corresponding patent clearly showed the interesting features of several complex PU formulations for the separation of benzene from cyclohexane [162]. Later on, the Exxon Research and Engineering Company also showed its strong interest in such block copolymers and patented a great deal of PU and PUU membranes for the separation of aromatics from alkanes [32,33,163–167]. Researchers of this company even described in their patents a few qualitative structure–property relationships that

were really interesting and certainly helped the rational design of new PU membranes with improved properties [33,164,167]. In addition to that strong industrial interest, the scientific literature also confirmed the unique feature of several PU and PU materials that displayed outstanding flux and selectivity for the separation of aromatics from alkanes. In the following, the key results are analyzed in terms of structure–property relationships to reveal some very interesting trends for both an improved fundamental understanding and obvious industrial potential applications.

#### 3.1.2.2.1. Influence of the chemical nature of the soft block

3.1.2.2.1.1. *Simple soft blocks.* The nature of the soft block plays a great role on the overall membrane performances as shown by both industrial and academic researchers for the separation of aromatics from alkanes [6,38,80,164,167,168]. A general trend is the much better selectivity of polyester soft blocks as compared with polyether soft blocks. As a result, most of the patented PU and PUU membranes involved polyester rather than polyether soft blocks, with an obvious preference for poly(ethylene adipate)-based formulations [32,163,165,166]. In a patent assigned to the Exxon and Research Engineering Company, Schucker reported experimental flux and selectivity data for the perstraction of a complex model feed for heavy cat naphtha (boiling range: 149–221 °C) using PUU membranes with different types of soft blocks (i.e. polyester: PEA, and polyether: PPO, PTMO). Even if the polymers also slightly differed in their hard blocks (e.g. TDI/ODA and MDI/MOCA) therefore limiting the bearing of the data analysis, the permeability sharply increased in the order  $PEA \ll PTMO < PPO$  for a constant soft block molecular weight ( $M_n \approx 1000$ ) while the selectivity towards the aromatics followed an opposite trend with very poor values for the polyether soft blocks PTMO and PPO [167]. At the same time, Ohst et al. working at the Bayer Company reported the results of the first systematic investigation of PU membranes for the separation of toluene/cyclohexane mixtures by pervaporation [6]. After having shown that the diisocyanate (e.g. MDI or TDI) used for the PU synthesis had almost no influence on the membrane permselective properties, the strong influence of the soft block nature was analyzed by comparing the properties of the polyetherurethane PTMO700/MDI/1,4-BD and the polyesterurethane PBA700/TDI/1,4-BD. As a way of example, the pervaporation of a mixture toluene/cyclohexane (50/50 wt%) at 30 °C led to total permeability values of 90 and 13 kg  $\mu\text{m}/\text{h m}^2$  for the polyetherurethane and polyesterurethane, respectively. In the same conditions, the pervaporate samples contained 73 and 86 wt% toluene, respectively, reflecting the better selectivity of the less permeable polyester soft block. As an interesting attempt to rationalize the selective permeability in terms of structure–property relationship, the solubility parameter concept was used to analyze the membrane properties qualitatively, pointing out that the solubility parameter of the PTMO soft block ( $\delta = 17.0\text{--}17.5 \text{ J}^{1/2}/\text{cm}^{3/2}$ ) was intermediate between the solubility parameters of toluene and cyclohexane ( $\delta = 18.3$  and  $16.7 \text{ J}^{1/2}/\text{cm}^{3/2}$ , respectively). The close solubility parameter values were related to the good affinity of the polyetherurethane membrane for both toluene and cyclohexane. The much higher solubility parameter value of the polyester soft block ( $\delta = 19.5 \text{ J}^{1/2}/\text{cm}^{3/2}$ ) favored the polymer swelling in toluene in detriment of cyclohexane which had a much lower solubility parameter. Worthy of mention, that first qualitative structure–property relationship motivated the design of new polyester soft blocks by substituting aliphatic adipic acid units for aromatic isophthalic acid units in order to increase the solubility parameter (thus the selectivity) of the corresponding polyesterurethane membrane. However, the impact on the pervaporation selectivity was fairly low with a limited increase of a few points while the pervaporation flux decreased very significantly (almost –50%). A later study by Enneking et al. allowed a finer analysis of the selective permeability of a closely related PU with a PBA polyester soft block and a fairly complex hard block which was also prepared by the Company Bayer. At

30 °C, systematic sorption experiments with pure vapors (activity = 0.8) revealed that the polyesterurethane absorbed four times more benzene and toluene than cyclohexane, thus confirming the strong affinity of the polyesterurethane for aromatics species. An analysis of the polymer swelling in binary mixtures toluene/cyclohexane and benzene/cyclohexane over the whole composition range showed that the polyesterurethane membrane was highly selective towards aromatics, especially for the mixtures enriched in aromatics species (typically  $C_{\text{aromatics}} > 80 \text{ wt}\%$ ) and the selective sorption was accounted for by a UNIQUAC thermodynamic approach. The diffusion coefficients obtained for toluene and benzene were very close whereas slightly lower values were found for cyclohexane, therefore corresponding to a very low diffusion selectivity. The pervaporation of *benzene/cyclohexane* mixtures at the same temperature (30 °C) led to cyclohexane flux values that were fairly low and almost constant over all the composition range ( $J_{\text{cyclohexane}} \approx 0.2 \text{ kg/h m}^2$  for an unspecified membrane thickness). The total flux was fairly high and sharply increased with the feed benzene content (i.e. from 1.3 to 3 kg/h m<sup>2</sup> for feed mixtures containing 50 and 80 wt% benzene, respectively). In the same conditions, the pervaporation selectivity was particularly high with pervaporate samples containing from 85 to 92 wt% benzene. The pervaporation of *toluene/cyclohexane* mixtures over the whole composition range obeyed the same general trends with lower flux values (typically  $\sim 30\%$ ) and almost identical selectivities. A complete modeling of the pervaporation mass transfer was achieved on the basis of the Stefan–Maxwell equations. More recently, Wolinska-Grabczyk et al. described the extremely high permeability ( $J = 42 \text{ kg } \mu\text{m/h m}^2$  at 30 °C) and poor selectivity ( $C'_{\text{benzene}} = 15 \text{ wt}\%$ ) of a polyetherurethaneurea PTMO2000/2,4-TDI/MDA (stoichiometry 1/4/3) for the pervaporation of a benzene/cyclohexane mixture containing 5 wt% benzene [168]. In a related paper, Wolinska-Grabczyk et al. then compared the selective permeability of this polymer with that of a related polyesterurethaneurea PBA2000/2,4-TDI/MDA (stoichiometry 1/4/3) [17]. As a way of example, for the pervaporation of a benzene/cyclohexane mixture containing 24 wt% of benzene at 25 °C, the polyether and polyester-based polymers led to total permeability values of 152 and 1.28 kg  $\mu\text{m/h m}^2$ , respectively, while the selectivity followed an opposite trend (permeate samples containing 43 wt% ( $\alpha = 2.4$ ) and 75 wt% ( $\alpha = 9.7$ ) of benzene, respectively). These results again confirmed the much higher selectivity of polyester rather than polyether soft blocks with a heavy price to pay in terms of permeability. Another comparison between PU with polyether (PEO600) or polyester (PCL530) soft blocks was made by Roizard et al. for the separation of toluene/*n*-heptane mixtures and the same conclusions were also drawn [37,38].

**3.1.2.1.2. Mixed soft blocks.** PU and PUU with mixed soft segments were also described for the separation of aromatics from non-aromatics. As it has been shown already in the previous sections of this paper, mixed soft segments can sometimes offer new opportunities to tailor block copolymers with much improved characteristics (e.g. better mechanical properties, optimized flux and selectivity). Following this approach, Feimer et al. [164] reported PUU membranes with mixed soft blocks for the separation of aromatics from aliphatics in a patent assigned to the Exxon Research and Engineering Company. As way of example, two polyesterurethaneureas with the same hard block MDI/MDA and soft segments made of either PEA1000 or mixed soft blocks PEA2000/PEA500 with almost the same average soft block molecular weight ( $M_n \approx 940$ ) were tested for the pervaporation of a heavy cat naphtha (feed mixture containing 51 vol% aromatics, 28 vol% saturates and 21 vol% olefins) at different temperatures [164]. The polymer with the mixed soft blocks presented several advantages over the polyesterurethaneurea with a simple soft block of almost the same molecular weight. First, the more complex PU was much stronger and could tolerate much higher temperatures. A temperature of 140 °C was initially reported for

the PU with the mixed soft blocks PEA2000/PEA500 while the maximum temperature (before a very sharp selectivity decrease indicative for membrane degradation) was 120 °C for the membrane with the simple soft block PEA1000. Clearly, the mixed soft segment PEA2000/PEA500 enabled to improve the mechanical withstanding of the PU membranes which became capable of working in extreme conditions. Second, the increase in working temperature led to a sharp increase in flux that was multiplied by a factor of almost 3 between 120 and 140 °C. At the same time, the selectivity remained quasi-constant and very high with permeate samples containing about 85 vol% of aromatics. Globally, the use of mixed soft segments enabled to triple the productivity. In another later patent assigned to the same company, Schucker [167] reported that this polymer with the mixed soft blocks PEA2000/PEA500 could even be used at a temperature as high as 170 °C without any loss in selectivity, thus leading to pervaporation membranes with outstanding properties for the separation of heavy cat naphtha.

*3.1.2.2. Influence of the polymer soft block content.* In the same way as what had been observed for the permeation of pure species, the separation of purely organic mixtures by PU and PUU can be strongly influenced by the polymer soft block content.

One way of demonstrating this influence was to analyze the properties of block copolymers obtained from soft block precursors of different molecular weights while keeping the reactant stoichiometry constant. For example, polyesterurethanes PHMS/MDI/1,4-BD obtained from poly(hexamethylene sebacate) (PHMS) telechelic oligomers with increasing molecular weights ( $M_n = 890 \rightarrow 2200$ ) were described by Cao and Kajiuchi for the separation of styrene/ethylbenzene mixtures by pervaporation [169], in an extension of their former work on cross-linked PHMS membranes [170]. In addition to a true relevance to another separation problem of strong industrial interest, that work showed that the total flux increased by a factor 2 when the PHMS molecular weight increased from 890 to 1600. Unfortunately, the reactant stoichiometry was not fully reported, therefore preventing from correlating the pervaporation flux to the polymer soft block content in a quantitative way. At the same time, the permeate styrene content decreased significantly from 48 wt% ( $\alpha = 2.76$ ) to 33 wt% ( $\alpha = 1.45$ ) for a feed mixture containing 25 wt% of styrene. The polyesterurethane with an even longer soft block ( $M_n = 2200$ ) could obviously not withstand the pervaporation conditions (i.e. membrane failure reflected by an extremely high flux and a nil selectivity) [169]. Another very interesting approach was reported by Schucker who varied the soft block average molecular weight by using *mixed soft segments* made of PEA2000 and PEA500 in various proportions [10,167]. A family of PUU PEA2000 + PEA500 ( $M_n = 580 \rightarrow 1930$ )/MDI/MDA (stoichiometry 1/2/1) was assessed for the extraction of aromatics from a complex model mixture for heavy cat naphtha by perstraction at 80 °C. The permeability was found to increase linearly with the number average molecular weight of the soft block  $M_n$  (correlation coefficient  $r = 0.993$ , seven data points) [10]. This linear variation could be considered as rather unexpected because a systematic analysis of the literature for different systems involving polyesterurethane block copolymers shows that the most usual variation of permeability is linear as a function of the polymer soft block content  $W_{SB}$  (rather than the soft block molecular weight). Nevertheless, Fig. 11 shows that the permeability also increased quasi-linearly with the polymer soft block content despite a significant scattering of the experimental data (correlation coefficient  $r = 0.978$ ). Quite surprisingly, the perstraction selectivity was almost independent of the polymer soft block content for most of the permeated species (i.e. pentamethylbenzene, isodurene, mesitylene and 1-decene) while it decreased significantly for *p*-xylene and naphthalene.

Another systematic way of varying the polymer soft block content consists of using different reactant stoichiometries with a constant soft block molecular weight, which corresponds to an increase in the

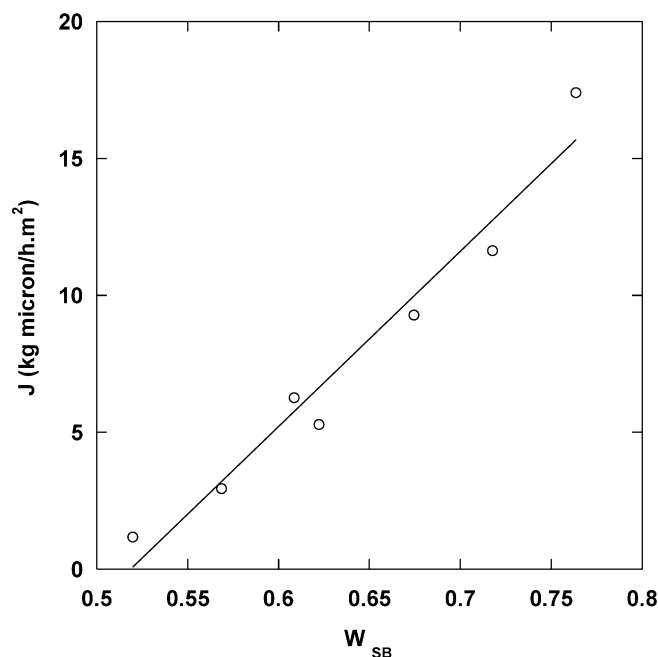


Fig. 11. Influence of the polymer soft block content on the total permeability for the pervaporation of a complex model mixture for heavy cat naphta at 80 °C using polyesterurethaneureas with mixed soft segments PEA2000 + PEA500 of increasing number average molecular weight ( $M_n = 580 \rightarrow 1930$ ) and hard blocks MDI/MDA (from the permeation data and polymer compositions reported by Schucker [10]).

average hard block length. In the first paper to describe systematic qualitative relationships between the PU structure and its permeation features for the separation of aromatics from aliphatics, Ohst et al. considered polyesterurethanes PBA2600/MDI/1,4-BD with different stoichiometries. The permeability data were reported for the pervaporation of toluene/cyclohexane mixtures over the whole composition range at 30 °C [6]. As a way of example, Fig. 12 shows that the total flux increased linearly with the polymer soft block content  $W_{SB}$  for pure toluene and for a binary mixture containing 72 wt% toluene (correlation coefficients  $r = 0.989$  and  $0.999$ , respectively). Moreover, the pervaporation selectivity did not depend upon the polymer soft block content and was fairly high (e.g.  $C'_{\text{toluene}} = 91$  wt% for  $C_{\text{toluene}} = 72$  wt%). Therefore, by a simple variation of the average hard block length, the flux was improved with no influence on the selectivity. This particular behavior is highly interesting because it overcomes the compromise between flux and selectivity that has usually to be made in pervaporation. The same trends can be observed for the pervaporation of a styrene/ethylbenzene mixture ( $C_{\text{styrene}} = 25$  wt%) using polyesterurethanes PHMS1270/HMDI/1,4-BD obtained from four different reactant stoichiometries [169]. From the reported polymer compositions, the polymer soft block content  $W_{SB}$  can be calculated and the following relationship can be determined:  $J$  (g/h m<sup>2</sup>) = 151.4 + 933.6  $W_{SB}$  (correlation coefficient  $r = 0.991$ ) at 25 °C. For these polyesterurethanes differing in their average hard block length, the selectivity again remained independent of the polymer soft block content ( $C'_{\text{styrene}} = 34$  wt%,  $\alpha = 1.56$ ).

As we have shown from a systematic analysis of the literature, the polymer soft block content  $W_{SB}$  is

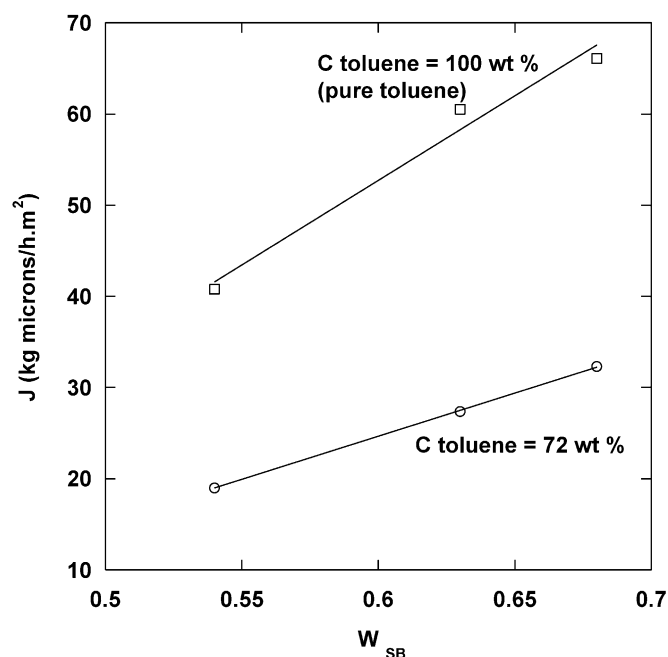


Fig. 12. Influence of the polymer soft block content on the total permeability for the pervaporation of pure toluene or a mixture toluene/cyclohexane (72/28 wt%) at 30 °C using polyesterurethanes PBA2600/MDI/1,4-BD with different reactant stoichiometries (from the polymer composition and permeation data reported by Ohst et al. [6]).

very useful to correlate the permeability of pure or mixed species in PU varying in either their soft block molecular weight or in their reactant stoichiometry. However, when both latter parameters are varied simultaneously in a same polymer family (which is rather unusual anyway), it seems that the permeation behavior is much more complex and cannot be easily related to the polymer soft block content. A very good example was recently given by Muszynski et al. for the pervaporation of benzene/cyclohexane mixtures using PTMO-based polyetherurethanes varying in both their soft block molecular weight and reactant stoichiometry [17]. The influence of the simultaneous variation in the average length of the soft and hard blocks could not be accounted for by the simple polymer soft block content.

**3.1.2.2.3. Influence of the chemical nature of the hard block.** By using different diisocyanates (e.g. aliphatic or aromatic) or chain extenders (e.g. diols or diamines), the chemical nature of the hard block can be varied to a great extent. Its influence on the selective permeation of purely organic mixtures through PU and PUU was reported only for the separation of aromatics from aliphatics. Most generally, the chemical nature of the hard block determined the extent of the polymer physical cross-linking and thus the polymer ability to withstand exposure to high temperatures or solvating power. However, its impact on the permeation features depended on the systems investigated and was not easy to generalize. For a few systems, the flux and selectivity were independent of systematic changes in the hard block chemical nature [6,33]. In other cases, the permeability was strongly affected while the selectivity remained quasi-unchanged [10,17]. The former systems sometimes allowed extreme working conditions (e.g. temperature as high as 170 °C) whereas the latter systems were also really interesting because they offered a way of circumventing the problem of duality between flux and selectivity usually observed in membrane separation processes.

In 1991, Ohst et al. reported that two polyesterurethanes differing in their aromatic or aliphatic diisocyanate precursor, PBA1000/2,4-TDI/1,4-BD and PBA1000/HMDI/1,4-BD ( $W_{SB} = 85$  wt%), led to the same permeability and selectivity for the separation of toluene/cyclohexane mixtures at 30 °C [6]. The same conclusion was also drawn for a polyesterurethane and a polyesterurethaneurea obtained from a diol or diamine chain extender, respectively, with no mention about the full polymer chemical structure. Ho et al. observed the same trends for halogenated polyesterurethaneureas with a PBA2000 soft block and hard blocks containing an increasing number of chlorine atoms (i.e.  $n_{Cl} = 0, 2, 6, 8$  and 10) [33]. A systematic investigation of the pervaporation of a mixture toluene/isooctane (50/50 wt%) revealed that the flux and selectivity were independent of the number of chlorine atoms in the hard blocks. Nevertheless, the hard blocks enriched in chlorine atoms were responsible for a much better physical cross-linking of the block copolymers. The higher the number of chlorine atoms in the hard blocks, the higher the working temperature for the pervaporation experiments. As a way of example, the control polyesterurethaneurea membrane with no chlorine atom was able to withstand a working temperature of 100 °C for the pervaporation of a mixture toluene/isooctane (50/50 wt%). When the hard blocks contained two and six chlorine atoms, the maximum temperature before membrane damaging increased up to 150 and 170 °C, respectively. For this family of halogenated polyesterurethaneureas, the net result of increasing the hard block chlorine content was a sharp increase in productivity obtained at much higher working temperatures.

In other systems, changes in the hard block chemical structure had an influence on the permeability at a given temperature while the selectivity was not or very slightly affected. A good example for this kind of behavior was reported by Schucker for the separation of a complex model mixture for heavy cat naphtha using polyesterurethaneureas PBA1000/MDI/4,4'-diaminodiphenylmethane and PBA1000/MDI/4,4'-diaminodiphenylsulfone [10]. A simple substitution of the methane bridge for the sulfone bridge in the hard block chemical structure had a dramatic impact on the permeability (almost –70%) while the selectivity remained unchanged for all the permeated species but naphthalene and *p*-xylene for which a very slight increase was observed. Muszynski et al. also showed how the chemical hard block structure could sometimes provide a way of tailoring the polymer permeability without any impact on selectivity (Table 2) [17]. Two families of polyetherurethaneureas and polyesterurethaneureas

Table 2

Influence of the chemical structure of the hard block on the properties of poly(ether or ester)urethaneureas for the pervaporation of benzene/cyclohexane mixtures at 25 °C

Polymer (reactant stoichiometry)	$C_{\text{benzene}}$ (wt%)	$J$ (kg $\mu\text{m}/\text{h m}^2$ )	$C'_{\text{benzene}}$ (wt%)	$\alpha_{\text{benzene/cyclohexane}}$
<i>Polyetherurethaneureas</i>				
PTMO650/2,4-TDI/Bz (1/2/1)	5	1.2	27	7.1
PTMO650/2,4-TDI/PDA (1/2/1)	5	2.1	25	6.4
PTMO650/2,4-TDI/1,5-DAN (1/2/1)	5	1.4	26	6.7
PTMO650/2,4-TDI/MDA (1/2/1)	5	1.3	25	6.4
<i>Polyesterurethaneureas</i>				
PBA2000/2,4-TDI/Bz (1/4/3)	40	5.7	82	6.9
PBA2000/2,4-TDI/PDA (1/4/3)	40	9.8	81.5	6.6
PBA2000/2,4-TDI/MDA (1/4/3)	40	6.9	82	6.9

Bz: benzidine, PDA: *p*-Phenylenediamine, 1,5-DAN: 1,5-diaminonaphthalene, MDA: 4,4'-methylenedianiline (from the data reported by Muszynski et al. [17]).



were obtained from various aromatic diamine chain extenders (i.e. benzidine, *p*-phenylene diamine, 1,5-diamino naphthalene and 4,4'-methylenedianiline). All the hard blocks but that obtained from *p*-phenylene diamine led to similar permeation features for the separation of benzene/cyclohexane mixtures at 25 °C. The *p*-phenylene diamine was the only aromatic diamine that contained a single aromatic ring as compared to two aromatic rings for all the other aromatic diamines used for that work. The corresponding decreased hard block size is most likely responsible for the very significant increase in permeability (multiplied by a factor 2) that was observed for the *p*-phenylene diamine-based PUU. Worthy of mention, this sharp increase in flux did not lead to any significant loss in selectivity for both families of poly(ether or ester)urethaneureas.

*3.1.2.2.4. Influence of other structural or morphological parameters.* Chemical cross-linking was also reported as an efficient way of reinforcing the polymer physical cross-linking when the latter was not strong enough to prevent the PU damage in working conditions. Its influence on the selective permeation of purely organic mixtures through PU block copolymers really depended on the different synthesis schemes proposed for the chemical cross-linking.

Ohst et al. reported different ways of polyesterurethane cross-linking by using either a triisocyanate or trifunctional polyesters for introducing cross-links between hard blocks or soft blocks, respectively [6]. The properties of the corresponding membranes were analyzed for the pervaporation of toluene/cyclohexane mixtures over the whole composition range at 30 °C. The chemical cross-linking between the hard blocks had no effect on the selective permeation. However, reducing the mobility of the soft blocks by introducing cross-links between the polyester soft segments led to a dramatic decrease in permeability, of one or two orders of magnitude depending on the systems investigated, and the selectivity was not significantly enhanced.

The influence of two different ways of PU cross-linking was also reported by Roizard et al. for the pervaporation of toluene/*n*-heptane mixtures [37,38]. The PU with an almost constant soft block weight fraction ( $W_{SB} = 61–67$  wt%) were obtained either by simple thermal cross-linking of a macrodiisocyanate precursor (route 1) or by reaction of a macrodiisocyanate precursor with a triol (2,2',2''-nitrilotriethanol) (route 2). The properties of the polyetherurethanes PEO600/HMDI (via route 1) and PEO600/HMDI/2,2',2''-nitrilotriethanol (via route 2) were systematically compared for the sorption, diffusion and pervaporation of pure or mixed toluene and *n*-heptane. The *n*-heptane swelling was very low and independent of the cross-linking route while the toluene swelling increased from 32 to 52 wt% when the second route was preferred to the first route. The same general trends were found for the sorption of binary mixtures of toluene and *n*-heptane. Moreover, the second route led to higher diffusion coefficients (multiplied by a factor 1.6 and 3 for *n*-heptane and toluene, respectively). The pervaporation features were in good agreement with the sorption and diffusion analysis and gave a clear advantage to the second synthesis scheme that obviously led to a more open macromolecular network. The outstanding properties of the polyetherurethane PEO600/HMDI/2,2',2''-nitrilotriethanol deserves a special attention with a very high permeability ( $J = 40$  kg  $\mu\text{m}/\text{h m}^2$ ) and very high selectivity (pervaporate toluene content  $C'_{\text{toluene}} = 87$  wt%) for the pervaporation of a mixture toluene/*n*-heptane (50/50 wt%) at 80 °C.

The *polymer morphology* could be another factor controlling the selective permeation of purely organic mixtures through PU and PUU block copolymers. Cao et al. reported the properties of polyesterurethanes obtained by a one-stage (i.e. 'one pot') or two-stage polymerization for the separation of a styrene/ethylbenzene mixture by pervaporation. It is well known that the two-stage polymerization generally allows a better control of the polymer structure relative to the single-stage synthesis, with an

obvious improvement in the material morphology and mechanical properties [171,172]. The polyesterurethanes were synthesized from PHMS soft blocks with four different molecular weights ( $M_n = 890 \rightarrow 2200$ ) in the one- and two-stage polymerization conditions, therefore leading to  $2 \times 4 = 8$  different membranes which were systematically assessed in pervaporation. The polyesterurethane with the longest soft segment ( $M_n = 2200$ ) led to extremely permeable membranes with no selectivity, reflecting the material failure in the pervaporation conditions owing to an insufficient physical cross-linking of the PU material. Otherwise, the polyetherurethanes obtained by the two-stage polymerization method systematically gave very slightly lower total fluxes (typically  $-4$  or  $5\%$ ) with small gains in selectivity (about 1 to 2 points) as compared with the polymers obtained by the 'one-pot' polymerization.

### 3.2. Polyimides

#### 3.2.1. Rigid polyimides as hard block models for polyimide block copolymers

Although they are not strictly speaking block copolymers and could thus be considered as out of the scope of the present review, rigid polyimides are interesting materials that can be seen as homopolymer models for hard blocks involved in more complex polyimide block copolymers. Therefore, systematic investigations made on rigid polyimides can give precious information about the permeation features of hard blocks in polyimide block copolymers. In the following, key examples will be chosen to help understand the relationship between the chemical structure of rigid polyimides and their (selective) permeability towards liquids or vapors.

*3.2.1.1. Rigid polyimides for the dehydration of air or organic solvents.* A great number of studies have shown that water, which is a very small and highly polar molecule, permeates rather easily through rigid polyimides while most of these materials are extremely poorly permeable towards organic solvents. Therefore, many works on liquid or vapor permeation through rigid polyimides took advantage of this particular feature and proposed polyimide membranes for the highly selective extraction of water from air or organic solvents. As way of example, Ube Industries, Ltd. Japan, has already commercialized air drying systems using rigid polyimide hollow fiber membranes [173]. Moreover, dehydration of organic solvents by rigid polyimide membranes has mainly been reported for alcohols (i.e. EtOH [174–180], *i*-PrOH [181,182]) and very rarely for other solvents (e.g. acetic acid [183]). As clearly shown by Huang and Feng [175] or Qariouh et al. [178] for the separation of water/ethanol mixtures by pervaporation using a membrane made of a commercially available aromatic polyetherimide (i.e. Ultem 1000, General Electric Co.), homogeneous dense membranes of rigid polyimides are usually poorly permeable towards water/ethanol mixtures (e.g.  $J < 100$  g/h m<sup>2</sup> for a membrane thickness of 35 μm at 40 °C [178]). To overcome this strong limitation of rigid polyimides, asymmetric [174,176,180] or composite [177,179] polyimide membranes have been reported for this potential application. Such complex membranes have a dense active layer which is much thinner (typically less than a few micrometers) than homogeneous dense membranes and a very significant increase in permeation fluxes can thus be obtained. As a way of example, Yanagishita et al. reported a pervaporation flux of 1 kg/h m<sup>2</sup> and a pervaporate water content of 97.9 wt% ( $\alpha \approx 900$ ) at 60 °C for the dehydration of ethanol starting from the aqueous azeotropic mixture containing 5 wt% of water [176]. The asymmetric membrane used was made of a commercially available aromatic polyimide BTDA/TDI + MDI (Polyimide PI-2080, Dow Chemical Co.). Compared to the azeotropic distillation, ethanol dehydration by hybrid processes involving vapor permeation

through asymmetric aromatic polyimide membranes enabled very significant savings in energy costs [174,180]. Following their first study of ethanol dehydration using a dense Ultem membrane [175], Huang and Feng reported the properties of asymmetric Ultem membranes obtained in various casting conditions for *iso*-propanol dehydration by pervaporation [181,182]. All the membranes permeated water preferentially. However, the pervaporation flux and selectivity were strongly dependent on the casting conditions (i.e. polymer concentration, solvent evaporation temperature and time before gelation).

*3.2.1.2. Rigid polyimides for the recovery of volatile organic solvents from air or water.* More surprising considering the general features of most rigid polyimides, a few authors reported the study of those materials for the recovery of volatile organic species from air or even water. Deng et al. described the control of volatile hydrocarbon emissions using an asymmetric aromatic polyetherimide membrane [184]. The vapor permeation experiments were first carried out with a model mixture containing *n*-pentane, *n*-heptane, toluene and cyclohexane at different dilutions in dry nitrogen. Even at the highest dilution, the total mole fraction of hydrocarbons in the permeate was more than 0.88 (i.e. six times the total mole fraction of hydrocarbons in the corresponding feed mixture). However, the permeation flux was very low (estimated as less than 100 g/h m<sup>2</sup> at 80 °C). When the feed mixture was slightly humidified (feed water mole fraction in the range of 0.001–0.003), water permeated very preferentially (mole fraction of water in the permeate in the range of 0.68–0.82) to the detriment of the hydrocarbon compounds for which the membrane did not show important selectivity any longer. The study of the separation of gasoline from air confirmed that the aromatic polyetherimide membrane had a much too low permeability to apolar hydrocarbons to be useful for this kind of application. Nevertheless, it again showed the very strong affinity of this membrane to polar species (especially water, and to a much slighter extent pentanol). Chung et al. [185] also described their attempts to recover a chlorofluorocarbon (CFC-12) from air using polyimide hollow fiber membranes developed by Ube Industries, Ltd. Japan. However, in all cases (i.e. permeation of pure air, pure CFC-12 or mixtures of air and CFC-12), the permeation rates were much higher (by at least one order of magnitude, depending on the experimental conditions) for air than for CFC-12. More recently, Kim and coworkers took up the challenge of really reversing a rigid polyimide selectivity by incorporating highly fluorinated side groups to the polymeric backbone with the monomer 2-(perfluorohexyl)ethyl-3,5-diaminobenzoate (PFDAB) [186]. Unlike the corresponding polyimides without fluorinated side groups, the new polyimides PFDAB/6FDA and PFDAB/ODPA had a strong hydrophobic character as reflected by their much lower surface energy (almost –30%). Systematic pervaporation experiments with dilute aqueous solutions containing different organic solvents (e.g. MEK, ethyl acetate, methylene chloride and trichloroethylene) showed that the incorporation of fluorinated side groups increased *both* permeability and selectivity towards the organic species. As a way of example, the polyimide PFDAB/6FDA led to a total permeability of almost 0.80 kg μm/h m<sup>2</sup> for the pervaporation of an aqueous mixture containing 0.11 wt% of trichloroethylene at 30 °C. Owing to the strong hydrophobic character of the highly fluorinated polyimide, the membrane permeated preferentially trichloroethylene, corresponding to a very interesting inversion of selectivity as compared to that of most usual aromatic polyimides, and the pervaporation selectivity was fairly high (permeate containing 45 wt% of trichloroethylene,  $\alpha = 750$ ).

*3.2.1.3. Rigid polyimides for the separation of purely organic mixtures.* As expected from their usually very poor permeability towards organic solvents [187,188], reports on the permeation of purely organic

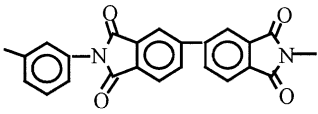
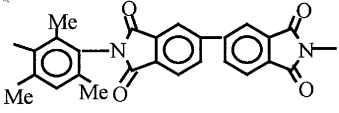
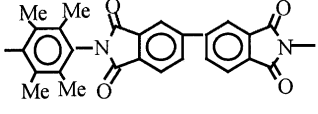
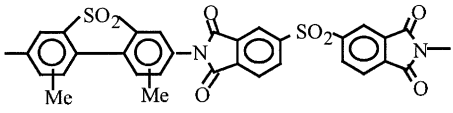
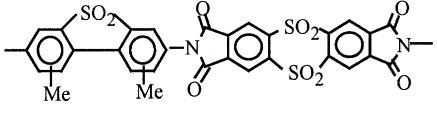
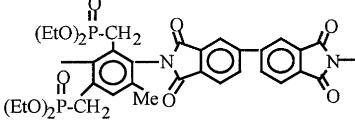
mixtures of liquids or vapors through rigid polyimides are really scarce in the literature. A very good exception to the rule is the important work that has been carried out over the last years by Okamoto's research team to demonstrate the influence of various side groups on the selective permeability of rigid polyimides towards aromatic/aliphatic hydrocarbon mixtures [187,189–192]. In addition to describing interesting approaches to new polyimides for membrane applications, Okamoto and coworkers obtained several rigid polyimide materials that displayed both high flux and selectivity for separations of strong industrial interest. As way of example, the main results obtained for the separation of benzene/cyclohexane mixtures (i.e. one of the most challenging potential applications thoroughly investigated by Okamoto and coworkers) are summarized in Table 3. The influence of methyl side groups was first reported by Tanihara et al. for rigid polyimides with methyl-substituted phenylenediamine moieties [187]. Compared to the corresponding rigid polyimide without methyl side groups (i.e. polyimide MPD/BPDA) that was almost impermeable in the same conditions ( $J < 0.003 \text{ kg } \mu\text{m}/\text{h m}^2$ ), the polyimide containing three methyl side groups per repeating unit led to a high flux ( $J = 9.1 \text{ kg } \mu\text{m}/\text{h m}^2$ ) and a rather good selectivity ( $C'_{\text{benzene}} = 88 \text{ wt}\%$ ,  $\alpha = 7.1$ ) for the pervaporation of a mixture benzene/cyclohexane (50/50 wt%) at 50 °C. Increasing the number of methyl-side groups from 3 to 4 had a great impact on the permeability (+54%) while the selectivity was affected very slightly ( $C'_{\text{benzene}} = 85 \text{ wt}\%$ ,  $\alpha = 5.7$ ). Therefore, the work of Tanihara et al. confirmed the key role of methyl-side groups which, owing to steric hindrance, minimized the packing of polyimide chains and thus induced much higher permeability. Sulfolane is known as a very good extraction agent for aromatics in the petrochemistry industry. By analogy, polyimides containing sulfonyl groups are expected to be interesting candidates for aromatic/aliphatic separation. A rigid polyimide with two sulfonyl groups per repeating unit (entry line 4, Table 3) was described by Hao et al. for the highly selective extraction of benzene from cyclohexane (i.e.  $C'_{\text{benzene}} = 98 \text{ wt}\%$  for a feed mixture containing 60 wt% of benzene at 50 °C) [189]. However, the permeability was fairly low ( $J = 0.56 \text{ kg } \mu\text{m}/\text{h m}^2$ ). Another related polyimide with three sulfonyl groups per repeating unit (entry line 5, Table 3) was also recently described by Wang et al. with a slightly decreased permeability (–16%) and the same very high selectivity in almost the same conditions [190]. Okamoto et al. also assessed the influence of pendant diethylphosphonate groups in aromatic polyimides [192], following a former work of Cabasso who had reported the extremely good properties (in fact, one of the best performances reported so far for the separation of benzene/cyclohexane mixtures by membrane separation processes) of blends of poly(styrene diethylphosphonate) and cellulose acetate for the extraction of benzene from cyclohexane [193]. Although the experimental fluxes were fairly scattered for those complex cross-linked polyimides, they were generally in the high range (typically  $J \approx 9 \text{ kg } \mu\text{m}/\text{h m}^2$  at 70 °C) and high selectivity values were also obtained ( $C'_{\text{benzene}} = 93 - 95 \text{ wt}\%$ ,  $\alpha = 13 - 20$ , for a feed mixture containing 50 wt% of benzene), confirming the very positive role of diethylphosphonate groups in the separation of benzene/cyclohexane mixtures.

### 3.2.2. Polyimide block copolymers

Rigid aromatic polyimides are generally very poorly permeable towards organic solvents, except for very particular cases as shown in Section 3.2.1.3. By associating highly permeable soft blocks with quasi-impermeable imide hard blocks which provide a very strong physical cross-linking, polyimide block copolymers have offered new ways of tailoring the (selective) permeability of polyimides. As way of example, in the 1990s, the very strong involvement of the Exxon Research and Engineering Company in research projects to develop new polyimide block copolymers for membrane applications was a very

Table 3

Influence of various side groups on the properties of rigid polyimides (here considered as models for hard blocks in polyimide block copolymers) for the pervaporation of benzene/cyclohexane mixtures

Polyimide	C <sub>benzene</sub> (wt%)	T (°C)	J (kg μm/h m <sup>2</sup> )	C' <sub>benzene</sub> (wt%)	α	References
MPD/BPDA	50	50	<0.003	–	–	[187]
						
3MMPD/BPDA	50	50	9.1	88	7.1	[187]
						
4MPPD/BPDA	50	50	14	85	5.7	[187]
						
DDBT/DSDA	60	50	0.56	98	29	[189,190]
						
DDBT/TADATO	55	60	0.47	98	35	[191]
						
P-3MMPD/BPDA (5.9 wt% P) <sup>a</sup>	50	70	2.5	95	20	[192]
						
P-3MMPD/BPDA (7.7 wt% P) <sup>a</sup>	50	70	9.9	94	15	[192]
P-3MMPD/BPDA (8.3 wt% P) <sup>a</sup>	50	70	7.9	93	13	[192]

MPD: *m*-phenylene diamine, 3MMPD: 2,4,6-trimethyl-1,3-phenylenediamine, 4MPPD: 2,3,5,6-tetramethyl-1,4-phenylenediamine, DDBT: 2,8 (or 6)-dimethyl-3,7-diaminobenzothiophene-5,5-dioxide, BPDA: 3,3',4,4'-biphenyltetracarboxylic dianhydride, DSDA: 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride, TADATO: thianthrene-2,3,7,8-tetracarboxylic dianhydride.

<sup>a</sup> Complex cross-linked phosphorylated polyimide.

good reflect for the highly interesting prospects of those particular materials for a broad range of challenging industrial separations [29–31,34,36,194–200].

Even if the reports on the permeability of polyimide block copolymers are still relatively scarce in the literature as compared to those on PU block copolymers, they have already shown several specific advantages of the former in terms of thermal stability, overall performance and scope of application that can be extended to the separation of purely organic mixtures containing polar species (e.g. alcohol/paraffin, alcohol/ether), for which simple PU usually fail owing to their insufficient physical cross-linking.

### 3.2.2.1. Poly(ester or ether)imides

3.2.2.1.1. *Polyesterimides*. Extending its former work on polyesterurethanes, the Exxon Research and Engineering Company patented several formulations of polyesterimide block copolymers [30,194–196] and their application for membrane separations of industrial interest (e.g. aromatics/alkanes [30,36,194–196] and also mixtures containing polar organic species like alcohols/*n*-paraffins [198] and alcohols/ethers [29]). Even if the data disclosed in the former patents were usually obtained in experimental conditions which differed in a lot of parameters, therefore limiting the bearing of any systematic analysis, they had the merit of first indicating some tendency relationships between the chemical structure of polyesterimide block copolymers and their selective permeability.

Following a fairly complex synthesis scheme that involved the reaction of two telechelic prepolymers (not detailed here for the sake of simplicity), Schucker compared the membrane properties of an aromatic rigid polyesterimide with those of a very closely related polyesterimide which contained a highly flexible soft block (PEA2000) and the same hard block for the pervaporation of a multi-component mixtures of aromatics and alkanes (i.e. toluene 10 wt%, *p*-xylene 40 wt%, *i*-octane 20 wt%, *n*-octane 30 wt%) [195]. The aromatic rigid polyesterimide was highly selective towards aromatics with selectivity factors  $\alpha_{\text{aromatic}/n\text{-octane}}$  of 20.8 and 17.5 for toluene and *p*-xylene, respectively, while the permeability was extremely low ( $J = 1.12 \text{ kg } \mu\text{m}/\text{h m}^2$  at the very high temperature of 220 °C). As expected, the corresponding polyesterimide containing the highly flexible soft block PEA2000 displayed much higher permeability values (e.g.  $J = 25.3 \text{ kg } \mu\text{m}/\text{h m}^2$  at the much lower temperature of 80 °C) and still high selectivity factors  $\alpha_{\text{aromatic}/n\text{-octane}}$  of 10.1 and 7.1 for toluene and *p*-xylene, respectively.

In other related patents on polyesterimide block copolymers with pendent carboxylic acid groups [30,194], Ho et al. also clearly provided interesting qualitative guidelines for the design of new membranes with targeted selective permeability. Compared to a related polyesterurethane (i.e. PEA2000/dichloro-MDI/MOCA (stoichiometry 1/2/1)) that had been patented for its particularly high thermal stability (up to 170 °C) and good separation performances for the same applications (discussed in Section 3.1.2.2.3) [33], the polyesterimide PEA2000/PMDA (pyromellitic dianhydride)/MOCA (stoichiometry 1/2/1) led to the same values of permeabilities with very close separation factors for the pervaporation of a mixture toluene/*i*-octane (50/50 wt%). However, the polyesterimide block copolymer had a much higher thermal stability (up to 210 °C) than the corresponding polyesterurethane, therefore leading to a sharp increase in the membrane permeability ( $J = 417 \text{ kg } \mu\text{m}/\text{h m}^2$ ) while the selectivity remained fairly high ( $C_{\text{toluene}}^I \approx 86 \text{ wt}\%$ ,  $\alpha \approx 6$ ) at 210 °C. When the same comparison was made for the polyesterurethane and polyesterimide with a much shorter polyester soft block (PEA1000), the same increase in thermal stability was observed whereas the polyesterimide based on PEA1000 displayed an improved selectivity in detriment of permeability that decreased significantly. Changing the chemical nature of the soft block X had also a strong influence on the selective permeability of polyesterimide block

copolymers X/PMDA/MOCA (stoichiometry 1/2/1). When compared to the soft block polyethylene-succinate (PES2000), the soft block polyethyleneadipate (PEA2000) led to a strong increase in permeability (by a factor 5) and the separation factor lost 4 points to reach the value of  $\alpha_{\text{aromatic/alkanes}} = 5$  for the pervaporation of a multi-component mixtures of aromatics and alkanes (i.e. toluene 10 wt%, *p*-xylene 40 wt%, *i*-octane 20 wt%, *n*-octane 30 wt%) at 150 °C. The influence of an accumulation of methylene groups within the polyester soft block was clearly detrimental to the selectivity while the opposite was found for the block copolymer permeability. A mixed soft block PEA500/PEA2000 (with an average number molecular weight of 950) was also used instead of the soft block PEA1000 to give much higher permeabilities (increased by a factor of more than 2) with slightly decreased selectivity factors (i.e. loss of a few points) that still remained fairly high and constant ( $\alpha = 10$ , corresponding to a pervaporate toluene content of 91 wt%) for the pervaporation of a mixture toluene/*i*-octane (50/50 wt%) at temperatures in the range 150–200 °C. Those results were in very good agreement with previous observations made on PU block copolymers with mixed soft blocks for the separation of aromatics from alkanes [164,167]. They confirmed that mixed soft segments were very promising for the design of block copolymer membranes with much improved productivity for this type of separation. For the pervaporation of a mixture toluene/*i*-octane (50/50 wt%) using the same type of polyesterimide block copolymers X/PMDA/MOCA, Ho et al. also showed that decreasing the soft block molecular weight increased selectivity but decreased permeability. Moreover, for this family of polymers obtained with various molecular weights of soft segments (i.e. PEA500, PEA1000, PEA2000 and PEA3000), the selectivity was shown to correlate linearly with the permeability in a log-log scale, providing an interesting tradeoff relationship for further polymer optimization [30]. The use of polyesterimide block copolymers *without pendent carboxylic acid groups* was also disclosed by Ho et al. for the same type of separation [196]. Typically, those polymers were obtained by a two-step synthesis scheme implying the end-capping of a polyester diol with trimellitic anhydride acid chloride followed by the chain extension using an aromatic diamine (e.g. PEA2000/TMAACI/MDA with the stoichiometry 1/2/1). No significant differences in selective permeability were found for the related polyesterimide block copolymers with or without pendent carboxylic acid groups [196].

**3.2.2.1.2. Polyetherimides.** Polyetherimide block copolymers were also described by Tanihara et al. for the separation by pervaporation of a mixture benzene/cyclohexane containing 60 wt% of benzene. The block copolymers were obtained by reaction in solution of an aromatic dianhydride (e.g. BPDA) with a mixture of a telechelic  $\alpha$ - $\omega$ -diamino polyether (i.e. soft block precursor) and comonomer aromatic diamines (e.g. ODA + DABA (3,5-diaminobenzoic acid)) followed by thermal imidization [111]. *The influence of the chemical structure of the soft block X* (i.e. PEO, PPO or PTMO) was very strong on the polyetherimide permeability which sharply increased with the number of methylene groups in the polyether soft segment: from 31 kg  $\mu\text{m}/\text{h m}^2$  for the soft block PEO to 290 kg  $\mu\text{m}/\text{h m}^2$  for the soft block PTMO at 50 °C. In the same conditions, the pervaporate benzene content dropped from 89 to 74 wt% corresponding to selectivity factors  $\alpha_{\text{benzene/cyclohexane}}$  of 5.5 and 1.9, respectively. In the same way as what had been observed for various other block copolymers, minimizing the number of methylene groups in the soft block was clearly required for improving the polyetherimide selectivity towards aromatics while a compromise had to be found in terms of permeability. Fig. 13 shows *the influence of the polymer soft block content* on the total permeability from the permeation data and polymer compositions reported by Tanihara et al. for polyetherimide block copolymers PEO (530 or 1150) + ODA + BADA/BPDA obtained with different reactant stoichiometries. The permeability was found to increase exponentially with the polymer soft block content for each of both polyetherimide

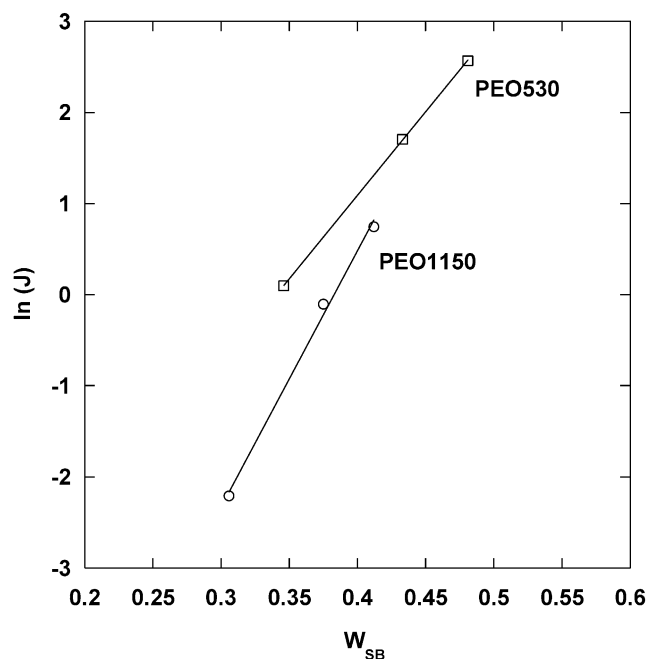


Fig. 13. Influence of the polymer soft block content on the total permeability ( $J$  in  $\text{kg } \mu\text{m/h m}^2$ ) for the pervaporation of a benzene/cyclohexane mixture containing 60 wt% of benzene at 50 °C using polyetherimide block copolymers PEO (530 or 1150) + ODA + BADA/BPDA with different reactant stoichiometries (from the polymer composition and permeation data reported by Tanihara et al. [11]).

families obtained either from PEO530 or PEO1150, for polymers whose soft block content  $W_{SB}$  exceeded a critical value of about 30 wt%. For the polymers highly enriched in hard blocks (corresponding to  $W_{SB} < 30$  wt%), the permeability were generally smaller than what would have been expected from the former exponential relationships. All of these observations are in very good agreement with the general trends that have been described for poly(ether(urethane or urea)) block copolymers in several previous sections of this work. It also confirms that, when *both* reactant stoichiometry and the molecular weight of the polyether soft block vary at the same time, the general behavior is too complex to be described by a single exponential permeability law as a function of the polymer soft block content [17]. Here, two different relationships are indeed required to describe the behaviors of the two polymer families obtained with different stoichiometries and either PEO530 or PEO1150 soft blocks. However, even if the polymer soft block content is clearly not the single parameter to account for the total permeability of block copolymers, this new example certainly shows that it still remains very useful to describe the permeability of block copolymer families that differ either in their soft block molecular weight or in their reactant stoichiometry.

**3.2.2.2. Poly(urethane or urea)imides.** Poly(urethane or urea)imide block copolymers contain highly polar and rigid hard blocks that combine urethane or urea with imide groups which act as reinforcing agents. The main consequence is a sharp improvement in the physical cross-linking of the PUI block copolymers, as compared to that of the related PU materials, with a tremendous positive impact on their stability in extreme conditions (e.g. exposure to high temperature or highly solvating media, etc.).



*3.2.2.2.1. Permeability to purely organic apolar mixtures.* In the 1990s, the Exxon and Research Engineering Company patented several polyester(urethane or urea)imides for the separation of aromatics from aliphatic compounds by membrane separation processes like pervaporation and perstraction [31,199,200]. Even if the PUI formulations and the aromatics/aliphatics mixtures were usually fairly complex and did not allow any broad interpretation in terms of structure/property relationship, the different patents clearly showed that the new polyurethaneimides were able to work at temperatures much higher than what had been allowed with closely related PU which generally did not withstand working temperatures higher than 100 °C [33]. Worthy of mention, a working temperature as high as 175 °C was even reported by Schucker for a complex PUI membrane [199]. Moreover, at such high temperatures, the poly(ester(urethane or urea) imides) were usually extremely permeable, while still maintaining a fairly high selectivity. As a way of example, the polyesterurethaneimide PEA2000/MDI/PMDA (stoichiometry 1/2/1) led to a total permeability of 206 kg  $\mu\text{m}/\text{h m}^2$  with a selectivity factor of 7 (i.e. corresponding to a pervaporate content in aromatics of 88 vol%) for the pervaporation of a heavy cat naphtha containing 51 vol% of aromatics at 160 °C.

*3.2.2.2.2. Permeability to purely organic polar mixtures.* More than simply allowing much higher operating temperatures, the very strong physical cross-linking of poly((urethane or urea) imides) offered new opportunities for the separation of purely organic mixtures that contained *polar* species (e.g. alcohol/ether or alcohol/ester mixtures). Therefore, PUI clearly overcame the usual limitations of the related poly(urethanes or ureas) which were generally not able to withstand exposure to such highly solvating media.

Jonquière et al. have thoroughly investigated the properties of a wide range of poly((urethane or urea)imide) block copolymers for the sorption (pure vapors [67,201] and binary liquid mixtures [70]) and pervaporation (mass transfer modeling [82] and structure/property relationships [9,12,13]) of alcohol/ether and/or alcohol/ester mixtures. One of the main subjacent purposes was the purification of ethyl-*tert*-butyl ether (ETBE), a fuel octane enhancer, widely used in the European Union instead of lead derivatives, for the protection of environment [18]. However, the industrial synthesis process of ETBE involves the separation of an excess of ethanol from the final product which is quite energy-intensive by common techniques because ethanol forms an azeotrope with ETBE. Membrane hybrid processes combining pervaporation and distillation have been proposed as interesting alternatives to common separation processes for the purification of ETBE [135,202] and several PUI block copolymers displayed interesting features for this kind of separation [9,12,13].

*3.2.2.2.2.1. Influence of the polymer structural parameters.*

*Influence of the polymer soft block content.* The properties of two families of PUIs with either polyether (Jeffamine JFAED) or polyester (PCL) soft blocks of increasing molecular weights ( $M_n$  in the range of 530–2000) and the same pyromellitimide hard blocks (MDI/PMDA) were reported by Jonquière et al. for the pervaporation of the azeotropic mixture EtOH/ETBE (20/80 wt%) at 30 °C and the total permeability was shown to increase sharply with the polymer soft block content [12]. The increase was exponential for the polyether soft blocks, while it was linear for polyester soft blocks. To the best of our knowledge, the strong influence of the soft block chemical nature on the former variation was first emphasized. In this review paper, we have shown that the former types of laws can be generalized to a great number of systems involving the permeation of small molecules through block copolymers containing either polyether or polyester soft blocks.

*Influence of the chemical nature of the soft block.* The influence of the chemical nature of the soft

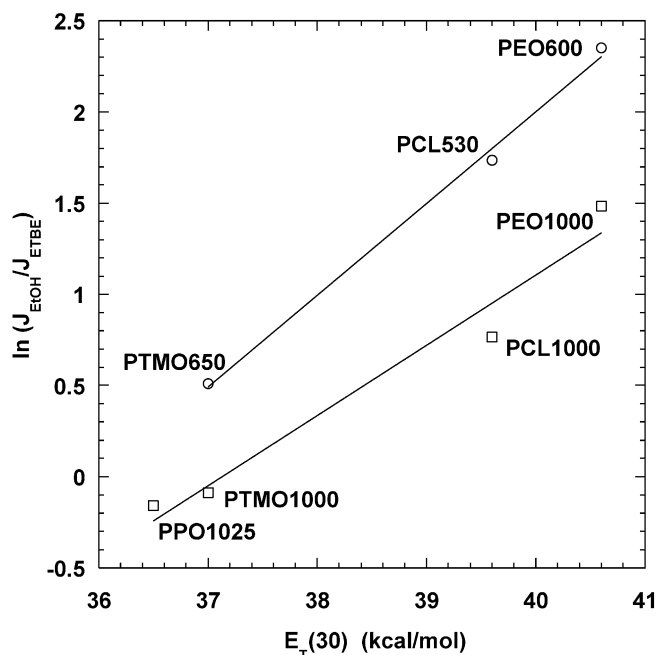


Fig. 14. Influence of the polarity parameter  $E_T(30)$  of the soft block X on the pervaporation selectivity of polyurethaneimides X/MDI/PMDA (stoichiometry 1/2/1). Separation of the azeotropic mixture EtOH/ETBE (20/80 wt%) at 30 °C (reproduced with permission from Jonquière et al. [9], copyright © 1995 John Wiley and Sons).

block (i.e. PEO, PPO, PTMO, PCL) on the pervaporation selectivity was also reported for various polyurethaneimides X/MDI/PMDA (stoichiometry 1/2/1) [9,13].

On the basis of polarity measurements on suitably end-capped soft blocks using a new solvatochromic probe, the pervaporation selectivity was correlated quantitatively to the soft block polarity parameter [9] in the  $E_T(30)$  polarity scale of Dimroth and Reichardt which had been initially reported to describe solvent polarity and its effect on various phenomena in organic chemistry [203] (Fig. 14). The former approach was original for block copolymers and provided an easy way of predicting the selectivity of new PUIs from the simple measurement of the polarity of their soft blocks.

In another related work [13] based on the Scatchard-Hildebrand theory [204], the solubility parameters of the soft block X, ethanol and ETBE were used to correlate the pervaporation selectivity in a quantitative way on the basis of a new semi-empirical parameter called interaction selectivity  $IS = |\delta_X - \delta_{\text{EtOH}}|/|\delta_X - \delta_{\text{ETBE}}|$  (Fig. 15). Despite the well-known inherent limitations of the solubility parameters, the former approach had the merit of allowing an a priori estimation of the pervaporation selectivity of any related polyurethaneimide X/MDI/PMDA provided the chemical structure of the soft block be known. The former correlation was indeed predictive because only the chemical structure of the soft block was required to estimate the pervaporation selectivity, the soft block solubility parameter  $\delta_X$  being then reported in the literature or calculated from group contribution methods [205,206]. Conversely, the design of a soft block providing a target selectivity was possible to some extent if the related  $\delta_X$  was compatible with a coherent chemical structure.

*Influence of the chemical nature of the hard block.* Recently, new related polyamideurethaneimide block copolymers with different hard block structures (i.e. PTMO650/MDI/Z, stoichiometry 1/2/1) were

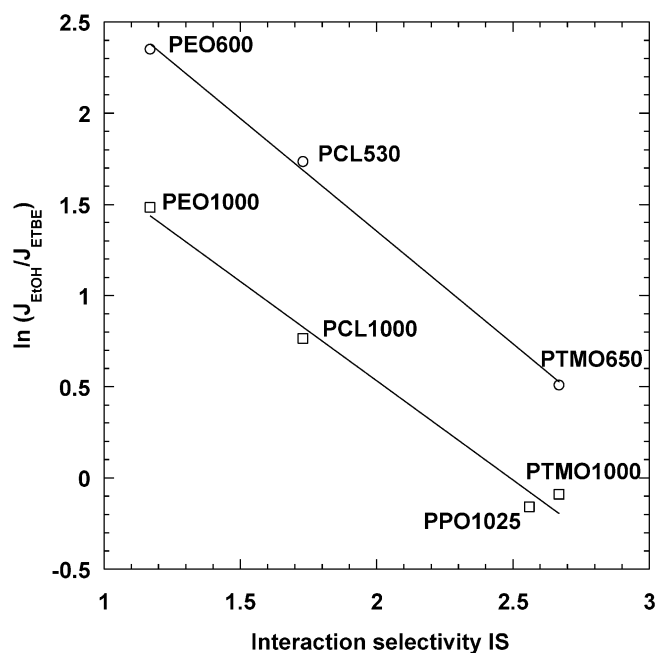
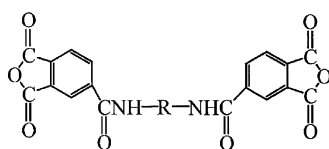


Fig. 15. Influence of the interaction selectivity  $IS = |\delta_X - \delta_{\text{EtOH}}|/|\delta_X - \delta_{\text{ETBE}}|$  on the pervaporation selectivity of polyurethaneimide block copolymers X/MDI/PMDA (stoichiometry 1/2/1) with different soft blocks X. Separation of the azeotropic mixture EtOH/ETBE (20/80 wt%) at 30 °C (reproduced with permission from Jonquière et al. [13], copyright © 2002 Elsevier Science).

obtained by substituting PMDA for dianhydride monomers containing amide functions [21]:



Those dianhydride monomers Z were synthesized from trimellitic anhydride acid chloride (TMAACl) and six aromatic diamines (i.e. 1,4-phenylene diamine, 2,2-bis(4-aminophenyl) propane, 4,4'-oxydianiline, 4,4'-methylene dianiline, 1,1-bis(4-aminophenyl)cyclohexane and bis(4-aminophenyl)-sulfone). Compared to the former related polyurethaneimide PTMO650/MDI/PMDA, the new block copolymers had an even more reinforced physical cross-linking owing to rigid hard blocks containing up to eight aromatic rings. This particular feature enabled to analyze the influence of the hard block chemical structure on their selective permeability to the azeotropic mixture EtOH/ETBE (20/80 wt%) at 30 °C. The former analysis revealed an interesting trend: changing the chemical nature of the hard block had almost no influence on the pervaporation selectivity whereas it greatly affected the total permeability. As way of example, the total permeability doubled when the junction  $R = \text{Ph}-\text{O}-\text{Ph}$  was replaced by the junction  $R = \text{Ph}$  while the pervaporate ethanol content remained almost unchanged (67 → 64 wt%). In addition to that interesting behavior which overcame the duality flux/selectivity

usually observed in pervaporation, the new PAUI block copolymers displayed very high permeability values as compared to those of polyamideimides so far described in the literature. A permeability as high as  $5.3 \text{ kg } \mu\text{m}/\text{h m}^2$  was even obtained at  $30 \text{ }^\circ\text{C}$  for the PAUI block copolymer with the junction  $R = \text{Ph}$ .

*3.2.2.2.2. Influence of the penetrant structural parameters.* Several approaches based on the polarity or solubility parameters were also reported for the analysis of the sorption and permeability of PUI block copolymers towards different *solvents*. The systems investigated associated a given polyurethaneimide block copolymer (i.e. PTMO650/MDI/PMDA, stoichiometry 1/2/1) with different mixtures EtOH/ether or alcohol/ETBE with a constant ether or alcohol penetrant activity at  $30 \text{ }^\circ\text{C}$  [13]. A comparative analysis showed that the solubility parameters were inappropriate to describe the behavior of systems differing in the nature of the ether species, owing to specific problems encountered for estimating the solubility parameters of ethers from additive group contributions or even thermodynamic data, problems that had been also mentioned by Hansen and Beerbower for other ethers in 1971 [207]. Highly contrasting with the solubility parameters, the polarity parameters proved to be highly powerful tools to correlate the sorption properties of systems differing in the nature of the penetrant. Linear relationships were first established to describe the *molar* swelling  $G_m$  of families of pure alcohols and ethers as a function of the solvent polarity parameter  $E_T(30)$  for the polyurethaneimide block copolymer PTMO650/MDI/PMDA at  $30 \text{ }^\circ\text{C}$  [67]. A systematic analysis of a great number of literature sorption data showed that the former original approach could be generalized to a wide range of polymer/solvent systems (i.e. involving polar and apolar polymers and solvents) [67]. When the sorption of binary liquid mixtures EtOH/ether or alcohol/ETBE were considered in the same conditions, the same type of linear relationships were obtained for the *partial molar* swellings of ethers or alcohols [13]. However, the sorption selectivity could generally not be simply related to the penetrant polarity parameter owing to strong sorption synergy effects which involved cooperative sorption of both species. Moreover, the correlative analysis of the pervaporation properties of the same systems as a simple function of the penetrant polarity parameter usually failed because, as expected, this simple thermodynamic parameter was not able to account for both thermodynamic and kinetic effects which were involved in the pervaporation mass transfer of penetrants with different polarities and molecular sizes [13].

### 3.3. Polyamides

Polyamide block copolymers described in the literature generally combine rigid polyamide hard blocks (e.g. PA6, PA11, PA12 or mixed hard blocks PA6/PA12) with flexible polyether soft blocks. Depending on the nature of their polyether soft block (i.e. PTMO or PEO), polyamide block copolymers can be either hydrophobic or hydrophilic. Their very strong physical cross-linking, good film-forming ability and great structure variability has led to a wide range of permeability investigations and several related patented applications.

#### 3.3.1. Permeability to pure vapors or liquids

Water vapor permeation through polyamide block copolymers has been widely investigated by the Elf Atochem Company (now Atofina) which took advantage of their high water permeability to develop a wide range of patented applications based on their commercial PEBAX<sup>®</sup> copolymers [208,209].

In 1990, the waterproof breathable PEBAX<sup>®</sup> films were for instance patented for high performance clothing, medical or surgical textiles or gloves, and under-roof film protection [210]. New developments based on the selective water permeability of PEBAX<sup>®</sup> block copolymers are still in progress. High

performance packaging films for conserving fresh produce (e.g. fruit, vegetables, cheese or meat) were recently described by Frey et al. based on the selective permeability of PEBAX towards water vapor and carbon dioxide [211]. In 1999, the OSMOFILM<sup>®</sup> technology [212] was also developed by the French Company Alyzee (i.e. a subsidiary company of Biotel [213]) for clean and low cost drying using PEBAX<sup>®</sup> closed bags (i.e. OSMOBAG<sup>®</sup>). At the end of the year 2001, a worldwide operating license has been acquired by Atofina for this innovative drying technology with a wide range of applications in various industries (e.g. food drying or controlled storage, chemicals and pharmaceuticals industry, waste limitation and control, etc.) [214].

Moreover, in order to improve the mechanical, surface or optical properties of films made of pure PEBAX<sup>®</sup> while retaining their high water permeability, polyamide block copolymers have also been developed by different industrial companies in various systems like blends, multi-layer films and films containing inorganic particles with several patented applications in high performance packaging [215, 216], waterproof breathable wind resistant textile [217], agriculture [218], and the medical field [219–221].

The experimental data obtained for water permeability through highly permeable films of polyamide block copolymers strongly depended upon the conditions of measurement, as clearly shown, for example, by the permeability data reported by Flesher for different standard methods [210]. Very recently, this fact has been thoroughly discussed by Nguyen et al. who have clearly shown the strong limitations of usual standard methods (i.e. ASTM E96 E and ASTM E96 BW [222,223]) for the measurement of water permeability through highly permeable PEBAX<sup>®</sup> films and proposed pervaporation as an alternative measurement method with the obvious advantage of well-determined mass transfer boundary conditions [224]. Therefore, a global comparison between the different literature data for water permeability through polyamide block copolymers is not an easy task.

Even if it still suffers from limitations inherent to the standard method used for the water permeability measurement, Table 4 has the merit of compiling the water permeability data [210] measured according to the *same* standard method (i.e. NF G52-019 [225,226]) for PEBAX with the same polyamide hard blocks PA12 and different soft blocks PTMO or PEO. The PTMO-based PEBAX<sup>®</sup> (i.e. PEBAX<sup>®</sup> of first generation) displayed water permeability in the range of 0.2–2.3 kg  $\mu\text{m}/\text{m}^2 \text{ h}$ , depending on the

Table 4

Water vapor permeability (kg  $\mu\text{m}/\text{m}^2 \text{ h}$ ) of various poly(ether-*block*-amides) PEBAX<sup>®</sup> with polyamide hard blocks PA12 and soft blocks PTMO or PEO (adapted from Ref. [210])

PEBAX <sup>®</sup>	$W_{\text{SB}}$ (wt%)	Film thickness ( $\mu\text{m}$ )	$J$ (kg $\mu\text{m}/\text{m}^2 \text{ h}$ ) <sup>a</sup>
<i>PTMO-based PEBAX<sup>®</sup> (PEBAX<sup>®</sup> of first generation)</i>			
PTMO650/PA5000	12	18	0.20
PTMO1000/PA4000	20	18	0.23
PTMO1000/PA2000	33	18	0.62
PTMO2000/PA2000	50	18	0.96
PTMO2000/PA850	70	30	2.3
<i>PEO-based PEBAX<sup>®</sup> (PEBAX<sup>®</sup> of second generation)</i>			
PEO1500/PA4500	25	18	2.7
PEO1500/PA1500	50	18	4.0

<sup>a</sup> Permeability measured according to the standard method NF G52-019 [225,226].

polymer composition. From the composition data reported by Flesher [210], we found an exponential variation of the water permeability as a function of the soft block content for this family of PEBAX<sup>®</sup>:

$$\ln J \text{ (kg } \mu\text{m/m}^2 \text{ h)} = -2.144 + 4.3W_{\text{SB}} \quad (r = 0.9964, 5 \text{ data points})$$

Even though the lack of a complete set of experimental data did not enable the same analysis for PEO-based PEBAX<sup>®</sup>, the influence of the polymer soft block content on their water permeability appeared very strong. The water permeability of the PEBAX<sup>®</sup> of second generation almost doubled when the polymer soft block content increased from 25 to 50 wt%. For the same soft block content, the PEO-based PEBAX<sup>®</sup> were much more permeable towards water than the PTMO-based PEBAX<sup>®</sup> (e.g. four times more permeable for a polymer soft block content  $W_{\text{SB}}$  of 50 wt%), reflecting the very strong influence of the chemical nature of the soft block on the water mass transfer. As expected, the hydrophilic PEO soft blocks enabled a very significant improvement in the water vapor transmission rate and thus the breathable character of the PEBAX films.

Based on a gravimetric analysis of the sorption transient regime using an automatic electro-microbalance, Rezac et al. also reported the sorption and diffusion coefficients for pure water and pure methanol through rather thick films (thickness of about 400  $\mu\text{m}$ ) which were obtained by melt extrusion of PEBAX<sup>®</sup> of first generation (i.e. PEBAX<sup>®</sup>2533, PEBAX<sup>®</sup>3533, PEBAX<sup>®</sup>5533, PEBAX<sup>®</sup>6333) [227]. Quite surprisingly for block copolymers, the water and methanol sorption coefficients were almost independent of the polymer PTMO content. In the same conditions, the diffusion coefficients of water and methanol were shown to decrease exponentially with the inverse fractional free volume of the polymer, defined as the ratio of the specific free volume to the observed specific volume, with correlation coefficients  $r$  of 0.996 and 0.993 for water and methanol, respectively [15]. The permeability coefficients were then estimated as the product of the sorption and diffusion coefficients. Unlike the rather poor exponential correlation that had been initially reported (i.e. correlation coefficients  $r$  of 0.966 and 0.990 for water and methanol, respectively), we found from the tabulated experimental data that the permeation coefficients were in fact linearly correlated to the polymer soft block content with much better correlation coefficients  $r$  (i.e.  $r = 0.9975$  and  $0.9982$  for water and methanol, respectively). This fact is worthy of mention because it disagrees with the related exponential correlation that we obtained for the water vapor permeability data reported by Flesher for PEBAX<sup>®</sup> of first generation [210]. Nevertheless, the work of Rezac and John clearly showed that these polyamide block copolymers could be used to extract methanol from contaminated air in the pulp and paper industry, with the limitation of a simultaneous water extraction in case of wet air [15].

PEO-based PEBAX copolymers (i.e. PEBAX 4011 (PEO/PA6,  $W_{\text{SB}} = 59$  wt%), PEBAX 1074 (PEO/PA12,  $W_{\text{SB}} = 55$  wt%) were also evaluated for ‘ultrafiltration’ (most likely nanofiltration) asymmetric composite membranes by Nunes et al. [228]. Dense top layers of PEBAX as thin as 0.15  $\mu\text{m}$  were obtained on PVDF porous membranes as confirmed by scanning electron microscopy, AFM and gas permeation measurements. The best compromise between water permeability and membrane cut-off was obtained for PEBAX 4011 with a water permeability of 6.4  $\text{l/m}^2 \text{ h bar}$ , very close to that obtained with the commercial Amicon YM30 cellulose membrane. However, the membrane with the PEBAX top layer was much less susceptible to fouling than the Amicon YM30 membrane, which is a determining advantage for ultrafiltration of oil/water emulsion wastes.

### 3.3.2. Permeability to hydro-organic mixtures

**3.3.2.1. Extraction of volatile organic compounds (VOCs) from water.** PTMO-based PEBAX<sup>®</sup> are hydrophobic polyamide block copolymers which have been widely investigated for the recovery of VOCs from water with several related patented applications [229–231]. Unlike PDMS which is a purely hydrophobic material, the PEBAX<sup>®</sup> of first generation combine hydrophobic PTMO soft blocks with fairly polar hydrophilic groups (i.e. ester and amide). This particular feature let anticipate some kind of compromise in the hydrophobic/hydrophilic balance that would be particularly welcome for the extraction of rather polar VOCs from water.

Morin and Thompson first investigated the pervaporation of dilute alcohol (1 and 5 wt%)/water solutions using PEBAX<sup>®</sup> 3533, PEBAX<sup>®</sup> 4033 and PEBAX<sup>®</sup> 5533 [3]. For a given PEBAX<sup>®</sup> membrane, the permeability and selectivity decreased in the following order: *i*-PrOH > EtOH > MeOH. That order corresponded to an increase in alcohol polarity which was clearly detrimental to the alcohol recovery by the hydrophobic PEBAX<sup>®</sup> membranes. Moreover, we found from the tabulated pervaporation data that the total permeability increased exponentially with the polymer PTMO content (i.e.  $W_{SB}$ ) for the different membranes, alcohols and feed compositions tested. Fig. 16 shows this trend for one set of examples. A striking and unusual fact was the concomitant pervaporate enrichment in alcohol, which enabled a double gain on permeability and selectivity by simply increasing the polymer soft block content. Very recently, Sampranpiboon et al. also reported the properties of PEBAX<sup>®</sup> 3533 membranes for the pervaporation of *iso*-propanol aqueous solutions with higher alcohol contents (from 10 to 40 wt%) and revealed a coupling effect in favor of water which was thus detrimental to the

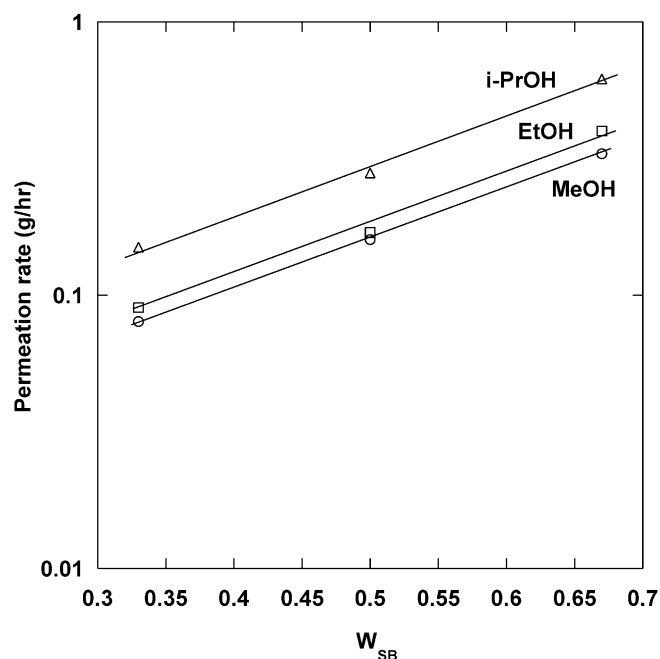


Fig. 16. Influence of the polymer soft block content on the total permeation rate of PTMO-based PEBAX<sup>®</sup> polyamide block copolymers for the pervaporation of dilute alcohol (5 wt%)/water solutions (from the polymer composition and permeation data reported by Morin and Thompson [3]).

*iso*-propanol recovery in this high concentration range [232]. In the same order of idea, Bøddeker et al. compared PEBAX<sup>®</sup> 40 with PDMS and a polyetherurethane (whose chemical structure was unspecified) for the recovery of butanol isomers from dilute aqueous as typically encountered in fermentation broths [24]. For a given alcohol concentration in the feed solutions ( $C_{\text{alcohol}} = 1 \text{ wt}\%$ ) and as discussed in Section 3.1.2.1.2 on the properties of PU block copolymers, the PEBAX<sup>®</sup> permeability and selectivity both increased with the alcohol polarity (i.e. in the order *tert*-BuOH, 2-BuOH, *iso*-BuOH, *n*-BuOH) (Table 1). Moreover, the highest values of the productivity factor were systematically obtained for the GKSS PEBAX<sup>®</sup> 40 membrane, reflecting the best compromise in terms of selective permeability which was obtained with this polyamide block copolymer irrespective of the butanol isomer.

Volatile organic esters like ethyl acetate, ethyl propionate or ethyl butyrate are model aroma compounds with fruity flavors that can be easily recovered from saturated aqueous solutions by pervaporation using PTMO-based PEBAX<sup>®</sup> membranes as shown by Kaddour Djebbar et al. [14,233]. For a given membrane, the total permeability decreased in the order ethyl acetate > ethyl propionate > ethyl butyrate whereas the enrichment factor towards ester,  $\beta$ , increased very significantly. A further interpretation of those results would certainly require the ester activity be evaluated for the corresponding ester saturated aqueous solutions. Nevertheless, a systematic analysis of the selective permeability of PTMO-based PEBAX<sup>®</sup> differing in their PTMO soft block content revealed that the ratio of the number of ether groups to the total number of ether and amide groups, called thereafter according to the authors ‘ether unit content’ for the sake of simplicity, was a key parameter for the selectivity and flux. The ester pervaporate content varied linearly with the ether unit content and the total permeability also increased linearly but with two different slopes. The partial permeability values displayed also the same trend with a sharp increase at the same critical ether unit content of 73% (corresponding to a polymer soft block content of about 50 wt%). That very particular behavior was ascribed to a phase inversion in the polyamide block copolymer, the highly permeable polyether phase becoming the continuous phase above that critical value. However, a systematic comparison of the properties of the PTMO-based PEBAX membranes with those of PDMS membranes in the same conditions revealed better flux and selectivity for PDMS [14]. In a related work which investigated the pervaporation features of PEBAX<sup>®</sup> 3533 membranes for the recovery of ethyl butyrate (i.e. a pineapple aroma compound) from much dilute aqueous solutions, Sampranpiboon et al. showed as expected that both permeability and selectivity increased with the feed ester content for the concentration range of 0–900 ppm [232].

PTMO-based PEBAX<sup>®</sup> membranes were also assessed for the extraction from water of miscellaneous volatile organic solvents like toluene [234–237], acetone [238], and halogenated solvents (1,1,1-trichloroethane, methylene chloride) [235]. For these applications, PDMS membranes were generally performing better than the PEBAX<sup>®</sup> membranes. Moreover, the apparent permeability was usually strongly limited [234,235] by the phenomenon of concentration polarization which, depending on the conditions, occurs for the pervaporation of VOCs from dilute solutions through highly permeable and selective membranes [52,239,240].

**3.3.2.2. Recovery of high boiling species from water.** One of the striking features of hydrophobic PEBAX membranes is their ability to extract not only VOCs but also *high boiling species* from dilute aqueous solutions. The recovery of pure vanillin (boiling temperature of 285 °C) by pervaporation of aqueous solutions through GKSS PEBA membranes is an extreme example which clearly shows the potential of PEBAX membranes for this kind of challenging applications [26].



**3.3.2.2.1. Recovery of phenols.** The recovery of phenols from dilute aqueous solutions by PEBAX<sup>®</sup> membranes was thoroughly investigated with a strong contribution of Bøddeker and coworkers [236, 241–245] and patented [23,246]. As a way of example, Bøddeker et al. reported a total permeability of 60 g  $\mu\text{m}/\text{m}^2 \text{ h}$  and an enrichment factor  $\beta$  of 75 for the pervaporation of a dilute aqueous solution containing 100 ppm of phenol through a GKSS PEBAX<sup>®</sup> 40 membrane at 50 °C [236]. Raghunath and Hwang later found very close permeability data for a related investigation and pointed out the strong limitations imposed by concentration polarization for the recovery of phenol from dilute aqueous solutions (50–500 ppm) [234]. The boundary layer mass transfer resistance accounted for almost 65% of the total mass transfer resistance for the pervaporation of an aqueous phenol solution containing 370 ppm of phenol at 60 °C using a PEBA membrane (unspecified chemical structure) with a thickness of 50  $\mu\text{m}$ . Further experiments carried at higher phenol concentrations (typically  $C_{\text{phenol}} = 1\text{--}5 \text{ wt}\%$ ) revealed a very strong increase in the total permeability that easily reached values higher than a few kg  $\mu\text{m}/\text{m}^2 \text{ h}$  whereas the phenol pervaporate content remained fairly high ( $C' = 50\text{--}85 \text{ wt}\%$ , depending on the feed phenol concentration) [244,247,248]. Taking advantage of the former results, Bøddeker et al. demonstrated the feasibility of phenol recovery on a pilot plant scale using a 40 l batch of aqueous phenol solution with an initial phenol content of 2 wt%. Phenol depletion to 50 ppm was obtained within 24 h with an overall permeate recovery of about 10 kg/day with a total PEBAX<sup>®</sup> membrane area of 2.3 m<sup>2</sup> at 50 °C [244]. Moreover, other phenols (e.g. *o*-cresol, *p*-xylenol, *o*-nitrophenol, *o*-chlorophenol) were also easily recovered from water solutions using GKSS PEBAX<sup>®</sup> 40 membranes and the phenol mass transfer increased with a decrease in the phenol solubility in water (corresponding to an increase in the activity coefficient of the phenolic compound) [236]. Gross and Heintz recently reported sorption and diffusion coefficients of aromatics through PEBAX<sup>®</sup> membranes and confirmed the very good permeability of chlorinated and nitro-phenols [237,249]. The very high sorption of bisphenol A (about 66 times that of phenol) was also emphasized, leading to fairly close permeability values for phenol and bisphenol A despite the very low diffusion coefficient of bisphenol A.

**3.3.2.2.2. Recovery of aniline.** As could be expected from the former results on phenol, aniline [25, 237] can also be easily recovered from dilute aqueous solutions using PEBAX membranes. Meckl and Lichtenthaler emphasized the outstanding separation characteristics of a GKSS PEBAX<sup>®</sup> membrane for the extraction of aniline by pervaporation at 80 °C [25]. For an aqueous feed containing 5.5 wt% of aniline, the total flux reached 1.7 kg/m<sup>2</sup> h for a membrane active layer thickness of 70  $\mu\text{m}$  (note that it corresponds to an extremely high total permeability of 119 kg  $\mu\text{m}/\text{m}^2 \text{ h}$ ) and the selectivity was very high with a pervaporate aniline content of 90 wt%. In the same conditions, the total flux of a PDMS membrane (i.e. a reference organophilic membrane) was 9.2 kg/m<sup>2</sup> h for a membrane active layer thickness of 1  $\mu\text{m}$ . However, PDMS was much less selective, the pervaporate aniline content only reaching 22 wt%. An evaluation of the economics of a hybrid process combining pervaporation with liquid-liquid phase separation gave a fair advantage to the PEBAX membrane for the recovery of aniline from dilute aqueous solution ( $C_{\text{aniline}} = 3.5 \text{ wt}\%$ ) [25]. The sorption and diffusion data reported recently by Gross and Heintz confirmed the very high permeability of PEBAX<sup>®</sup> membranes to aniline, and pyridine was also found to permeate fairly easily through PEBAX<sup>®</sup> membranes even though to a much slighter extent (– 80%) than aniline [237].

**3.3.2.2.3. Recovery of aromas and flavors.** Aromas and flavors can be thermo-sensitive compounds with high boiling temperature. In this case, their recovery from aqueous solutions is not easily achieved by conventional techniques (e.g. distillation) and pervaporation could be a very good alternative operating at low temperature. Dettwiler et al. compared the performance of a PEBAX<sup>®</sup> membrane

(provided by SEMPAS Membrantechnik GmbH) with that of a GFT PDMS membrane for the recovery of acetoin (i.e. an aroma with butter flavor,  $T_{\text{eb}} = 140\text{--}144\text{ }^{\circ}\text{C}$ ) from a fermentation broth [250]. The PDMS membrane showed no selectivity for acetoin whereas enrichment factors higher than 2 were obtained for the PEBAX<sup>®</sup> membrane with real fermentation solutions. A simulation of a hybrid system coupling a fermentor with a pervaporation system equipped with a PEBAX<sup>®</sup> membrane showed that such low enrichment factors were yet enough to prevent the fermentation inhibition which usually occurs above a critical acetoin concentration in the bioreactor. In the same order of idea, Baudwot and Marin investigated the recovery of dairy aroma compounds from model aqueous solutions using GFT PDMS silicalite-filled membranes and GKSS PEBAX<sup>®</sup> 40 homogeneous membranes [251,252]. The PDMS membranes displayed higher flux and selectivity for 2,3-butanedione (also known as diacetyl, the major aroma compound used in margarine for its butter flavor,  $T_{\text{eb}} = 88\text{ }^{\circ}\text{C}$ ). However, the PEBAX<sup>®</sup> membranes were more selective ( $C' = 94\text{ wt}\%$  against  $59\text{ wt}\%$  for PDMS) and more permeable ( $\times 2.5$ ) to *S*-methylthiobutanoate (i.e. an hydrophobic aroma with cheese flavor,  $T_{\text{eb}} = 142\text{ }^{\circ}\text{C}$ ) for the pervaporation of an aqueous solution containing 15 ppm of the cheese aroma compound at  $30\text{ }^{\circ}\text{C}$ . As briefly emphasized earlier, pervaporation through PEBAX<sup>®</sup> membranes even provided an easy way of recovering natural vanillin (a particularly high boiling aroma,  $T_{\text{eb}} = 285\text{ }^{\circ}\text{C}$ ) directly from the acidified culture broth ( $C_{\text{vanillin}} = 0.6\text{ wt}\%$ ) during the biosynthesis of this aroma from natural precursors (i.e. eugenols) [26]. The vanillin flux was about  $10\text{ g/m}^2\text{ h}$  for a GKSS PEBAX<sup>®</sup> 40 membrane of  $100\text{ }\mu\text{m}$  at  $65\text{ }^{\circ}\text{C}$  and vanillin was obtained as crystalline needles of high purity (higher than 99%), irrespective of the concomitant water flux which by-passed the crystalline product without affecting its purity.

### 3.3.3. Permeability to purely organic mixtures

To the best of our knowledge and quite surprisingly, publications on the permeation of purely organic mixtures through polyamide block copolymer membranes are extremely scarce in the literature.

In 1991, Sheng tested more than 20 different polymeric membranes for the separation of 1,1-dichloroethane (DCE)/1,2,2-trichloroethylene (TCE) mixtures by pervaporation [253]. Amongst all the polymers under evaluation, PEBAX<sup>®</sup> copolymers were the only ones to withstand exposure to DCE/TCE mixtures and to show a selectivity for DCE. However, the enrichment factor was much too low (i.e.  $\beta_{\text{max}} = 1.2$  for  $C_{\text{DCE}} = 0.2\text{ wt}\%$ ) to enable a potential application of PEBAX<sup>®</sup> membranes for this separation. A very few other works investigated the properties of PEBAX<sup>®</sup> membranes for the challenging separation of aromatics from aliphatics. Sorption experiments as well as the simulation of pervaporation selectivity from sorption and diffusion data showed that a GKSS PEBAX<sup>®</sup> membrane (unspecified structure) was fairly selective towards aromatics over aliphatics for mixtures of benzene, cyclohexene and cyclohexane but to a lesser extent than a Bayer PU membrane (unspecified structure) in the same conditions [35,254]. Nevertheless, certain PEBAX<sup>®</sup> membranes could be very promising for the removal of aromatics from aliphatics as shown by recent data reported by Roizard et al. for an unspecified polyetheramide block copolymer [255]. A very high permeability ( $40\text{ kg }\mu\text{m/m}^2\text{ h}$ ) and a good selectivity ( $C'_{\text{toluene}} = 63$ ;  $\beta = 3.15$ ) was obtained during the pervaporation of a mixture toluene (20 wt%)/heptane at  $80\text{ }^{\circ}\text{C}$ .

### 3.4. Block copolymers containing polysiloxane segments

PDMS is usually considered as one of the best organophilic polymers for the extraction of a wide range of VOCs from water [140,243] and PDMS membranes can even be purchased from different

suppliers for this particular purpose [150]. Nevertheless, PDMS is a very soft rubber with rather poor mechanical properties. This strongly limits the thickness of the defect-free dense PDMS layer that can be obtained and, eventually, the fluxes of the PDMS composite membranes. Block copolymers containing PDMS segments could be a good alternative to PDMS. By providing a physical (rather than chemical) cross-linking of the PDMS blocks, they could offer an interesting way of improving the polymer mechanical properties while maintaining a certain polymer solubility in organic solvents which is another advantage for membrane casting. However, despite the promising features of block copolymers containing polysiloxane segments, systematic investigations on their permeability towards vapors or liquids were reported only rarely.

#### 3.4.1. Poly(urethane or urea)siloxanes

Takegami et al. compared different polyurethaneureasiloxanes PDMS/MDI/1,4-BD, obtained from  $\alpha$ - $\omega$ -diaminopropyl PDMS telechelic oligomers with increasing molecular weights, with chemically cross-linked PDMS networks for the pervaporation of ethanol/water mixtures at 40 °C [256]. All of these polymeric materials differed in the average molecular weight of their PDMS segments between (physical or chemical) cross-links. The membranes permeated ethanol selectively and the separation factor  $\alpha_{\text{EtOH/water}}$  increased with the molar mass between cross-links  $M_c$ , for PDMS segments containing less than 50 dimethylsiloxane units. For longer PDMS segments, the separation factor reached a plateau at a value of about 8 for the pervaporation of an aqueous feed mixture containing 16.5 wt% of ethanol. Moreover, the separation factors of a polyurethaneureasiloxane and a chemically cross-linked PDMS network with the same molar mass between cross-links were identical. This suggested that the PUU hard blocks played exactly the same role as the cross-links in the chemically cross-linked PDMS networks. However, a complete comparison between both polymer families would have required the knowledge of the corresponding total fluxes which were not reported for the polyurethaneureasiloxane block copolymers. Later on, Schnabel et al. described the synthesis and properties of non-fluorinated and fluorinated polyureasiloxane block copolymers for the removal of the four butanol isomers from aqueous solutions [257]. The non-fluorinated polyureasiloxanes (i.e. PDMS/TDI, PDMS/TXDI (1,3-bis-(1-isocyanato-1-methylethyl)benzene) and PDMS/IPDI) displayed improved mechanical properties and higher permeability than simply chemically cross-linked PDMS networks, with identical or slightly higher selectivity for the pervaporation of aqueous butanol solutions with a constant butanol activity of 0.1 at 40 °C. This clearly confirmed the interesting potential of PDMS-based polyureas for the extraction of butanol isomers from water. The fluorinated polyurethaneureasiloxanes were synthesized using fluorinated diol chain extenders (i.e. aliphatic: 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diol, or aromatic: 1,4-bis-(2-hydroxyhexafluoro-isopropyl) benzene). Owing to their high number of fluorine atoms, the fluorinated block copolymers were expected to be more organophilic than their non-fluorinated homologues. However, beyond all expectation, the experimental permeability data showed that the fluorinated block copolymers were less permeable and less selective than the related non-fluorinated copolymers in the same conditions. The understanding of this unexpected behavior would require further investigation.

#### 3.4.2. Polyimidesiloxanes

Compared with polyurethanesiloxanes, polyimidesiloxane block copolymers should offer an even stronger physical cross-linking of the PDMS soft blocks owing to their more polar and rigid imide hard blocks. As way of example, Schauer et al. described the selective permeability of polyimidesiloxanes

with rather complex polyimide hard blocks and PDMS soft blocks [258]. A systematic analysis of the pervaporation of water–ethanol mixtures at 25 °C showed that these copolymers displayed selectivity very close to that of the corresponding polyimide homopolymer, and were thus water selective, for PDMS contents less than 20 wt%. For higher PDMS contents, an inversion of selectivity occurred and the polyimidesiloxanes permeated ethanol preferentially with separation factors almost identical to those of PDMS membranes over the whole range of ethanol concentration. The corresponding permeation fluxes were not reported. Nevertheless, the very sharp transition observed for the PDMS content of 20 wt% was ascribed to a percolation phenomenon which involved the formation of a continuous PDMS phase within the polyimidesiloxane material above this critical content in PDMS. The influence of the PDMS content on the selective permeability towards water–ethanol mixtures was a little more complex for other polyimidesiloxanes as described by Lai et al. [259]. For polyimidesiloxanes PDMS/BTDA with PDMS contents ranging from 55 to 80 wt%, the permeability increased sharply whereas the selectivity decreased very significantly, the most permeable membrane showing almost no selectivity owing to an excessive polymer swelling. Reinforcing the polymer physical cross-linking by extending the hard block with an aromatic chain extender (i.e. ODA) enabled to maintain both the high permeability and the membrane selectivity towards ethanol. However, the separation factors remained fairly low ( $\alpha_{\max} = 1.7$ ) which corresponded to a pervaporate ethanol content of 16 wt% for a feed mixture containing 10 wt% of ethanol at 80 °C. Therefore, the pervaporation selectivity through the polysiloxaneimide block copolymers PDMS/BTDA/ODA was much less than what would have been obtained from a single distillation stage of the feed mixture ( $C^{\text{LVE}} \cong 40$  wt%). The influence of the hard block structure on the selective sorption and permeability of polyimidesiloxane block copolymers was also analyzed by Chang et al. for polymers obtained from an  $\alpha$ - $\omega$ -diaminopropyl PDMS telechelic oligomer ( $M_n = 800$ ) and different aromatic dianhydrides (i.e. BTDA, 6FDA and PMDA) [260]. The sorption of dilute organic aqueous solutions containing 0.05 wt% of ethanol, methylene dichloride, ethyl acetate, trichloroethylene or toluene was independent of the hard block chemical structure. However, it increased very significantly in intensity and selectivity with the hydrophobicity of the organic species (i.e. in the following order EtOH < CH<sub>2</sub>Cl<sub>2</sub> < trichloroethylene < toluene). Almost identical conclusions were drawn for pervaporation in the same conditions, despite a slight influence of the hard block chemical structure on the membrane permeability towards trichloroethylene and toluene. For both solvents, the pervaporation flux increased as expected in the following order BTDA < PMDA < 6FDA. Worthy of mention, the pervaporation selectivity of these block copolymers was extremely high for trichloroethylene ( $C' > 99$  wt%) and toluene ( $C' = 99.8$  wt%) for total permeability values in the range of 4.05–7.2 kg  $\mu\text{m}^2$  h at 30 °C.

### 3.4.3. Hybrid block copolymers containing siloxane segments

More than simply providing a way of reinforcing the very soft PDMS rubber, block copolymers containing a PDMS phase have also allowed recently a better understanding of the influence of the polymer morphology on the selective permeability of those complex materials thanks to the very good work of Miyata et al. [16,261]. Following the related precursor works of Barrie and Munday [262] and Kerres and Strathmann [263] who had shown the very strong influence of the polymer morphology on the selective permeability of block and graft copolymers and complex cross-linked materials, respectively, for systems out of the scope of the present review, Miyata et al. focused on the pervaporation of aqueous ethanol solutions ( $C_{\text{EtOH}} = 10$  wt%) using block and graft copolymer membranes containing PDMS and PMMA segments whose choice was certainly determining for the

success of the work [16]. PDMS is indeed a very soft rubber selective towards ethanol whereas PMMA is a water-selective glassy polymer; both of the chosen segments thus display strongly antagonistic features in terms of permeability and selectivity. As expected, the block and graft copolymers were water selective for PDMS contents less than a critical value which depended upon the type of copolymers investigated. For the block copolymers PMMA-*block*-PDMS, the threshold was obtained at 55 mol% of PDMS whereas it was inferior (i.e. 35 mol%) for the graft copolymers PMMA-*graft*-PDMS (Fig. 17). Above the critical PDMS content, the membranes were selective towards ethanol and the pervaporate ethanol content sharply increased with the PDMS content to reach the selectivity of a pure PDMS membrane for copolymers containing more than 80 mol% of PDMS. The total permeability followed almost the same trend with a very sharp increase above the critical PDMS content for the block copolymers whereas a less acute linear increase was observed for the graft copolymers. Clearly, block and graft copolymers with the same PDMS content in the range of 35–55 mol%, and thus the same chemical composition, displayed neither the same selectivity nor the same permeability. These interesting experimental results indicated that the chemical composition was not the single parameter governing the selective permeability which was also controlled by the material morphology in a significant way. A thorough morphology analysis based on different complementary techniques showed that a microphase inversion, leading to the formation of a continuous PDMS phase, occurred for a PDMS content of 55 and 35 mol% for the block and graft copolymers, respectively. This corresponded to a percolation point for which the membrane permselectivity sharply increased up to values very close to that of the pure PDMS phase (Fig. 17). In order to enhance the mobility of the polymer chains and facilitate their reorganization, thermal annealing of the block and graft copolymers was also investigated

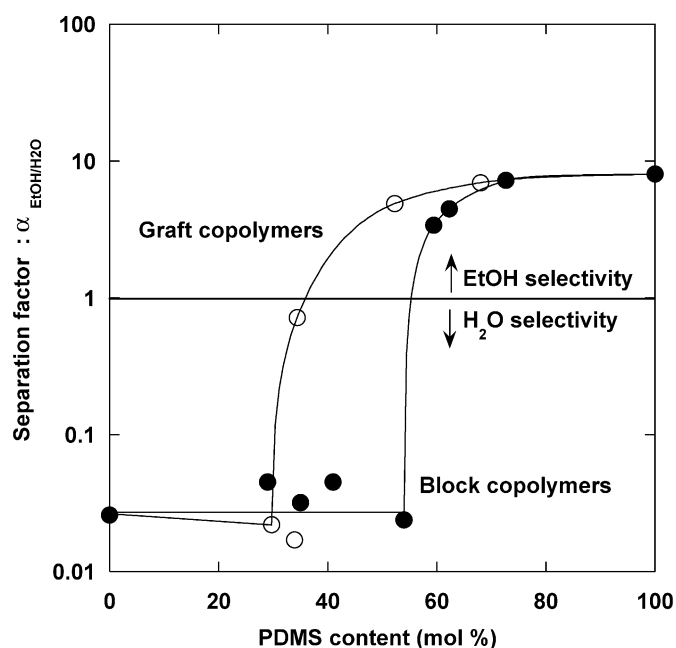


Fig. 17. Influence of the PDMS content on the separation factors for PMMA-*block*-PDMS and PMMA-*graft*-PDMS membranes for the pervaporation of aqueous ethanol mixtures containing 10 wt% of ethanol at 40 °C (reproduced with permission from Miyata et al. [16], copyright © 1999 American Chemical Society).

for controlling the material microphase separation [261]. Its influence was not significant for the graft copolymers but the percolation point of the annealed block copolymer membranes occurred at a much lower PDMS content (i.e. 37 mol%), very close to that of the graft copolymer membranes.

### 3.5. Hydrocarbon block copolymers and related materials

Systematic permeability studies on hydrocarbon block copolymers are really scarce in the literature as compared with those on other block copolymers (e.g. PU, polyimides and polyamides). Nevertheless, one of their interesting features is to have brought another insight into the morphology of these particular materials. Sorption, diffusion and permeability of small molecules through hydrocarbon block copolymers or related materials are indeed usually sensitive to small changes in the block copolymer morphology and have been used as fundamental indicators to investigate their phase separation and block mobility.

#### 3.5.1. Permeability to pure vapors or liquids

The first related works focused on the properties of common thermoplastic elastomers, with polystyrene and polybutadiene (or polyisoprene) blocks, towards pure alkanes (cyclohexane or *n*-hexane) [2,264,265]. As a way of example, Chiang and Sefton [264] reported that the diffusion of cyclohexane vapors through SBS elastomers deviated from the Fickian behavior that is usually observed with conventional rubbers like the related homopolymer polybutadiene. That particular feature was ascribed to the heterogeneous morphology of the SBS thermoplastic elastomer which restricted the mobility of the polybutadiene soft block owing to the constraints imposed by the rigid impermeable polystyrene blocks. In the same order of idea, Odani et al. later compared the sorption and diffusion of *n*-hexane for styrene–butadiene block copolymers with almost the same chemical composition but different morphologies [2]. One of the polymer (i.e. SBS) was made of PS rods embedded in a PB matrix whereas the other one (i.e. (SB)<sub>n</sub>) was a series of alternating lamellae of PS and PB. Unlike the former sample which displayed general features much closer to those of homogeneous rubbers, the lamellar block copolymer led to sorption values that were slightly higher (typically +20% for a solvent activity of 0.5) than what would have been expected from its polybutadiene content. Moreover, the diffusion study of the lamellar sample revealed relaxation phenomena with two-stage transient sorption curves that are very typical of non-Fickian behavior and confirmed the former conclusion of Chiang and Sefton on related systems [264]. In another work, French and Koplos investigated the sorption of cyclohexane in triblock copolymers with styrene endblocks and midblocks of butadiene, isoprene or hydrogenated butadiene [265]. Despite the strong limitations imposed by the quartz crystal microbalance used for the sorption measurements in the transient regime (e.g. captor response linear only for sorption typically less than 20 wt%), an analysis of the tabulated sorption data shows that, for the same styrene content, polybutadiene and polyisoprene midblocks led to the same cyclohexane sorption isotherms. Hydrogenation of the polybutadiene midblock increased very slightly (+15%) the copolymer affinity towards cyclohexane at high activity. Quite surprising, the sorption isotherms of cyclohexane in styrene/isoprene/styrene thermoplastic elastomers did not depend upon their styrene (i.e. hard block) content between 15 and 30 wt%, at least for the common activity range investigated ( $a < 0.5$ ). Mateo et al. also recently discussed the influence of UV cross-linking of SBS elastomers on their permeability towards pure organic solvents (i.e. chloroform and toluene) [266]. Two times higher for chloroform than for toluene, the sorption was analyzed on the basis of the Flory–Rehner theory which enabled to calculate

the molar mass between cross-links  $M_c$  for different times of UV exposure. The values obtained for  $M_c$  did not depend upon the solvent tested and, as expected, sharply decreased with the UV exposure time. The diffusion of both solvents was characterized by a systematic slight deviation from the Fickian behavior. That deviation decreased when the cross-linking degree increased, which was related to a decrease in microphase separation, corresponding to an improved homogeneity of the block copolymer sample.

So far, the properties of hydrocarbon block copolymers have been discussed for systems in which the permeation of pure molecules mostly occurred through a rubbery phase (e.g. polybutadiene, polyisoprene, etc.). For those block copolymers, mass transfer was usually limited by the glassy phase which restricted the soft block mobility. Another interesting work reported by Odani et al. described the very particular case of related block copolymers in which the penetrant diffusion mainly took place through the *glassy* phase rather than through a rubbery phase [267]. Sorption, diffusion and permeability of pure methanol was investigated for two diblock copolymers, poly(2-vinylpyridine)-block-polystyrene and poly(2-vinylpyridine)-block-polyisoprene, with almost the same content in the glassy phase P2VP (i.e. about 50 wt%). Methanol is a good solvent for the homopolymer poly(2-vinylpyridine) while being almost insoluble in polystyrene and polyisoprene, thus mostly transferring through the glassy phase P2VP in those diblock copolymers. For both copolymers, the sorption of methanol was slightly higher (+10 wt%) than what would have been expected from their P2VP content, in the same way as what had been reported by the same authors for the sorption of *n*-hexane in styrene–butadiene block copolymers [2]. The deviation from purely Fickian behavior was small and the methanol average diffusion coefficient was slightly lower for poly(2-vinylpyridine)-block-polystyrene and much greater ( $\times 10$ ) for poly(2-vinylpyridine)-*block*-polyisoprene as compared with the homopolymer poly(2-vinylpyridine). The same observation was also made for the methanol permeability and indicated the positive role played by the elastomeric block polyisoprene, unlike the glassy block polystyrene which again penalized the penetrant mass transfer.

### 3.5.2. Permeability to vapor or liquid mixtures

Styrene/butadiene/styrene triblocks and related styrene-based block copolymers were also reported for the recovery of alcohol's or VOCs from water, based on their selective permeability towards hydro-organic mixtures [268–270]. Sun and Ruckenstein described the properties of triblock copolymers styrene/butadiene/styrene and styrene/butadiene-ethylene/styrene for the challenging extraction of methanol, ethanol and 2-propanol from aqueous solutions by pervaporation [268]. Unlike what could have been anticipated from their hydrophobic features, the uncross-linked polymeric membranes were poorly permeable and absolutely not selective towards the organic species. The block copolymer cross-linking using divinylbenzene led to an unexpected simultaneous increase in both selectivity and flux for ethanol aqueous solutions, most likely by stabilizing a more disorganized structure than the initial morphology which was characterized by a long-range order. However, the influence of the cross-linking degree was fairly complex, leading to an optimum for about 10 wt% of divinylbenzene, critical value above which a simultaneous decrease in selectivity and flux was observed. That optimum could result from a compromise between the morphology disorganization and the rigidifying of the block copolymer during the chemical cross-linking, both factors having antagonistic influences on permeability. As expected for purely hydrocarbon membranes, the pervaporation performances improved with a decrease in alcohol polarity (i.e. in the following order MeOH < EtOH < 2-PrOH). Dutta and Sikdar further investigated a SBS copolymer for the recovery of pure and mixed VOCs (i.e. trichloroethane

(unspecified), trichloroethylene and toluene) from water [269]. The sorption increased in the order toluene < TCE < TCA while the average diffusion coefficient increased in a slightly different order toluene < TCA < TCE. The selective permeability was not affected when the organics were mixed in model aqueous mixtures, revealing an absence of any coupling effect in those dilute systems. However, the phenomenon of concentration of polarization played an important role in the overall mass transfer, in the same way as what had been reported for the recovery of organics from dilute aqueous solutions through highly selective and permeable membranes [52,239,240]. Another interesting approach was described by Schauer et al. who tailored the selective permeability of hydrogenated polystyrene-block-polyisoprene copolymers by functionalizing the polystyrene block with different types of polar or apolar side groups (i.e. alcohol: CH<sub>2</sub>OH, ester: COOCH<sub>3</sub>, trimethylsilyl Si(CH<sub>3</sub>)<sub>3</sub>) [270]. Composite membranes made of the unsubstituted hydrogenated polystyrene-block-polyisoprene were poorly permeable and slightly selective towards water for the pervaporation of aqueous mixtures containing either ethanol or 1,4-dioxane at 25 °C. Moreover, for feed mixtures containing more than 50 wt% of 1,4-dioxane, the membranes were much too swollen to withstand the pervaporation conditions. The highly polar hydroxymethyl substituents were responsible for an even higher swelling of the membranes which soon damaged even for low organic concentrations of the feed mixture. The slightly less polar ester substituents COOCH<sub>3</sub> led to much higher permeability while the selectivity towards water was almost the same as that of the unsubstituted copolymer for low organic contents ( $C < 30$  wt%). In contrast, the trimethylsilylated block copolymer produced an inversion of selectivity, very typical of a strongly organophilic membrane, with the same total permeability as the parent copolymer.

#### 4. Conclusion

An analysis of the literature of the past 40 years shows the richness and variety in publications about permeability of block copolymers and their related elementary phenomena of sorption and diffusion.

The systematic investigation of permeability of block copolymers with closely related structures has contributed to a better fundamental understanding of their permeability.

Different factors were shown to be determining for the mass transfer of small molecules through block copolymers. The chemical nature, polarity and molecular weight of the hard blocks usually govern the hard block aggregation. These parameters have a great impact on the physical cross-linking of the polymeric material and its ability to withstand exposure to strong solvents. Most generally, hard blocks are impermeable towards small molecules and act as simple cross-links to reduce the overall permeability. The influence of the soft blocks is determining for permeability. It is generally much more complex and involves different factors like their chemical structure and polarity, the weight ratio of soft blocks to hard blocks, the phase separation and material morphology. For systems with closely related structures, structure–property relationships have been found to correlate the permeability with the soft block copolymer structure in a quantitative way. By revealing important parameters governing the (sometimes selective) mass transfer of small molecules through polymeric materials, such structure–property relationships can be considered as precious tools for the design of new polymeric materials with improved permeability properties.

Many patents on permeability of block copolymers also reflected a strong industrial interest in related applications. Block copolymers are indeed ‘tailor-made’ polymeric materials which usually allow a fairly good control of their properties for a wide range of systems including packaging, barrier materials,



bio-materials for controlled release or encapsulating membranes, high performance impermeable breathable clothing, protective films, permselective membranes, etc. A sharp increase in the related patents for the past 10 years certainly shows the strong potential of block copolymers to take up several current challenges in the medical, chemical and petrochemical fields.

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