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Investigations of rubbery copolyimides for the preparation of asymmetric pervaporation membranes

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ABSTRACT

It is known that membrane technologies may have a major role to play in the development of environmental-friendly processes, either in gas or liquid separations. In liquid separations, one of the challenging issues is to get membranes with suitable separation properties able also to survive to the exposure of liquid solvents at various temperatures. Aromatic polyimides are known to exhibit a very good stability to a great number of solvents, but their permeability are low because of their rigid carbon skeleton and of their low available free volume; so their uses are mainly limited to gas separations or to filtration processes (MF, UF). To broaden the application area of polyimides in liquid separations, we have prepared and studied the properties of a block ether aromatic copolyimide series where the ether soft block acts both as a selective and a permeable block; we describe attempts to get asymmetric polyetherimide (PEI) membranes having molecular separation properties using various experimental conditions of dry/wet phase inversion. The PEI physical properties and morphologies (SEM) are reported together with their pervaporation properties for water–ethanol separation. The PV results showed that rubbery copolyimides can lead to promising asymmetric membranes for liquid–liquid separations.

Keywords: Rubbery copolyetherimides; Phase inversion; Asymmetric PEI membranes; Pervaporation

1. Introduction

Polyimides are well known as polymer materials and they have been used since the last three decades as specialty polymer in numerous applications [1]. One of the reasons is the outstanding physical properties of aromatic polyimides (PI): the polymer backbone induces high thermal stability, high electrical insulating properties and good chemical resistance in addition to mechanical toughness [2]; therefore PI have been widely employed in various technical fields such as coatings, composite matrices, adhesives, fibers, foams moldings, and also in the field of membranes [3,4].

From 1950 to 1970, the interest for the polymeric membranes mainly remained in laboratories and almost no application emerged. It is the preparation of asymmetric membranes demonstrated by Loeb and Sourirajan in the sixties [5] that definitively pushed the polymeric membranes towards the application field and helped them to be ranked as industrial processes. Indeed the sudden progress caused by the phase inversion technology gave rise to the production of new membranes combining better thermal and mechanical

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properties than natural polymers with attractive transport properties, i.e. high permeability and selectivity. However it turns out from practice that the more selective membranes usually have a low permeability and vice versa.

This was clearly established by Robeson [6] who first correlated the gas permselectivity data of numerous polymers, and then theoretically justified by Freeman [7]. This trend, existing both for glassy and rubbery polymers, is also true for the separation of liquid mixtures like in pervaporation (PV). Hence, once a selective polymer material has been identified for a given separation, it is always a challenge to find an adequate route to get high flux membranes preserving the initial selectivity.

This challenge is even more complicated for liquid separations like PV than for gas separations, because usually some significant swelling of the membrane occurs during the permeation [8,9]. PV process is recognized to be an alternative technology for liquid separations when more classical technologies are either not efficient (too close boiling points, thermal sensitive compounds) or too expensive; for instance, breaking azeotropes can be an easy task by PV [10] and also an energy-saving process [4,11]. PV can be used either for organic liquid separations [12–15] or for dehydration of organic liquids [16]. According to the separation type, the permeate or the retentate can be valorized [8]; in addition, an interesting feature of PV is that it is a clean technology which does not emit pollutant [17].

To tackle the permeability-selectivity problem, we decided to use aromatic polymers like polyimides, which are well-known to be solvent resistant; this approach has been previously reported with oligooxyethylene [18,19] or oligosiloxane blocks [20]. The objectives was to prepare asymmetric membranes thanks to the glassy properties of the rigid block, and to modify the aromatic PI structure by the incorporation of a water-selective block, in order to get asymmetric PV membranes able to combine selectivity and high permeability. However, it was not possible to predict the exact influence of this second type of block on the preparation of asymmetric membranes or to know if a molecular separation could be achieved in PV with such asymmetric membranes.

This work explores this synthesis approach, using α,ω-alkoxyether diamines, i.e. Jeffamine® ED-series, as precursor blocks for selective water permeation. Both dense and asymmetric copolyether-imide membranes (PEI) were prepared with different ether-aromatic block contents; the inversion phase procedure was tuned to favor the formation highly porous sub-structure retaining on its top side a tight film as thin as possible under the conditions used. The PV properties of these membranes were compared for the separation of ethanol-water mixture chosen as a feed model.

2. Materials and method

2.1. Materials

Jeffamine® ED-600 (Jeff), an α,ω-alkoxyether diamine of average Mw = 600 g, was purchased from Aldrich; others monomers 4,4′-oxydianiline (ODA), 1,2,4,5-benzenetetracarboxylic anhydride (PMDA) were purchased from Acros Organics Inc. and Fluka Chemical Corp. N,N-dimethylformamide (DMF) was obtained from Aldrich, purified and stored over molecular sieves (4 Å). Commercial poly(amic acid; PAA) 11 wt% solution in NMP/aromatic hydrocarbon was purchased from Aldrich.

2.2. Membrane preparation

2.2.1. Preparation of dense polyetherimide (PEI) and Kapton™ polyimide (PI) membranes

PAA and PEI membranes were prepared from Jeff, PMDA and ODA with three different Jeffamine®—ODA ratios (i.e. 0.4, 0.5 and 0.6 Jeff) at concentration of 25 to 30 wt% in DMF, following the two step procedure; Kapton™ (PI) was prepared from the commercial PAA in NMP/aromatic hydrocarbon solution. The PAA precursors were casted onto glass plates or Teflon using a film applicator. Then, the films were dried at 80°C for 12 h and subsequently the final dense PEI membranes cured under vacuum at 100°C, 150°C and 200°C for 1 h at each temperature while Kapton™ dense membranes were obtained with a thermal treatment up to 300°C.

2.2.2. Preparation of asymmetric PEI and PI membranes

The so called wet phase inversion method was used to induce the formation of homogenous asymmetric membranes with water as a non-solvent. The PAA solution was casted onto a glass substrate using a film applicator before immersion in a water bath to produce phase inversion. The studied parameters were the polymer dope concentration and the temperature of non-solvent bath used to induce the phase inversion.

2.3. Membrane characterizations

2.3.1. Scanning electron microscopy (SEM)

SEM was used to characterize the morphology of the asymmetric membranes. The samples were prepared by freeze cut in liquid nitrogen and metalized with gold using polaron sputter coater with magnetron head before SEM examination (Gold sputtering device: Jeol JFC-11-E, SEM: Jeol JSM-T330A). The registered pictures show the membrane morphology views of cross-sections.

2.3.2. Thermo-mechanical property

Tensile strength of PEI and PI were measured by using an Instron Tensile Tester 5569 (universal tensile testing machine). The mechanical properties of PEI prepared were determined using test specimens (length 23 mm, width 8 mm, area 50 mm^2). The test specimens were prepared as the standard method. These specimens are cut from PEI and PI films with thicknesses of ≈200 μm. Young modules, tensile stress and elongation at break reported are the average of several measurements.

2.3.3. Thermo-gravimetric analysis (TGA)

TGA was conducted with a SETARAM, Setsys TG-12 System at a heating rate of 10°C/min. The thermal stability and the loss of 10 wt% of the PEI and Kapton™ as a function of temperature were evaluated using a magnetic microbalance of high accuracy 2.10^{-6} mg. The PEI samples were cut from the prepared membranes and dried under vacuum. The TGA measurements were carried out in nitrogen atmosphere from 30 to 1,000°C at a heating rate of 10°C/min.

2.3.4. FTIR characterizations

The PAA, the PEI and Kapton™ synthesis steps were analyzed by FT-IR spectroscopy using a Thermo Nicolet 370 (FT-IR) using ATR method. The main attributions of the wavenumbers (cm^{-1}) are as follows: PAA 2,400–3,200: O-H (COOH) and NH_2; 1,660, 1,700, 1,710, 1,735, 1,775, 1,780 and 1,340, 1,370, 1,380: C=O group vibrations; 1,600: CONH amide deformation; PEI. 1,500: C-N; 1,230, 1,240, and 1,260: C-O-C; 811 and 720: CO imide.

2.3.5. Swelling properties

The membrane swelling degrees were determined under steady-state conditions. Well dried samples were precisely weighed and then immerged into liquids at room temperature until swelling equilibrium was reached. From time to time, the swollen samples were removed from solvent, quickly wiped of excess solvent with tissue paper and immediately weighed in a close flask. The initial sample weight recorded before immersion is noted as Wd and the final sample weight noted as Ws.

The swelling degree at equilibrium was calculated according to the formula:

$$\text{Swelling degree } (\%) = 100 \cdot (\text{Ws} - \text{Wd})/\text{Wd}.$$

2.4. PV experiments

PV experiments with mixtures of ethanol/water were carried out to determine the separation properties of the dense and asymmetric membranes under steady state conditions, with a downstream vacuum of ≈1 mmHg and at constant feed temperature. The permeate was condensed in liquid nitrogen traps and its composition was determined by gas chromatography (TCD detector, accuracy ±2%); the permeate enrichment and the permeation flux (J) were measured for several membrane samples to get averaged results. The specific membrane area was 2.1×10^{-3} m^2 and the feed tank capacity 100 cm^3. The effect of the temperature on the membrane performances was studied in the range of 30–60°C. For each mixture studied, experiments were carried out for several days. The PV performances were evaluated by the permeate selectivity β and the total permeation flux, J. The selectivity β is defined as:

$$\beta = C_p/C_f$$

where C_p (H_2O permeate enrichment, in weight) and C_f (H_2O feed concentration, in weight) are the weight fractions of water in the permeate and in the feed, respectively.

The permeation flux was calculated using the expression:

$$J = Q/(A \cdot T_t)$$

where Q (kg) is the total mass of the permeate collected through the effective area of membrane A (m^2) and during the time T_t (h), once the state has been reached. The PV experiments set-up is shown in Fig. 1.

3. Results and discussion

There are many different methods to prepare aromatic polyimides, the most popular method being the two steps procedure, i.e. the reaction of an aromatic dianhydride (1 equivalent) with an aromatic diamine (1 equivalent) to form a soluble PAA, followed by its thermal imidization to polyimide. For example, Kapton™, one of the very typical aromatic polyimide, is prepared from PMDA and ODA, leading to the

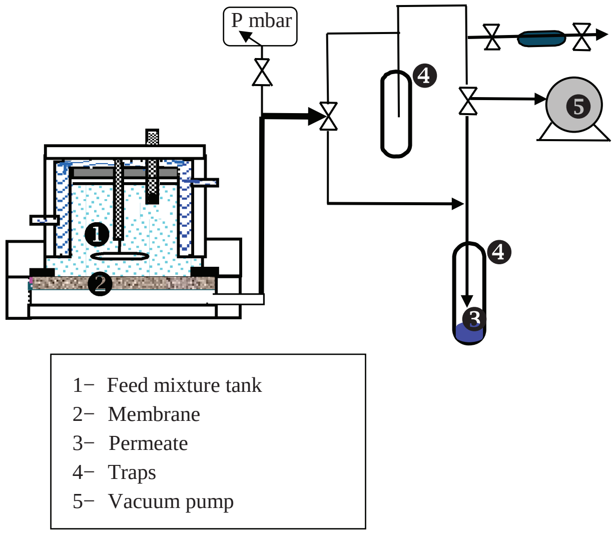


Fig. 1. Schematic diagram of the pervaporation experimental set-up.

corresponding PAA; then Kapton™ films can be subsequently obtained by thermal treatment. In this work we introduce alkoxy soft blocks in the basic PI structure to modify both the physico chemical properties of the polyimide structure and the permeation properties, the later one being known to be very small with fully aromatic polyimide. The prepared dense and asymmetric PEI membranes had stoechiometric amounts of Jeffamine® (Jeff) ranging from 0.4 to 0.6, the other amine used being the aromatic ODA. The physical features of this set of PEIs were studied comparatively to Kapton™ characteristics, and the ability of these polymers to give asymmetric structure determined. The purpose was to prepare rubbery asymmetric copolyimides with a self supported thin dense layer on the topside, thanks to the rigid properties of the aromatic part of the PEI structure.

However, if asymmetric morphologies can be easily formed by phase inversion methods with glassy polymer such as Kapton™, the effect of the soft blocks in polyimide structure on the ability of preparing such membranes was unknown, not predictable and not yet reported to our knowledge.

3.1. Membrane characterizations

3.1.1. Infrared spectra (FT-IR)

To follow the proper course of the PEI and PI synthetic steps, FTIR was used. The IR spectra obtained for dense PAA (Jeff-PMDA-ODA), dense and asymmetric PEI and dense PI membranes are presented on Fig. 2. These spectra exhibit the characteristic peaks expected for the PAA (Fig. 2a) and for the polyimide formations (Fig. 2b, c). These features indicate that the phase inversion procedure does not inhibit the polymer formation nor the subsequent imide cyclization carried out by thermal treatment, i.e. up to 200°C for PEI membrane and to 300°C for Kapton™ membrane.

3.1.2. Mechanical properties

Previous studies have shown that polyimides prepared with PMDA and ODA monomers (i.e. Kapton™ type) are endowed with a high Young modulus and a high tensile strength; conversely such polyimide have low elongations at break values [21–23] (Table 1).

To improve the permeability and the water affinity properties of these rigid aromatic polyimides, various contents of Jeff were incorporated in the first synthetic step to give rise to PEI structures. Mechanical behavior of PEI was recorded at ambient temperature leading to the characteristic parameters gathered in the Table 1: Young modulus determined from the initial slope, the tensile stress and the elongation at break. To evaluate the impact of the soft block on the mechanical properties of PEI, data related to Kapton™ are also given.

Furthermore, it was found that the Young modulus and the tensile strength of the PEI membranes decreased with increasing Jeff content in PEI membranes, while the elongation was increased. Comparison of the mechanical behavior of Kapton™ shows an increase of Young modulus and a decrease in the elasticity. The evolution of the mechanical properties are really impressive: compared to Kapton™ the elongation at break one is about one order of magnitude higher whereas the Young modulus is one or two order of magnitude lower.

3.1.3. TGA

The thermal stability of PEI membranes and PI was determined by TGA and the results are given in the Table 2. Compared to Kapton™, PEI exhibit two degradation steps starting at about 250–280°C and 510°C (Fig. 3); clearly the first step can be related to the presence of the alkoxyimide block: going from PEI 0.4 Jeff to PEI 0.6 Jeff, the peak intensity increases as shown on the Fig. 4; among PEI, the PEI 0.4 Jeff has the higher degradation temperature. However, the degradation of the aromatic block of the PEI has the same starting temperature than the aromatic block of Kapton™, i.e. 510°C. At last the TGA results showed that the total weight loss at 800°C is also related to the Jeff content showing that the decomposition of the PEI gives more volatile species than the fully aromatic structure (Table 2).

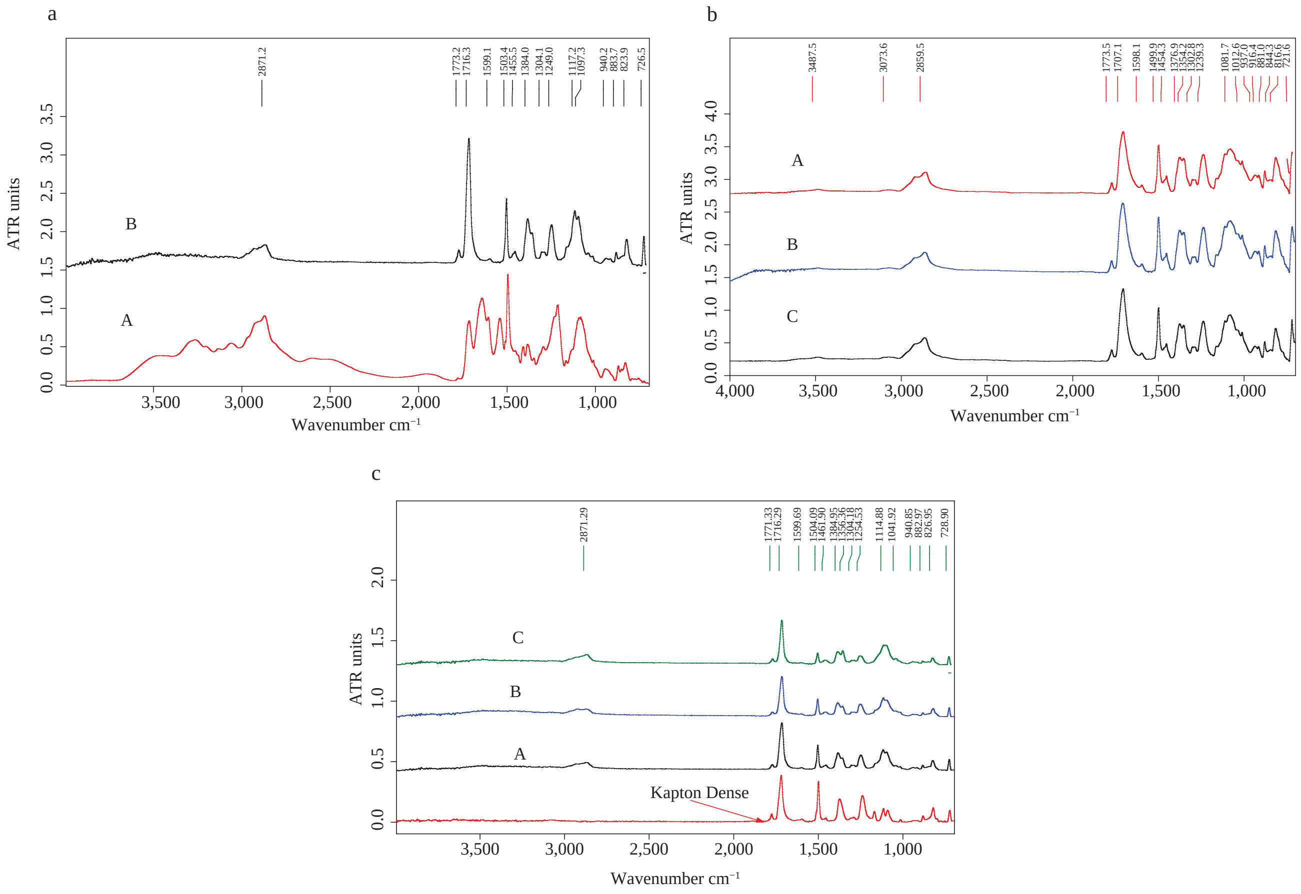


Fig. 2. a, b, c: Infra-red spectra for PAA, PEI and Kapton™ membranes. a. Infra-red spectrum for dense PAA (A) and PEI (B) dense membranes with 0.4 Jeff. b. Infra-red spectrum for dense PEI (A), asymmetric PEI 25PAA (B) and asymmetric PEI 30 PAA(C). c. Infra-red spectrum for dense Kapton™ and PEI dense membranes (A Jeff 0.4, B Jeff 0.5, C 0.6 Jeff).

3.1.4. Asymmetric membranes preparation

To get asymmetric membranes, PAA solutions were casted on glass substrate at room temperature. After casting (thickness 300 μm), the liquid film was allowed to concentrate for 1 min under room conditions; then the glass plate was immersed in the coagulation bath for one hour at least. This procedure led to the easy generation of asymmetric membranes when the PAA 0.4 Jeff was used. After drying of the asymmetric PAA film under room conditions, the final asymmetric PEI membrane was obtained by the thermal treatment, as already reported for the dense membranes preparation.

Effects of immersion bath temperature on preparation of asymmetric PEI membrane morphology are shown in Figs. 5 and 6 (membranes Mb-1 (30 wt% PAA) and Mb-2 (25 wt% PAA) in DMF). It was found that with asymmetric PEI membranes, the porosity increases with the increase of the immersion bath temperature. Raising the temperature increases mutual diffusivities between the non-solvent (water) and the solvent (DMF) in the casting solution during demixing process. At higher temperature, nucleuses of polymer-poor phase grow rapidly which consequently increases the formation of porous structure in the membrane leading to macrovoids. Conversely, the reduction of the temperature limits the speed of nucleus growth, giving rise to the formation of a large

Table 1
Mechanical properties of PEI and Kapton™ (present work and literature data)

Membrane	Young modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PI Ref. [21]	3.2	265	60.1
PI Ref. [22]	2.1	104.7	16
PI Ref. [23]	2.3	60.2	35
PI [this work]	1.4	66.8	16
PEI 0.4 Jeff	0.25	35.9	285
PEI 0.5 Jeff	0.1	15.7	287
PEI 0.6 Jeff	0.025	6.9	303

Table 2
TGA features of PEI membranes

Membrane type	T (°C) at 5% weight loss	T (°C) at 10% weight loss	Final degradation at 800°C (wt%)
PI (PMDA-ODA)	569	584	42
PEI Jeff/PMDA/ODA (0.4/1/0.6) dense	386	399	68
PEI Jeff/PMDA/ODA (0.5/1/0.5) dense	351	379	73
PEI Jeff/PMDA/ODA (0.6/1/0.4) dense	393	405	77

number of small nucleuses in every part of the cast film; hence a great number of little pores/voids are formed in the sublayer of the PAA membranes. Therefore, formation of macrovoids is prevented and denser PEI structures are obtained after cyclization as shown on Figs. 5 and 6. These results are in agreement with the literature [8,24].

For the others PAA having higher Jeffamine® contents, despite the variations of the phase inversion conditions, i.e. polymer dope concentration, concentration time, coagulation bath temperature, liquid film thickness, it was not possible up to now to prepare reproducible asymmetric films usable in PV experiments.

3.2. Separation properties

3.2.1. Swelling properties

Han et al. [25] reported that Kapton™ has a low water uptake; about 2–3 wt% at 20°C, and it was expected that the incorporation of alkoxyether groups (Jeff) would enhance the water uptake ability and consequently improved the water permeation properties.

The swelling degrees of PEI membranes having different contents of etherblock were compared to Kapton™ swelling in different solvents at ambient temperature; the swelling was calculated as the ratio of the liquid weight uptake per gram of dry polymer (Table 3). Whatever the liquid used, it was found that the swelling degree is strongly influenced by the content of Jeff incorporated in the PEI membranes; the more important effect is due to toluene, with a 10-fold increase for PEI 0.4Jeff for instance, whereas heptane has the lowest effect. In the case of water, the effect on PEI swelling degrees is also rather high and the values are 5–10 higher compared to Kapton™.

The increase of the hydrophilic degree of the PEI can be deduced from these measurements as well as a lower packing density compared to Kapton™, where the aromatic blocks act as physical crosslinker between

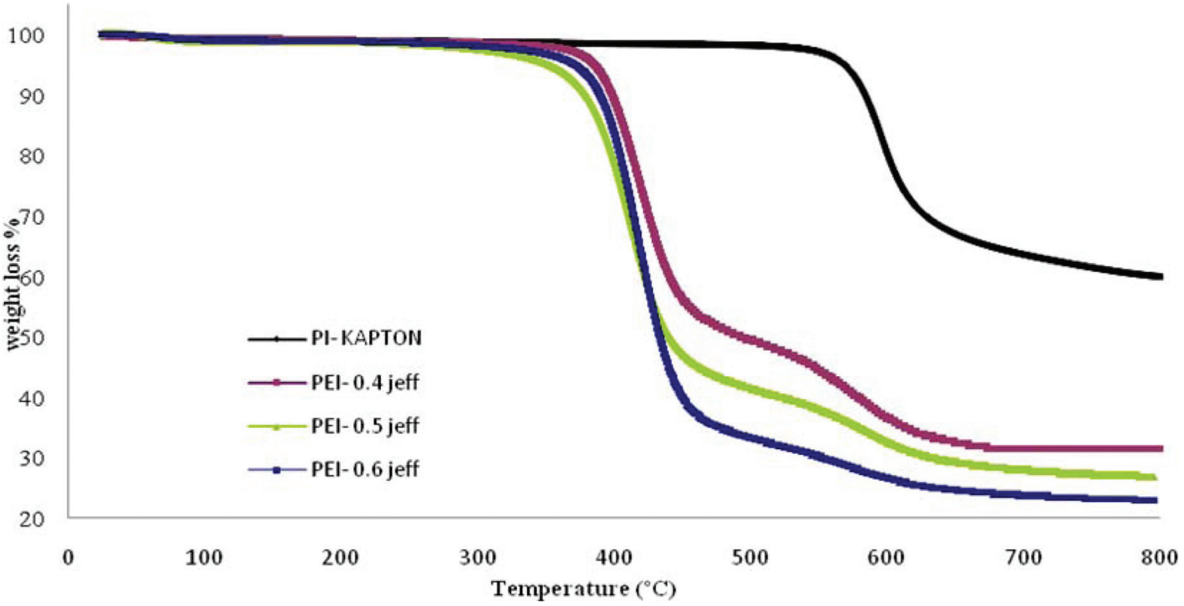


Fig. 3. TGA showing the membranes weight loss of PEI and Kapton™ (N2, heating rate: 10°C/min).

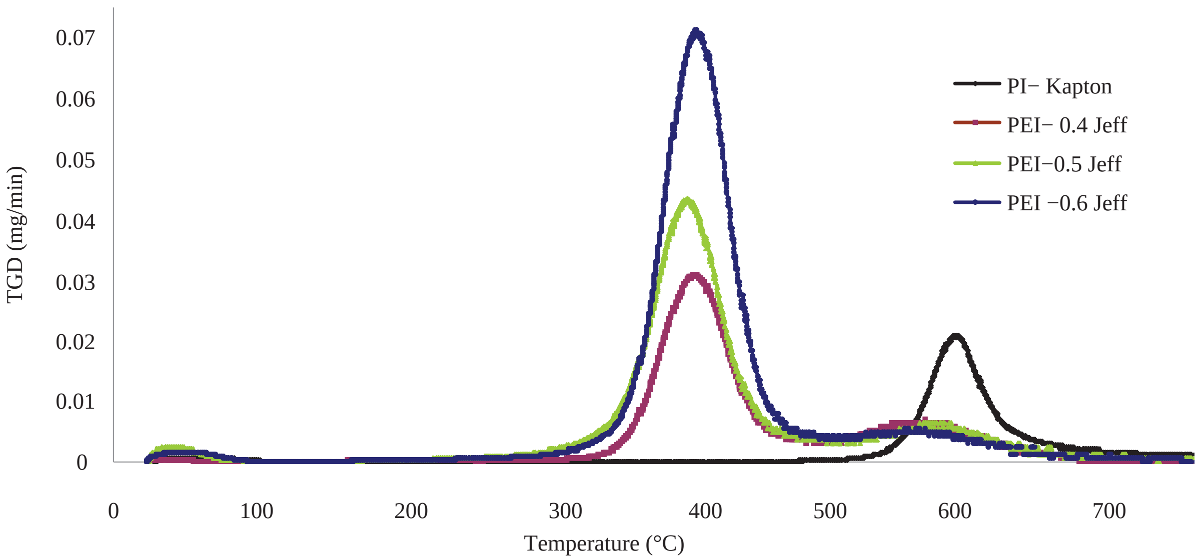


Fig. 4. Differential curves of the TGA signals of PEI and Kapton™. The influence of the Jeff content is very clear: the more Jeff, the higher rate of polymer degradation.

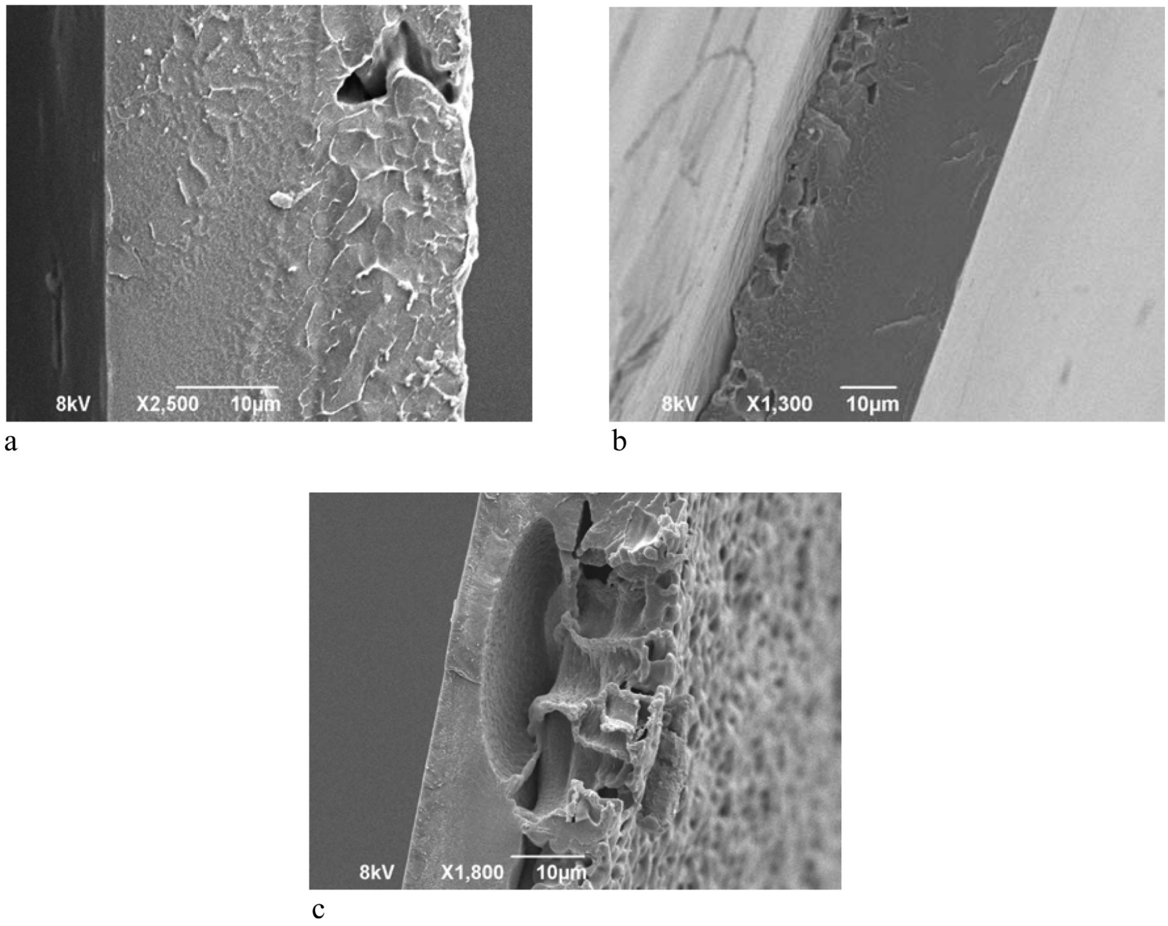
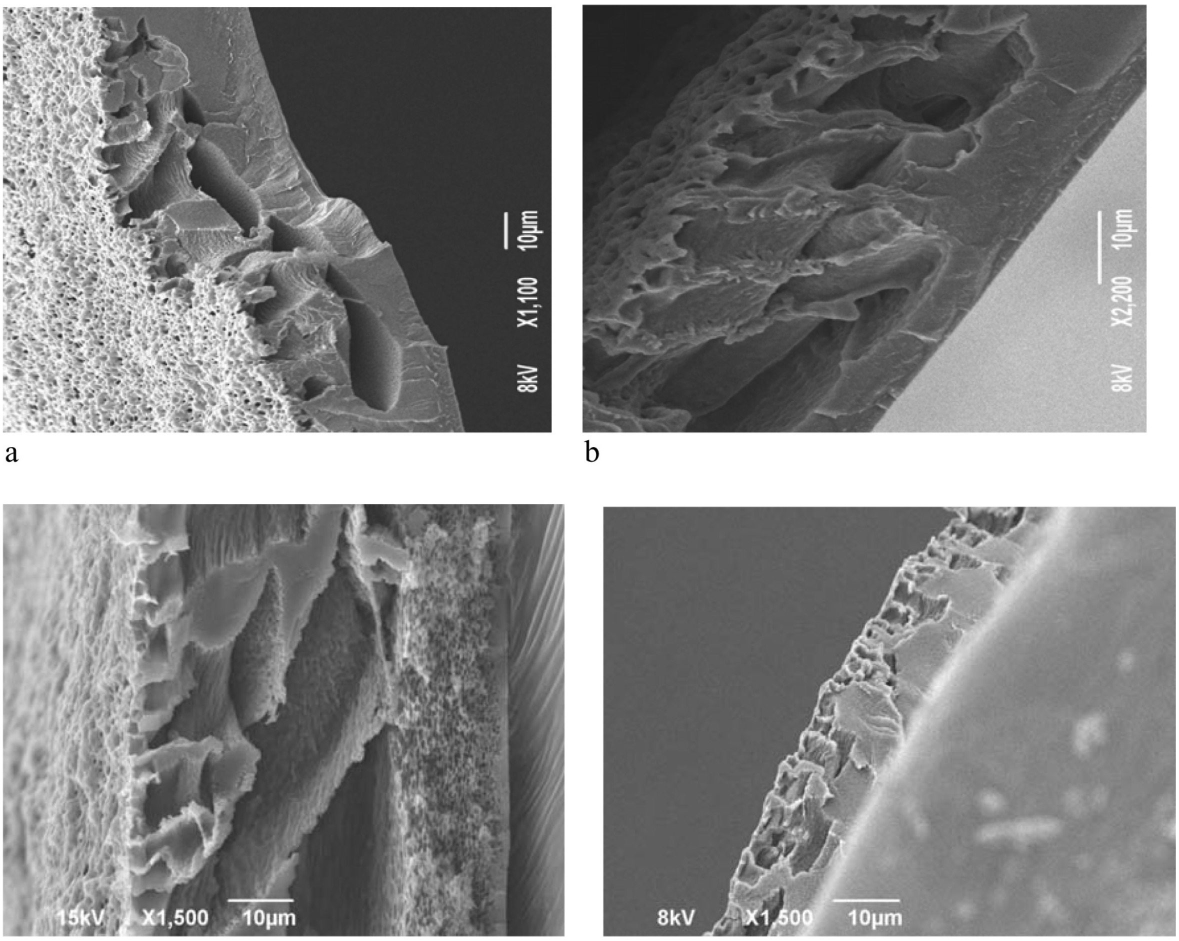


Fig. 5. Cross-section view of Mb-1 PEI asymmetric membrane 30 wt% PAA in DMF at immersion bath temperature 5°C, 7°C and 10°C. a. PEI membrane at immersion bath 5°C. b. PEI membrane at immersion bath 7°C. c. PEI membrane at immersion bath 10°C.



a b

c d

Fig. 6. Cross-section view of Mb-2 PEI membrane 25% PAA in DMF at immersion bath temperature 5°C, 7°C, 10°C and 20°C. a. PEI membrane at immersion bath 7°C. b. PEI membrane at immersion bath 10°C. c. PEI membrane at immersion bath 12°C. d. PEI membrane at immersion bath 20°C.

the polymer chains. As a consequence, it was clear that PEI membranes could be good candidates for applications requiring hydrophilic properties.

3.2.2. PV properties

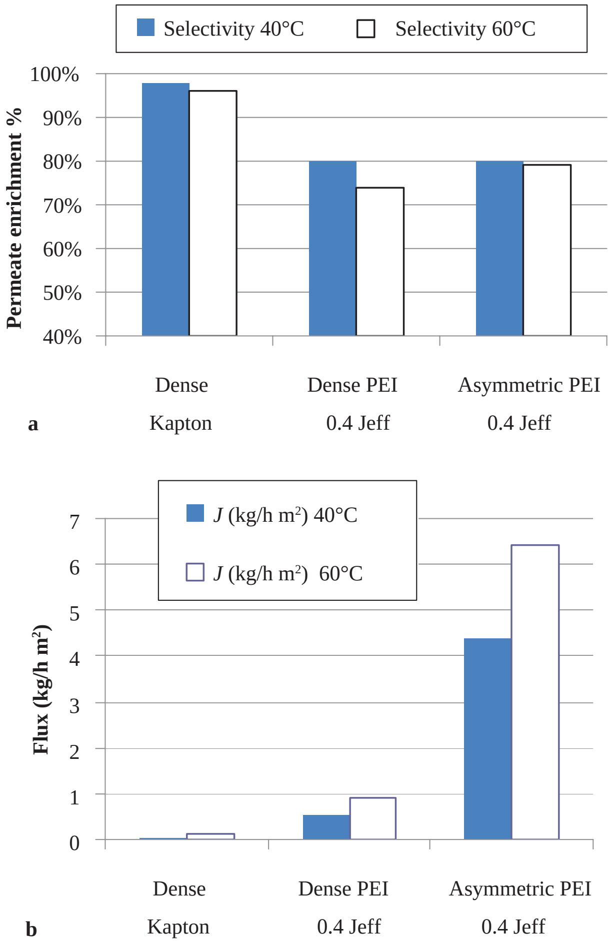
The PV experiments intended to know if it was possible to achieve molecular separation with the asymmetric PEI 0.4Jeff membrane (cf. Fig. 6c) keeping the selectivity close to that obtained with a dense PEI membrane, together with much higher flux. Water-Ethanol (50–50 wt%) mixtures were used to investigate the dense and asymmetric PEI and PI membranes performances and their PV temperature dependence in the range 30–60°C.

The PV results are presented the Fig. 7. First it should be underlined that all the PEI 0.4Jeff samples used were well stable during the PV experiments even at 60°C and long term PV experiments could be carried out to check the temperature dependence (up to 5 days).

The effect of membrane type and of membrane morphology on the selectivity, i.e. permeate enrichment is shown on the Fig. 7a. It should be noted that the fully

Table 3
Swelling measurements of Kapton and PEI for various solvents

		PEI: Jeff 600 content		
Solvents	Kapton	0.4 Jeff	0.5 Jeff	0.6 Jeff
Water	5%	16%	24%	31%
Methanol	6%	12%	14%	14%
Ethanol	3%	13%	13.5%	14%
Toluene	3%	20%	39%	55%
Heptane	0.5%	0.3%	0.9%	1.6%



Effect of membrane type on the permeate enrichments (a) and PV flux (b)

Fig. 7. a, b. PV results obtained with PI or PEI membranes either as dense or asymmetric membranes—feed mixture: 50 wt% water/ethanol (at 40°C and 60°C).

aromatic PI is much more selective for H_2O than the PEI membranes despite the fact that the water affinity of PEI is about three times higher than for the PI Kapton™ (Table 3). Two factors explain this result: first, the EtOH affinity is also higher for the PEI membranes than for the PI, resulting in lower intrinsic sorption selectivity; second, as far as PV deals with a binary mixture, it is known that a coupling effect can occur giving rise to a higher permeation rate than expected of the compound having the lowest membrane affinity; hence it is the combination of these two phenomena which led to the lower selectivity of PEI compared to PI. But one should note also that the PI flux is extremely low, about 15 times lower than PEI flux, meaning that dense PI membranes could not have any practical use ($J \approx 0.05$–0.1 kg/h m^2).

On the other hand, the H_2O permeate enrichment of the dense and of the asymmetric PEI 0.4Jeff membranes were almost the same, i.e. 80 wt% at 40°C. First these results mean the asymmetric membrane is really able to achieve molecular separation as well as the dense membrane does, showing that the phase inversion procedure used gave rise to the formation of a tight layer on the top of the asymmetric membrane.

The effect of the operating temperature on PV selectivity was at first glance rather conventional: the permeate enrichments recorded with PEI and PI membranes were smaller when the temperature was increased. This trend is well-known and has been reported many times in the literature [26]. The higher selectivity at lower temperature is explained by the lower coupling phenomena between H_2O and EtOH, that can be related to the lower plasticizing effects of the permeants; thus as the polymer free volumes are lower, the water permselectivity is favored.

But interestingly, it can be also noticed that the temperature increase led to a lower decrease of the selectivity recorded with the asymmetric membrane than with the dense one, respectively 79% and 74% at 60°C. Considering the classical solution–diffusion model this finding could not be predicted. So we can only postulate that phase inversion conditions do not lead to the formation of a thin dense layer having exactly the same PEI microphase separation structure than the dense layer prepared by a slow solvent evaporation procedure; but up to now, no analytical proofs of this hypothesis could be obtained.

Considering now the PEI flux obtained at 40 or 60°C (Fig. 7b), the results obtained were rather expected, showing a much higher flux of the asymmetric membrane up to ≈700% more (i.e. 4.4–6.4 kg/h m^2). But again, one can notice that the range of the temperature effect is different for the dense membranes (PEI or PI, 80% increase or more) and for the asymmetric one, for which the flux increase was relatively lower (only 40%). Hence these experimental results might also indicate that the structure of the dense top layer is not strictly the same for the two types of membranes. This phenomena could be related to the very different conditions prevailing to the formation of the two types of dense layers; for the homogeneous dense membrane, the structure is formed by slow solvent evaporation (DMF) where thermodynamic polymer chain rearrangements are possible to a large extent, i.e. until the Tg is reached, whereas in the other case, the structure of the dense layer is formed on the top of an asymmetric membrane obtained from a very fast polymer gelification due to the phase inversion conditions.

4. Conclusion

Phase inversion was found to be a suitable method to prepare asymmetric membranes from rubbery PEIs combining soft alkoxyether blocks (from Jeffamine®) and aromatic blocks (from ODA) after condensation with PMDA. Dense PEI membranes were easily obtained with various aliphatic/aromatic diamine ratios; with respect to the ODA-PMDA blocks, these membranes have a structural analogy with the Kapton™ structure.

Despite the various phase inversion conditions used, only the amine ratio 0.4/0.6 allowed the preparation of asymmetric membranes of good mechanical properties to be used further in PV. It was shown that the porosity of the membrane sublayers could be tuned according the initial polymer dope concentration and the temperature of the inversion bath. The FT-IR characterizations indicate that the PAA structures seem to be fully imidized to polyimide following the curing treatment which was limited to 200°C for PEI membranes; compared to the imidization temperature of Kapton™ i.e. 300°C, this lower value can be related to the presence of the Jeffamine® soft block of much smaller glass transition temperature. Nevertheless, the TGA analysis revealed that the PEI series had still a fairly good thermal stability, with degradation temperatures at 5 wt% loss in the range of 350–390°C.

The separation properties of the dense and asymmetric PEI 0.4Jeff were studied by PV with the water/ethanol mixtures, and the recorded permselectivity could be rationalized with the membrane swelling properties which were much higher than for Kapton™ for all the considered solvents. As for the dense membranes, it was first shown that the asymmetric membranes exhibited also molecular separation properties, leading to the selective water permeation from ethanol mixtures. It means that these asymmetric membranes combining rubbery alkoxy and rigid aromatic blocks in the polymer structure had a tight top layer. Compared to the dense membranes, the PEIs have obviously much higher flux, but also fairly good selectivity. Interestingly, the influence of the temperature on the PV performances seems to show that microstructure of the top layer of the asymmetric membrane is different from the dense one: when the temperature is increased, the flux increase is smaller and the selectivity almost unchanged; this finding must be related to the very different conditions prevailing to the formation of the two types of dense layer, i.e. slow solvent evaporation or very fast polymer gelification induced by phase inversion conditions.

Acknowledgments

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Symbols

C_p	weight fraction in the permeate (%)
C_f	weight fraction in the feed (%)
Wd	initial dry sample weight recorded before immersion (g)
Ws	final sample weight noted after immersion (g)
Q	total mass of permeate (kg)
A	effective area of membrane (m^2)
T_t	PV experiment duration (h)
J	total flux (kg/h m^2)

Abbreviations

SEM	scanning electron microscopy
PAA	poly(amic acid)
PI	aromatic polyimides such as Kapton™
PEI	polyetherimide
PV	pervaporation
ODA	4,4′oxydianiline
Jeff	Jeffamine® ED-600
PMDA	pyromellic dianhydride (1,2,4,5-benzenetetracarboxylic anhydride)
DMF	N,N-dimethylformamide

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