NRC Publications Archive Archives des publications du CNRC

Formation and thermal stability of BMI-based interpenetrating polymers for gas separation membranes

Kurdi, Jamal; Kumar, Ashwani

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version
acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien
DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1016/j.memsci.2006.01.024>

Journal of Membrane Science, 280, pp. 234-244, 2006

NRC Publications Archive Record / Notice des Archives des publications du CNRC :

<https://nrc-publications.canada.ca/eng/view/object/?id=02c2a0ba-d3c5-43fb-9a4c-53c48bdf626>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=02c2a0ba-d3c5-43fb-9a4c-53c48bdf626>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the
first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la
première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez
pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Formation and thermal stability of BMI-based interpenetrating polymers for gas separation membranes[☆]

Jamal Kurdi, Ashwani Kumar^{*}

*National Research Council of Canada, Institute for Chemical Process and Environmental Technology,
Montreal Road Campus, Ottawa, Ont., Canada K1A 0R6*

Received 24 March 2005; received in revised form 6 January 2006; accepted 13 January 2006

Available online 17 February 2006

Abstract

Semi-interpenetrating polymer networks (semi-IPNs) were prepared by sol–gel technique through in situ polymerization of bismaleimide (BMI) in thermoplastic polyetherimide (PEI) as well as in polysulfone (PSF). This synthesis route allows arresting thermoset/thermoplastic phase separation at an early stage by solidifying the semi-IPNs through membrane phase inversion. The phase separation could be observed visually in the casting solution or by optical microscope on the surface of the produced membranes. These semi-IPNs with a density lower than their thermoplastic base polymer allowed easier water penetration during membrane phase inversion. This led to improved membrane morphology that was confirmed by scanning electron microscopy. Membranes fabricated from these semi-IPN materials had thinner skin layers and longer straight fingers perpendicular to membrane surface. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) showed that these semi-IPNs membranes have improved glass transition temperatures but a lower thermal stability. However, at ambient conditions, these membranes with their improved structure and morphology showed superior gas separation characteristics compared to base polymers. For example, the permeance was increased by 12–15 times without a significant decrease in the selectivity of oxygen over nitrogen in air separation experiments. Crown Copyright © 2006 Published by Elsevier B.V. All rights reserved.

Keywords: Semi-IPN; BMI; PEI; PSF; DSC; TGA; Gas separation membranes

1. Introduction

Membrane-based separation is a rapidly growing green technology that has been commercially recognized in many industrial applications [1]. Most commercial asymmetric membranes are fabricated from engineering plastics using different techniques to obtain ideally ultra-thin skin layer having a high microporosity as well as selective gas permeation characteristics [2]. Additional requirements for membrane materials include ability to form flexible membranes, absence of defects, improved damage tolerance and durability under various operating conditions. It is hard to achieve all of the above characteristics and therefore improving membrane materials is still an active topic of research. In addition to this, the trade off between permeability and selectivity for most polymeric membrane materials

has to be overcome to increase productivity of gas separation membranes especially in some applications such as separation of oxygen from air [3].

Generally, most of the polymers require incorporation of additives to achieve desired characteristics for material performance [4,5]. Interpenetrating polymer networks (IPNs) introduced in the early 1960s, were successful in creating polymeric nano-scale blends having new extraordinary properties as reviewed elsewhere [6,7]. The importance of IPN synthesis has been recognized in engineering literature, patents and commercialized products since 1951 [8,9]. The concept of in situ polymerization within and through the structure of another polymer network as well as stabilizing this multiphase system was based on creating interpenetrating (i.e. physical interlocked or/and catenated) networks having multi-domains at supramolecular levels [8,9]. It was recognized that phase separation at macro-scale level that may arise from the mutual incompatibility inherent in multipolymer systems should be prohibited during formation, post-treatment, processing or/and end-use application in order to enhance IPN composite properties [10,11]. This was

[☆] NRCC No. 47870.

^{*} Corresponding author. Tel.: +1 613 998 0498; fax: +1 613 991 2384.

E-mail address: ashwani.kumar@nrc-cnrc.gc.ca (A. Kumar).

achieved by slowing down phase separation at an early stage at the onset of de-mixing through highly viscous solution by gelation or vitrification [12]. It was also reported that timing the two phenomena of gelation and phase separation is very important for governing the size of each domain in the polymeric network [8]. The concept of synthesis of IPNs seems to be useful for development of nano-size multiphase polymeric materials for gas separation membranes as it provides a distinct possibility to control composite material properties and morphology. However, in situ structuring and interfacial tailoring of IPNs is necessary to obtain desired properties and to overcome challenges such as defects in the fine structure [13], phase separation and incompatibility [10,11].

Bismaleimide (BMI) has been used successfully with many high performance thermoplastic polymers for forming semi-IPNs. For example, BMI/polysulfone semi-IPN was prepared from a casting solution of BMI, polysulfone and anionic initiator (1,4-diazabicyclo-[2,2,2]-octane) in *N*-methylpyrrolidone solvent. Thermal polymerization of BMI was achieved to gel the cast film. However, at magnification of 1200 the optical microscopy of the cured films showed phase separation [14]. This was attributed to heating the cast film above the glass transition temperature of PSF before and during polymerization of BMI that led to a phase separation as illustrated elsewhere [12,15]. However, an improvement in the synthesis of semi-IPN was achieved in the work of Liou et al. [16] when BMI oligomer/polyimide was mixed in a rotary roller for 24 h within a highly viscous NMP/polyimide solution. BMI oligomers acted as plasticizer for polyimides. An enhancement in miscibility of the low-molecular-weight BMI oligomer in polyimide was responsible for the formation of semi-IPN containing microphase domains, which were smaller than 0.25 μm that was beyond the resolution limit of polarized optical microscope [16]. However, their work was aimed at preparing semi-IPNs suitable for microelectronic industry and was not utilized for membrane formation.

We found that BMI could be polymerized at ambient conditions in the presence of a proton donor, polar aprotic solvent and polyetherimide or polysulfone without the need for an initiator or catalyst. Exploiting this discovery to prepare a new BMI-based semi-IPN in addition to combining this semi-IPN synthesis with membrane formation appears to be a promising way of preparing relatively high permeance gas separation membranes. Selection of an appropriate technique was found through combining the procedures for synthesis of BMI-based thermoset/thermoplastic semi-IPN with the membrane formation. This combination of IPN concept and membrane fabrication was disclosed in a US Patent [17]. However, the described route for semi-IPN synthesis was not set to have the ability to control polymer/polymer phase separation. The polymerization of vinyl monomers was carried out inside a stagnant film of a thermoplastic polymeric solution, which led to the formation of a gel within the polymeric solution before water coagulation and membrane formation. Termination of polymerizing vinyl monomers to control the size of growing microphase at different polymerization stages and enhancement of component dispersion by mixing, were not used in this patent. The major disadvantage of their process was a challenge in

producing membranes that had both high flux and a small molecular weight cut-off [17]. Therefore, to overcome this obstacle, a new route for semi-IPN synthesis combined with membrane formation to control thermo set/thermoplastic phase separation at different polymerization stages, is needed. The present work describes the synthesis of new semi-IPNs materials, formation of membranes and their characterization including microscopic, thermal and permeation studies.

2. Experimental

2.1. Materials

Aromatic polysulfone (Udel[®] P-1700 NT LCD) and aromatic polyetherimide (Ultem[®] 1000) were supplied in pellet form by Solvay Advanced Polymers, USA, and General Electric Plastics, USA, respectively. Both polymers were dried in an oven at 150 °C for 8 h to remove any possible absorbed water vapors. Anhydrous 1-methyl-2-pyrrolidinone (Aldrich, 99.5%, reagent grade, water <0.005%), anhydrous isopropanol 99.5% and 1,1'-(methylenedi-4,1-phenylene) bismaleimide 95% were supplied by Sigma–Aldrich Canada Ltd. Anhydrous ethyl alcohol was received from Commercial Alcohols Inc., Ont., Canada. Hexanes of ACS reagent grade were supplied by VWR, Canada. All solvents were used as supplied under a dry nitrogen atmosphere. Ultra high purity Helium and medical air were supplied by BOC Gases Canada Ltd. and used as received without further purification.

2.2. Membrane preparation

Formulations of polyetherimide (PEI) as well as polysulfone (PSF) with and without 1,1'-(methylenedi-4,1-phenylene) bismaleimide (BMI) were used to prepare flat asymmetric membranes by sol–gel technique [18]. Polymerization of BMI monomer was carried out in polymeric solutions containing anhydrous 1-methyl-2-pyrrolidinone (NMP) as an aprotic dipolar solvent and one of the non-solvents, i.e. anhydrous ethyl alcohol (EtOH) or isopropyl alcohol (i-PrOH) [19]. Polyetherimide (Ultem[®] 1000) was selected as a high performance engineering amorphous thermoplastic polymer to impart strength and toughness with excellent thermal, mechanical and electrical properties [20]. The polysulfone Udel[®] P-1700 NT LCD was also selected as it provides very good control of pore size and pore size distribution, high membrane strength, good film-forming properties, good resistance to degradation, low cost and low content of cyclic dimer that may precipitate in the polymeric solutions. Both PEI and PSF have ether groups and an electron acceptor moiety such as phthalimide or sulfone. The two protic non-solvents were selected because they act as diluents for forming the porous structure [21] and as a proton donor to enhance BMI polymerization. In addition to these criteria, i-PrOH and EtOH have a different polarity and dielectric constant that may influence mechanism of BMI polymerization and semi-IPNs formation. The weight ratio of BMI to PEI or PSF in all formulations was kept below 11% because a higher concentration led to a brittle IPN material. The weight ratio of

Table 1
Compositions of polymeric solutions used in this study

Samples	Composition (% w/w) of the total solution				
	Polymer	NMP	BMI	EtOH	i-PrOH
PEI-EtOH	19.5	67.2	0	13.3	0
PEI-i-PrOH	19.5	67.2	0	0	13.3
PEI-BMI-EtOH	17.6	67.2	1.9	13.3	0
PEI-BMI-EtOH-2	28	60	1	11	0
PEI-BMI-i-PrOH	17.6	67.2	1.9	0	13.3
PSF-EtOH	19.5	67.2	0	13.3	0
PSF-i-PrOH	19.5	67.2	0	0	13.3
PSF-BMI-EtOH	17.6	67.2	1.9	13.3	0
PSF-BMI-i-PrOH	17.6	67.2	1.9	0	13.3

the non-solvent was kept at one-fifth of NMP weight so that the final solution was close to its clouding point [19]. Based on these criteria nine different polymer solutions with compositions shown in Table 1 were prepared by mixing PEI or PSF and BMI in NMP. After PEI or PSF and BMI were completely dissolved, the non-solvent was mixed in this solution. Mixing of these solutions was continued under ambient light and temperature conditions for 30–100 days. To prepare membrane films, homogenous solutions with compositions shown in Table 1 were cast at room temperature on clean glass plates placed in a glove box equipped with a gas filter. After casting each sample with a doctor knife having a gap of 250 μm , the plate was quickly immersed in distilled water at ambient temperature. The membrane films were left in water for three days then washed and stored in anhydrous EtOH bath for one day. Membranes were subsequently placed in hexanes for one day before leaving them in a fume hood for one day. Drying was carried out at 80 °C in air-purging convection oven for one day and finally in vacuum oven at 80 °C and 9.66×10^4 Pa (725 mmHg) pressure for two days. Three circular coupons of 7.4 cm diameter were cut from each sample to be used in the permeation test while other pieces were cut from the same sample for characterization.

Membranes used in the permeation test were coated with silicon rubber. A solution of 3% Sylgard 184 with a catalyst to base rubber ratio of 1:10 in *n*-pentane was sprayed as a thin layer on the top surface of the membrane and the solvent was allowed to evaporate. Application of four coatings was found to be adequate for making gas separation membranes. Finally, the silicon coated membranes were cured in air purging convection oven at 80 °C for one day.

2.3. Permeation test

A cross-flow test cell having an effective permeation surface area of 9.6 cm² was used. Medical air was used at feed pressure of 665 kPa gauge (6.65×10^5 Pa (498.8 cmHg)) and the retentate was set at a flow rate of 400 ml (STP)/min. Permeate was discharged to atmosphere. The permeate flow rate was measured by a soap bubble flow meter and the oxygen concentration in permeate was determined by gas chromatography.

2.4. Microscopy studies

Surface of each membrane before silicon rubber coating was examined using a Leica DMRXE optical microscope (Leica Microsystems Wetzlar GmbH, Wetzlar, Germany) equipped for bright-/dark-field illumination. Microscope was set at reflected light mode using the reflected light bright-/dark-field objectives (Delta optics PL Fluotar series) at standard magnification of 50, 100, 200, 500 and 1000. Images were adjusted to be on a part of the surface that showed a thermoset/thermoplastic phase separation. These images were captured for magnification of 1000 times with Orthomat® E camera mounted on the microscope using Polaroid 72 black and white instant sheet films (ISO 400). An image of the microscope scale (graticule) was captured under identical conditions to scale all produced images.

Membrane samples without coating by silicon rubber were also examined by scanning electron microscopy (SEM) using JEOL 840A equipment at an accelerating voltage of 10 kV. Samples were prepared by cutting a strip from membrane, freezing in liquid nitrogen and fracturing to obtain a representative sample. They were mounted on carbon tape at 45° SEM stubs and sputter coated with gold. Photographs were taken at magnifications of 500, 2000 or 5000 times.

2.5. Thermal analysis

A TA instrument model 2920 Modulated differential scanning calorimetry, DSC V2.6 A, calibrated with Indium at 156.5985 °C and with Tin at 231.93 °C was used to measure the glass transition temperature (T_g). Under a nitrogen atmosphere, polymer samples were ramped to 50 °C at 1 °C/min, held isothermally for 10 min and then reheated to 350 °C at 10 °C/min. The T_g was calculated at the point of inflection of the DSC curve. A TA instruments, Model AutoTGA 2950HR V5.4A analyzer was used for measuring the degradation temperatures by thermogravimetric analysis (TGA). Under a nitrogen atmosphere, polymer samples were ramped to 40 °C at 1 °C/min, held isothermally for 60 min, and then heated to 800 °C at 10 °C/min.

3. Results and discussion

Synthesis procedure for PEI-BMI or PSF-BMI semi-IPNs combined with membrane fabrication was arrived at after several preliminary experiments. It was observed that BMI could be polymerized slowly inside and through PEI/NMP or PSF/NMP solutions at ambient conditions in the presence of a proton donor. This in situ polymerization process has many advantages such as avoiding the addition of complicated initiators or catalysts. Polymerization of BMI was visually observed through increasing viscosity of polymeric solutions accompanied by a change in color. In the case of EtOH as a proton donor, the color of the PEI-BMI polymeric solution underwent gradual change from light yellow to bright crimson color while in the case of PSF it changed to bright reddish-purple color. In the case of PEI it took up to 30 days to notice a change in the color and up to 60 days to reach the brightest color while for PSF, it took up to 40 days to notice a color change and up to 80 days to observe the

brightest color. After a long time (more than 80 days) both solutions started to be cloudy, less transparent with a decrease in the brightness and changing to a more brownish color. Phase separation was clearly observed through precipitation of one of the polymeric phases. This phenomenon is well known in literature for the phase separation of thermoset/thermoplastic polymeric blends particularly for BMI/PSF blends [14,22]. Through preliminary experiments, we found that membranes formed from those solutions, which had large separated phases did not have suitable gas separations characteristics.

Similar observations were made when isopropanol was used as a proton donor instead of EtOH. However, an increase in the brightness of yellow color was obtained. This may indicate that polymerization mechanism is different because it is known that purple or red color is obtained upon anionic polymerization of BMI that usually leads to a lower molecular weight polymer [23]. Absence of red or purple color in the case of isopropanol indicates that BMI probably underwent a free radical polymerization as reported elsewhere [24]. The chemical structures of modified BMI-PEI as well as modified BMI-PSF were analyzed by ATR-FTIR and XPS spectroscopy as found elsewhere [25,26].

In order to have a better understanding, additional experiments were carried out to polymerize BMI at the same conditions as discussed above but in the absence of PEI or PSF. There was no color change in the solution even after 100 days. This indicates that PEI or PSF in NMP has an important catalysis role in accelerating BMI polymerization. The catalysis role of PEI or PSF could be similar to the role of nano-crystalline titania [27]. We also found that polymerization of BMI at the above conditions did not occur in the absence of alcohol indicating the vital role of this proton donor in acceleration of BMI polymerization. As the above process required a long time, accelerating polymerization of BMI is necessary for economic reason. It is worth noting that the rate of polymerization of BMI is dependent on BMI and polymer concentrations as well as on solution viscosity and speed of mixing. Experimentally, we observe the change in the color would be faster for lower BMI concentration, lower viscosity and higher speed of mixing. We also found that increasing temperature to 60 °C during solution mixing lead to a decrease in the required time to change color to red (crimson) from 30 days to a less than 24 h. A significant decrease in solution viscosity and an improvement in the mixing were achieved when temperature was increased to 60 °C during solution mixing. It is worth noting that with increasing polymer concentration in the casting solution, it was possible to increase membrane gas selectivity but at the expense of membrane productivity.

3.1. Phase structure and morphology analysis

Surfaces of all membrane samples were examined by optical microscope. Phase separation was not observed in PEI-BMI or PSF-BMI semi-IPN membranes that were cast after 30 days in the case of PEI and after 40 days for PSF. The appearance of the surface of these membranes was similar to surfaces of membranes prepared from PEI or PSF without adding BMI. Membranes containing BMI and cast after 80 days using PEI or after 100 days for PSF had brown to orange-red dispersed

phase in some areas that represented thermoset BMI phase within a large area of continuous PEI or PSF phase. The dispersed phase might have circular or cylindrical shape and some of them could be seen with size that may exceed 10 μm (Fig. 1). The interface between two phases was observed to be more clear in membranes formed from isopropanol containing solution (Fig. 1(b and d)) while with ethanol (Fig. 1(a and c)) a diffused interface was observed. The dispersed phase in the PSF-based membrane prepared from solutions containing isopropanol (Fig. 1(d)) was shown to have a larger size than other membranes shown in Fig. 1(a–c). The phenomenon of phase separation influenced the membrane performance for gas separation as found through our preliminary experiments. We believe that polymeric solutions should be coagulated before the stage of significant thermoset/thermoplastic phase separation in order to form gas separation membranes.

Morphology of membranes was examined by scanning electron microscopy (SEM). The morphology of membranes prepared from solutions containing isopropanol was not significantly different from those obtained by using ethanol. Therefore, morphology analysis was conducted for only membranes produced from solutions containing ethanol. Membranes were labeled according to their solution composition. Symbols S and L refer to membranes coagulated after 30 and 60 days, respectively, for PEI and after 40 and 80 days, respectively, for PSF. SEM micrographs of cross-sections of PEI-EtOH, PEI-BMI-EtOH (S and L) are shown in Fig. 2. It was clear from micrographs (a) and (b) that the fingers penetrated along cross-section with changing direction between parallel and perpendicular to membrane surface. The beginning and end of these fingers were located at a distance far from both membrane surfaces and could be expressed, respectively, by top and bottom layers that were not penetrated by finger voids. The top layer thickness became smaller and the finger became straightforward and perpendicular to membrane surface as shown in micrographs (c) and (d) for membranes containing BMI. Although in both cases these fingers were well-developed but PEI-BMI-EtOH-L membrane (Fig. 2(d)) had slightly smaller top layer thickness and its finger started with a smaller diameter than those in PEI-BMI-EtOH-S (Fig. 2(c)). It was also clear that the diameter of the finger in the PEI-BMI-EtOH-L gradually increased towards the bottom of the membrane (Fig. 2(d)) while these fingers had approximately the same diameter along the cross-section of PEI-BMI-EtOH-S membrane (Fig. 2(c)). Although it was hard to see phase separation in L membranes within the resolution of optical microscope, the thermoset microphase domain might be larger than that in S membranes and could be responsible for a change in membrane morphology. The top homogeneous layer thickness of PEI-EtOH membranes was significantly larger than 10 μm while it did not exceed 10 μm for PEI-BMI-EtOH-L membranes as shown in micrographs (e) and (f) in Fig. 2. We will discuss the correlation between membrane morphology and superior gas permeance for PEI-BMI-EtOH-L later on.

Scanning electron micrographs of PSF-EtOH and PSF-BMI-EtOH-L membranes are shown in Fig. 3. It is clear that in the absence of BMI, morphology of PSF-EtOH was different from that of PEI-EtOH membranes shown in Fig. 2. In contrast to

Fig. 1. Optical micrographs at 1000 times magnifications for the skinned surface of semi-IPN membranes formed from solutions coagulated after 80 days in case of using PEI and after 100 days in case of using PSF. (a) PEI-BMI-EtOH membrane, (b) PEI-BMI-i-PrOH membrane, (c) PSF-BMI-EtOH membrane, (d) PSF-BMI-i-PrOH membrane.

PEI, PSF had the ability to form a very thin top layer as shown in micrograph (a) of Fig. 3. A gradual increase in finger size was obtained for all membranes containing PSF, the penetration did not reach the bottom of the membrane and the thickness of bottom layer is significantly higher than 10 μm . For membranes containing BMI as shown in micrograph (b) of Fig. 3, the penetration of fingers might have reached the membrane bottom and the thickness of the bottom layer became very small. Using 5000 magnification the thickness of the top layer did not exceed 1 μm as shown in micrographs (c) and (d) in Fig. 3. It is hard to see significant differences in the top part of all membranes containing PSF as shown in Fig. 3. From these observations, we might expect gas permeance values for PSF-BMI-EtOH-L were higher than those for other PSF membranes which might be attributed to a thinner bottom layer. These results indicated that using PEI-BMI or PSF-BMI semi-IPNs as membrane materials led to a different membrane phase inversion and membrane morphology compared to using PEI or PSF alone as shown in Figs. 2 and 3.

3.2. Membrane thermal stability

Thermal stability of PEI, PSF and their BMI semi-IPNs was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Glass transition temperatures of PEI, PSF and their BMI semi-IPNs membranes were measured by DSC as listed in Table 2. The glass transition tem-

perature (T_g) of PEI-BMI-EtOH-S membrane was found to be 199.7 $^{\circ}\text{C}$, which was lower than T_g of PEI-EtOH by 13.7 $^{\circ}\text{C}$. This could be attributed to weaker interactions between the thermoset BMI and thermoplastic PEI phases in the semi-IPN system than the inter chain forces in the individual polymers as reported elsewhere [28]. The large interface area between BMI and PEI was probably attributed to the small size of low-molecular-weight BMI oligomers. These oligomers might easily plasticize the imide-based polymer (PEI) caused by their higher dilution in the polymeric matrix as illustrated elsewhere [16,29]. Similar observation was reported for the decrease of T_g of polyimide/BMI semi-IPN by 10 $^{\circ}\text{C}$ compared to free polyimides. This may also be accompanied by a decrease in the softening point T_{g2} of BMI phase by 10–60 $^{\circ}\text{C}$ compared to the neat BMI network [29]. However, as the BMI dispersed phase grew, a lower interfacial area and plasticizing effect might reduce the mutual influences

Table 2

Glass transition temperatures of PEI, PSF and their BMI semi-IPNs membranes as measured by DSC at heating rate 10 $^{\circ}\text{C}/\text{min}$ in nitrogen

Sample	T_g ($^{\circ}\text{C}$)
PEI-EtOH	213.4
PEI-BMI-EtOH-S	199.7
PEI-BMI-EtOH-L	216.1
PSF-EtOH	185.1
PSF-BMI-EtOH-S	182.9
PSF-BMI-EtOH-L	188.9

Fig. 2. SEM micrographs for the cross-section of membranes at 500 times magnification: (a and b) PEI-EtOH at different cross-section locations, (c) PEI-BMI-EtOH-S and (d) PEI-BMI-EtOH-L, in addition to 2000 times magnification: (e) PEI-EtOH and (f) PEI-BMI-EtOH-L.

and magnitude of change in T_g of two phases. The T_g of neat BMI resin was reported to be 399 °C [29]. The T_g of the PEI-BMI-EtOH-L membranes was measured to be 216.1 °C, which was slightly higher (by 2.7 °C) than the T_g of PEI-EtOH. This might be attributed to the formation of a rigid microphase of BMI resin with a higher softening point, T_{g2} than the T_g of PEI that might restrict chain mobility of PEI. A similar explanation might also be given for PSF-BMI semi-IPN membranes. The measured T_g of PSF-EtOH was 185.1 °C, which was equal to the T_g of this polymer as reported elsewhere [14,30]. The T_g of PSF-BMI-EtOH-S was measured to be 182.9 °C, which was lower than the T_g of PSF by only 2.2 °C. Considering that the amount of this decrease was lower than that for PEI-BMI-EtOH-S (i.e. 13.7 °C) it indicates that plasticizing effect of BMI on PSF was less than that on PEI. On the other hand, the T_g of PSF-BMI-EtOH-L was measured to be 188.9 °C, which was higher than the neat PSF by 3.8 °C. This increase in T_g was slightly higher than that in the case of PEI and might be attributed to same reasons as for PEI. It was clear that the T_g of base polymer could be improved through synthesis of PEI-BMI and PSF-BMI semi-IPN. This improvement might depend on the formation of rigid

microphase dispersed in a base polymer such as PEI or PSF. The size of this microphase might have an important role on the properties of thermoset/thermoplastic composites. In case microphase comprised a low-molecular-weight BMI oligomer, it might act as a plasticizer that led to a decrease in the T_g , however if the microphase was large enough to form rigid domain, it might act as reinforcing particle that led to increase T_g compare to T_g of base polymer. In both cases, the microphase domain size should not exceed the resolution of optical microscope in order to maintain interpenetrating interactions of different components within the network. Also, a larger size for the thermoset phase would lead to a traditional polymer blend losing the beneficial features of IPN.

Thermal stability and heat resistances of PEI, PSF and their BMI semi-IPNs membranes were measured by TGA as shown in Fig. 4 for PEI as a base polymer and in Fig. 5 for PSF as a base polymer. From these figures, we will evaluate the thermal resistance of membranes through degradation temperatures at 2%, 10%, 20% and 50% weight loss and residual weights at 800 °C or temperature at complete degradation if it was less than 800 °C as summarized in Table 3. As shown in Fig. 4, the

Fig. 3. SEM micrographs for the cross-section of membranes at 500 times magnification: (a) PSF-EtOH and (b) PSF-BMI-EtOH-L, in addition to 5000 times magnification: (c) PSF-EtOH and (d) PSF-BMI-EtOH-L.

thermal degradation of PEI-EtOH membranes took place in two stages that agrees well with the TGA obtained for polyetherimide in nitrogen illustrated elsewhere [31]. For PEI-BMI-EtOH-S membrane, the thermal degradation weight loss of the first stage was at lower temperatures than that for PEI-EtOH membrane while in the second stage they were located at higher temperatures. For instance as seen in Table 3, at 2% weight loss, the degradation temperature was lower by 75 °C while in the second stage and at 20% loss, it was higher by 5 °C. A relatively low thermal stability of BMI/polyimides semi-IPN compared to the free linear polyimide was attributed to the less stable polymer-

ized maleimide structures as illustrated and reported elsewhere [29]. The increase in the thermal stability at higher temperatures within the second degradation stage was attributed to the BMI network as reported elsewhere [32]. The thermal degradation of PEI-BMI-EtOH-L membrane appeared at much lower temperatures compared to the other two membranes within the total range of the two stages (Fig. 4). The lower degradation temperature of this membrane might be attributed to the chemical structure of composite material which contained amic acid groups resulted from imide cleavage, substituted ethoxy moieties and complex NMP as was determined by a separate FTIR

Fig. 4. TGA curves of PEI-EtOH, PEI-BMI-EtOH-S and PEI-BMI-EtOH-L membranes.

Fig. 5. TGA curves of PSF-EtOH, PSF-BMI-EtOH-S and PSF-BMI-EtOH-L membranes.

Table 3

Thermal stability of PEI, PSF and their BMI semi-IPNs membranes as measured by TGA at heating rate 10 °C/min in nitrogen

Sample	Degradation temperatures (°C) at different percent weight loss				Residue at 800 °C or temperature at residue of 0%
	2%	10%	20%	50%	
PEI-EtOH	449	510	529	662	19%
PEI-BMI-EtOH-S	374	509	534	666	19%
PEI-BMI-EtOH-L	249	467	505	572	722 °C
PSF-EtOH	476	504	515	539	5%
PSF-BMI-EtOH-S	403	479	503	564	795 °C
PSF-BMI-EtOH-L	361	472	495	570	797 °C

and XPS analysis for PEI-BMI-EtOH-L membrane [25]. At a temperature of 325 °C in TGA curve in Fig. 4, this membrane has approximately 3.2% weight loss that might be attributed to loss of solvent as well as water resulting from imidization of amic acid as was illustrated to be in the range of 200–325 °C and also reported elsewhere [33]. A polymer containing amide group is usually less thermally stable than the one that has same structure but containing imide instead of amide group [34]. On the other hand, the decomposition of ethoxy group may also occur at 250 °C [35] or at a maximum temperature of 270 °C [36]. It was clear from Table 3 that PEI-BMI-EtOH-L membrane had a weight loss of 2% at thermal degradation temperature of 249 °C. This agreed well with the possible presence of amic acid groups, ethoxy moieties and NMP complexes.

The TGA curves of PSF-EtOH, PSF-BMI-EtOH-S and PSF-BMI-EtOH-L were shown in Fig. 5. The thermal degradation of these membranes took place in two stages, which was similar to reported literature [14]. In the first stage, PSF membrane had a better thermal resistance than PSF-BMI semi-IPN membranes that might be attributed to the presence of less stable polymerized BMI as illustrated elsewhere [14]. In the second stage, the thermal degradation was slowed for semi-IPN membranes between 530 and 580 °C and then a higher rate of degradation than that for a base PSF membrane was observed. The differences between the degradation temperatures of PSF-BMI-EtOH-S and PSF-BMI-EtOH-L at 2% weight loss as shown in Table 3 was 42 °C, which indicated that BMI microphase growth had smaller impact on the IPN structure in the case of PSF as a base polymer than the case of PEI where this difference was 125 °C. This also agreed well with the larger difference in T_g values between S and L membranes in case of PEI compared to those of PSF as discussed above. Comparing both base polymers, PSF-EtOH membrane had higher degradation temperatures within the first stage as seen at 2% and 10% weight loss in Table 3 but lower degradation temperatures than PEI-EtOH membrane within the second stage as seen at 20% and 50% weight loss. High thermal stability of PSF polymer within the first stage could be attributed to its strong chemical moieties such as aromatic, sulfone and ether as illustrated elsewhere [37] while it was lower for imide-based polymer particularly for incomplete imidization or hydrolysis imide that condensed within this first thermal degradation stage. However, in the second stage, rearrangement, condensation and cyclization products from imide-based polymer, such as naph-

thalene, anthracene and phenanthrene might be responsible for its higher degradation temperatures [38] compared to PSF-based polymer. For this reason, the residual weight at 800 °C for PEI was higher than that of PSF base membranes (Table 3). For PSF-BMI-EtOH S and L, there was no residue at temperatures 795 and 797 °C, respectively. The decrease in these temperatures for complete degradation was due to the lower stability of polymerized BMI and perhaps to the relatively low molecular weight of the BMI resin. The influence of molecular weight and its distribution on thermal stability of polymers was illustrated elsewhere [39]. On the other hand, it was interesting to see that PEI-BMI-EtOH-S membrane had the same residue of 19% at 800 °C as the one without BMI although the polymerization time of BMI was shorter than that for PEI-BMI-EtOH-L membrane. It appears that the low-molecular-weight BMI oligomer had higher interactions with PEI network that led to plasticization with the ability to condense or possibly crosslink with PEI that maintained a 19% residue at 800 °C. However, growth of BMI resin to a relative larger size as in PEI-BMI-EtOH-L membrane would decrease the area available for interactions with PEI and therefore the thermal degradation of BMI phase might take place independently. The presence of a less stable BMI resin led to a complete thermal degradation of PEI-BMI-EtOH-L membrane (0% residue) at 721 °C.

It was clear from the above results that formation route of PEI or PSF semi-IPN had significant influence on the glass transition temperature as well as the thermal stability of final polymer networks. Both thermoset micro-domain size and the ability to interact with the base thermoplastic polymer in IPN were found to be responsible for changing the composite properties. The PEI-BMI-EtOH-L membrane was suitable for gas separation application at ambient temperature but not at elevated temperature because the onset thermal degradation might occur at temperatures as low as 135 °C (see Fig. 4). Both permeance and selectivity of this membrane for air separation did not vary more than 1% in one month, which indicated a reasonable stability at ambient temperature.

3.3. Gas transport characteristics

The novel PEI-BMI and PSF-BMI semi-IPN membranes were characterized by a gas permeation test. Gas permeance and O₂/N₂ selectivity for separation of oxygen from air were shown in Table 4 and compared with literature [40–42]. It is well-known that cost-effective use of membranes would not only depend on membrane selectivity but also on its permeance. As a thick bulk film, material performance could be evaluated by both permeability and selectivity through 1991 Robeson upper bound trade off as shown elsewhere [43]. For homogeneous film, the flux is multiplied by the film thickness so that its permeability value would be independent of the thickness of the tested film. However, in commercial asymmetric membranes, gas permeance (pressure normalized flux) that could be increased by decreasing the thickness of the selective skin layer and the gas transport resistance of the sub-layer is an important factor that should be considered. Unfortunately, as the thickness of the selective layer (skin in asymmetric membranes or thin coated layer in compos-

Table 4

Comparison of permeance (total gas and oxygen) and O₂/N₂ selectivity for air separation with different membranes

Membranes	Total permeance (GPU ^a)	Oxygen permeance (GPU ^a)	Selectivity O ₂ /N ₂
PEI-EtOH	33	23	2.3
PEI-BMI-EtOH-S	126	87	2.2
PEI-BMI-EtOH-L	505	341	2.1
PEI-BMI-EtOH-2-L	9	7.9	7.2
PSf-EtOH	44	29	1.9
PSf-BMI-EtOH-S	153	103	2.1
PSf-BMI-EtOH-L	553	366	1.6
PVTMS [40]	–	219	3.5
EC/PAN [40]	–	74	3.0
PDMS/MDK [40]	–	126	2.0
Aromatic polyimide [40]	–	28	5.0
Polymeric blends	–	12	6.9
membranes ^b	–	121	2.1
[41]	–	127	1.5
Composite membrane ^c dried for 30 s, [42]	–	266–826	2.0–2.1
Composite membrane ^c dried for 75 s, [42]	–	143–334	2.2–2.3

^a Gas permeation unit, GPU = $1 \times 10^{-5} ((\text{m}^3 (\text{STP})) / (\text{m}^2 \text{ s Pa})) (1 \times 10^{-6} (\text{cm}^3 (\text{STP})) / (\text{cm}^2 \text{ s cmHg})))$.

^b Blends of polyethersulfones with aromatic polyimides, polyamides or polyamide-imides.

^c Polysulfone membrane coated with Teflon polymer.

ite membranes) decreases, the influence of material defects on gas selectivity becomes more prominent.

The intrinsic O₂/N₂ selectivity and O₂ permeability values for a dense PEI film, at 35 °C were 57.0×10^{-18} and $3.0 \times 10^{-18} \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and (7.6 and 0.4 Barrer) [44] whereas for a dense polysulfone film these values were 45.0×10^{-18} and $9.0006 \times 10^{-18} \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ (6.0 and 1.2 Barrer) [43]. Also, silicon rubber has O₂/N₂ selectivity of 2.22 and O₂ permeability of $5858 \times 10^{-18} \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ (781 Barrer). Although these numbers might provide an idea about material performance, the ability to form ultra thin film with less and/or smaller defects and good mechanical properties is a challenge for producing commercial membranes. Belyaev et al. [40] tested four commercial O₂-enriched-air membranes PVTMS, EC/PAN, PDMS/MDK and aromatic polyimide. The O₂/N₂ selectivity and O₂ permeance of these commercial membranes were shown in Table 4. It is clear that the O₂/N₂ selectivity of polydimethylsiloxane PDMS in commercial membranes is less than its intrinsic selectivity due to challenge in obtaining a homogenous ultra thin layer of silicon rubber. On the other hand, aromatic polyimide membrane has O₂/N₂ selectivity of 5 but Belyaev et al. [40] confirmed experimentally that this membrane was not economically suitable to produce O₂ enriched-air used in coal gasification process.

In one experiment where casting solution (PEI-BMI-EtOH-2) contained higher percentage of PEI than others listed in Table 1. We observed that the PEI-BMI-EtOH-2-L had an O₂/N₂ selectivity of 7.2, which is close to the intrinsic selectivity of bulk PEI with a reasonable permeance of 9 GPU as shown in

Table 4. However, in order to obtain a permeance, which is significantly higher than 9 GPU, it was necessary to use diluted casting solutions. It was an objective in this study to increase membrane permeance as much as possible without decreasing membrane selectivity below the intrinsic selectivity of coating silicon rubber. It is clear from Table 4 that membranes produced from blends of polyethersulfones with aromatic polyimides, polyamides or polyamide-imides reported in a European Patent have an O₂/N₂ selectivity of 6.9 and O₂ permeance of 12 GPU while at O₂ permeance of 127 GPU, the O₂/N₂ selectivity decreased to 1.5 which is less than the intrinsic selectivity of silicon rubber [41].

We used Sylgard 184 silicon rubber coating technique [45], the BMI/PEI semi-IPN membrane showed air separation performance that was comparable to a recent US Patent [42], which was aimed at developing the coating technique but not the membrane materials. The PEI-BMI-EtOH-L membrane has O₂ permeance of 341 GPU that is higher than that reported for composite membrane, which was prepared with polysulfone with a Teflon AFTM 1600 coating and dried for 75 s (334 GPU) in the above mentioned US Patent while the O₂/N₂ selectivity was comparable in two cases. The possibility of having very high O₂ permeance for composite membranes was reported to be 826 GPU at similar O₂/N₂ selectivity (i.e. 2). However, the significant drop of O₂ permeance upon increasing drying time from 30 to 75 s might be questionable. It is not clear from this patent if membranes having a high gas permeance are stable and do not need an additional drying. Although, the novel Teflon coating was applied on optimized membranes which is not the subject of this study, the gas permeance for PEI-BMI-EtOH-L was 505 GPU (341 GPU of pure oxygen in the mixture) with a calculated selectivity of 2.1 as shown in Table 4. Both PEI-BMI-EtOH-L and PSF-BMI-EtOH-L membranes had 12–15 times higher permeances than the corresponding thermoplastic membranes at similar O₂/N₂ selectivity. These permeances are also higher than the ones reported for membranes made with blends of polyethersulfones with aromatic polyimides, polyamides or polyamide-imides that were disclosed in a European Patent [41] (see Table 4).

The increase in the permeance for semi-IPN membranes compared to the base PEI or PSF membranes might be attributed to an increase in the free volume (i.e. decrease in material density) as was illustrated for similar semi-IPN by other workers [16]. As the selectivity was maintained constant upon increasing gas permeances, we might rule out the possibility of increasing pore size (or in other words the presence of large defects) especially in the top membrane skin. Therefore, increasing permeance might be attributed to an increase in material microporosity, which resulted from microphase separation or/and a decrease in the thickness of the top and bottom layers. The first possibility could be supported by X-ray diffraction (WAXD) measurements as reported elsewhere for similar semi-IPNs [16] and the second possibility could be supported by SEM analysis as discussed in this work. The permeance of PSF-BMI-EtOH-L membrane was higher than that for PEI-BMI-EtOH-L membrane as listed in Table 4 due to PSF's ability to form ultra-thin skin layer not exceeding 1 µm as shown in micrographs (c) and (d) in Fig. 3.

Skin with thickness lower than 1 μm is more prone to defects leading to a decrease in the PSF-BMI-EtoH-L selectivity to 1.6 that is lower than the intrinsic selectivity of 2.22 for silicon rubber. It is clear from our data that there is a limitation for increasing membrane permeance and for reducing gas transport resistance of sub-layer. This limitation occurs when the defects becomes large enough so that it is not possible to be sealed by silicon coating layer.

4. Conclusions

It was concluded that PEI-BMI or PSF-BMI semi-IPN membranes could be synthesized and assembled through in situ polymerization of BMI in PEI/NMP or PSF/NMP solutions at ambient conditions without the need for an initiator. Structure and properties of semi-IPN membranes could be varied by controlling the thermoset BMI micro-domain size interpenetrating within a thermoplastic polymer network. The size of this micro-domain depended on the polymerization time of BMI and the degree of thermoset/thermoplastic phase separation. Furthermore, for preparing suitable material the growth of micro-domain and phase separation should be arrested at an early stage when the phase separation in the casting solution was not visible. Both PEI-BMI and PSF-BMI semi-IPN membranes showed improved structures and morphology compared with the ones obtained from the corresponding base polymer. It was also concluded that the semi-IPN membranes showed an improved glass transition temperature but a decrease in their thermal stability. At ambient temperature, it was possible to increase the permeance of semi-IPN membranes by 12–15 times higher than membranes produced from the corresponding base thermoplastic polymer without sacrificing membrane gas selectivity at the same conditions. These semi-IPN membranes could be used for O_2 -enriched-air applications where high selectivity is not required but membrane productivity should be as high as possible.

Acknowledgements

Authors are thankful to Mr. David Kingston and Dr. Jim Tunney for their help with SEM experiments and optical microscopy, respectively.

References

- [1] D. Paul, S.K. Sikdar, Clean production with membrane technology, *Clean Product. Process.* 1 (1998) 39.
- [2] S.A. Stern, Polymers for gas separations: the next decade, *J. Membr. Sci.* 94 (1994) 1.
- [3] W.R. Baker, Future direction of membrane gas separation technology, *Ind. Eng. Chem. Res.* 41 (2002) 1393.
- [4] J. Bart, Additives in Polymers: Industrial Analysis and Applications, John Wiley & Sons Ltd., New York, 2005.
- [5] A. Bos, I. Pünt, H. Strathmann, M. Wessling, Special separations section suppression of gas separation membrane plasticization by homogeneous polymer blending, *AIChE J.* 47 (2001) 1088.
- [6] P. Mison, B. Sillion, Thermosetting oligomers containing maleimides and nadimides end-groups, *Adv. Polym. Sci.* 140 (1999) 137.
- [7] L.H. Sperling, Interpenetrating polymer networks: an overview, in: D. Klemperer, L.H. Sperling, L.A. Utracki (Eds.), *Interpenetrating Polymer Networks*, Advances in Chemistry Series, No. 239, American Chemical Society, Washington, DC, 1994, pp. 3–38.
- [8] L.H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum Press, New York, 1981.
- [9] L.H. Sperling, V. Mishra, The current status of interpenetrating polymer networks, *Polym. Adv. Technol.* 7 (1996) 197.
- [10] S.K. Kim, S.C. Kim, Polyurethane–polystyrene interpenetrating polymer networks synthesized in the presence of a common solvent, *Polym. Bull.* 23 (1990) 141.
- [11] E.G. Sommerfeld, Solvent dispersible interpenetrating polymer networks, US Patent 6,228,919, 2001, to E.I. du Pont de Nemours and Company, USA.
- [12] M.I. Giannotti, M.S. Solsona, M.J. Galante, P.A. Oyanguren, Morphology control in polysulfone-modified epoxy resins by demixing behavior, *J. Appl. Polym. Sci.* 89 (2003) 405.
- [13] T.P. Lodge, Block copolymers: past successes and future challenges, *Macromol. Chem. Phys.* 204 (2003) 265.
- [14] V. Gaina, C. Gaina, A. Stoleriu, D. Timpu, M. Sava, M. Rusu, New semi-interpenetrating polymeric networks from linear polysulfone and thermosetting bismaleimide and polyaminobismaleimide resins, *Polym. Plast. Technol. Eng.* 38 (1999) 927.
- [15] G.C. Kapantaidakis, S.P. Kaldis, G.P. Sakellaropoulos, E. Chira, B. Loppinet, G. Floudas, Interrelation between phase state and gas permeation in polysulfone-polyimide blend membranes, *J. Polym. Sci. Part B: Polym. Phys.* 37 (1999) 2788.
- [16] H.-C. Liou, P.S. Ho, B. Tung, Structure-property correlation for thin films of semi-interpenetrating polyimide networks. I. Miscibility, curing, and morphology studies, *J. Appl. Polym. Sci.* 70 (1998) 261.
- [17] H. Zhang, T. Anazawa, Y. Watanabe, M. Miyajima, Process for preparation of porous material and porous material, US Patent 6,319,404, 2001, to Dainippon Ink Chemicals, Inc. and Kawamura Institute of Chemical Research, Japan.
- [18] W.J. Koros, Y.H. Ma, T. Shimidzu, Terminology for membranes and membrane processes, *Pure Appl. Chem.* 68 (1996) 1479.
- [19] D. Wang, K. Li, W.K. Teo, Relationship between mass ratio of nonsolvent-additive to solvent in membrane casting solution and its coagulation value, *J. Membr. Sci.* 98 (1995) 233.
- [20] M. Friedman, G. Walsh, High performance films: review of new materials and trends, *Polym. Eng. Sci.* 42 (2002) 1756.
- [21] M. Aykurt, I. Küçük, A. Kuyulu, The effect of mixed diluent on the porous structure of crosslinked PMMA beads, *Polym. Bull.* 44 (2000) 325.
- [22] K. Mai, J. Huang, H. Zeng, Studies of the stability of thermoplastic-modified bismaleimide resin, *J. Appl. Polym. Sci.* 66 (1997) 1965.
- [23] P.O. Tawney, R.H. Snyder, R.P. Conger, K.A. Leibbrand, C.H. Stiteler, A.R. Williams, The chemistry of maleimide and its derivatives. II. Maleimide and *N*-methylolmaleimide, *J. Org. Chem.* 26 (1961) 15.
- [24] B.A. Rozenberg, E.A. Dzhevadayan, R. Morgan, E. Shin, High-performance bismaleimide matrices: cure kinetics and mechanism, *Polym. Adv. Technol.* 13 (2002) 837.
- [25] J. Kurdi, A. Kumar, Structuring and characterization of a novel highly microporous PEI/BMI semi-interpenetrating polymer networks, *Polymer* 46 (2005) 6910.
- [26] J. Kurdi, A. Kumar, Synthesis and characterization of modified bismaleimide/polysulfone semi-interpenetrating polymer networks, *J. Appl. Polym. Sci.*, in press.
- [27] X. Wang, D. Chen, W. Ma, X. Yang, L. Lu, Polymerization of bismaleimide and maleimide catalyzed by nanocrystalline titania, *J. Appl. Polym. Sci.* 71 (1999) 665.
- [28] H. Tang, Y. Zhuang, J. Zhang, L. Dong, M. Ding, Z. Feng, Study on structure-property relationship of thermosetting polyimide/thermoplastic polyimide blends, *Macromol. Rapid Commun.* 15 (1994) 677.
- [29] T. Pascal, R. Mercier, B. Sillion, New semi-interpenetrating polymeric networks from linear polyimides and thermosetting bismaleimides. 2. Mechanical and thermal properties of the blends, *Polymer* 31 (1990) 78.

- [30] I. Hamerton, P. Klewpatinond, Synthesis and characterization of functionalized thermoplastics as reactive modifiers for bismaleimide resins, *Polymer Int.* 50 (2001) 1309.
- [31] R. Torrecillas, A. Baudry, J. Dufay, B. Mortaigne, Thermal degradation of high performance polymers-influence of structure on polyimide thermostability, *Polym. Degrad. Stab.* 54 (1996) 267.
- [32] J.L. Han, K.Y. Li, Interpenetrating polymer networks of bismaleimide and polyether polyurethane-crosslinked epoxy, *J. Appl. Polym. Sci.* 70 (1998) 2635.
- [33] S. Srinivas, M. Graham, M.H. Brink, S. Gardner, R.M. Davis, J.E. McGrath, G.L. Wilkes, Influence of melt stability on the crystallization of bis(4-aminophenoxy) benzene-oxypipthalic anhydride based polyimides, *Polym. Eng. Sci.* 36 (1996) 1928.
- [34] K.P. Pramoda, T.S. Chung, S.L. Liu, H. Oikawa, A. Yamaguchi, Characterization and thermal degradation of polyimide and polyamide liquid crystalline polymers, *Polym. Degrad. Stab.* 67 (2000) 365.
- [35] J. Ryzkowski, IR spectroscopy in catalysis, *Catal. Today* 68 (2001) 263.
- [36] S. Raja, R. Dhamodharan, Synthesis and characterization of nitroglycerin-functionalized polystyrene, *J. Polym. Sci. Part A Polym. Chem.* 39 (2001) 1203.
- [37] L.H. Sperling, *Introduction to Physical Polymer Science*, second ed., John Wiley and Sons Inc., New York, 1992.
- [38] W. Xie, W.-P. Pan, K.C. Chuang, Thermal degradation study of polymerization of monomeric reactants (PMR) polyimides, *J. Therm. Anal. Cal.* 64 (2001) 477.
- [39] P.M. Hergenrother, The use, design, synthesis, and properties of high performance/high temperature polymers: an overview, *High Perform. Polym.* 15 (2003) 3.
- [40] A.A. Belyaev, Yu.P. Yampolskii, L.E. Starannikova, A.M. Polyakov, G. Clarizia, E. Drioli, G. Marigliano, G. Barbieri, Membrane air separation for intensification of coal gasification process, *Fuel Process. Technol.* 80 (2003) 119.
- [41] O.M. Ekiner, Blends of Polyethersulfones with aromatic polyimides, polyamides or polyamide-imides and gas separation membranes made therefrom, Eur. Patent, Publication Number: 0,648,812A3, 1994, to L'Air Liquide, France.
- [42] J.K. Nelson, B. Bikson, J.T. Macheras, Method of preparing composite gas separation membranes from perfluoropolymers, US Patent, No. 6,540,813, 2003.
- [43] L.M. Robeson, Polymer membranes for gas separation, *Curr. Opin. Solid State Mater. Sci.* 4 (1999) 549.
- [44] T.A. Barbari, W.J. Koros, D.R. Paul, Polymeric membranes based on bisphenol-A for gas separations, *J. Membr. Sci.* 42 (1989) 69–86.
- [45] J.M.S. Henis, M.K. Tripodi, Multicomponent membranes for gas separations, US Patent, No. 4,230,463, 1980.