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Effects of casting and post casting annealing on xylene isomer transport properties of Torlon® 4000T films

Raymond Chafin*, Jong Suk Lee, William J. Koros*

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA-30332, USA

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ABSTRACT

Procedures for Torlon® 4000T membrane formation were developed to provide attractive and repeatable xylene separation properties. Torlon® 4000T membrane films cast by our method were investigated in terms of thermally induced imidization, molecular weight enhancement, and solvent removal. After development of the Torlon® 4000T casting procedure, pervaporation of a xylene mixture (i.e. 30% para-xylene, 30% meta-xylene, 30% ortho-xylene, and 10% ethylbenzene) was performed in both Torlon® 4000T and post casting annealed Torlon® 4000T films. The xylene pervaporation in annealed Torlon® 4000T film at 200 °C gave a permeability of 0.25 Barrer and a selectivity of 3.1 (para/ortho) and 2.1 (para/meta) respectively. A so-called "permeability collapse" reflecting an accelerated reduction in the free volume is consistent with significant temperature-induced changes in the films observed after thermal annealing at 300 °C. This conditioning effect is induced by a combination of heat treatment and the presence of the interacting aromatic penetrants. Optical methods were used to verify that the density of annealed samples exposed to xylene for 5 days eventually increased, suggesting that the membrane is originally swollen upon initial xylene exposure, and then relaxes to a more densified, and more discriminating state.

1. Introduction

Xylene isomers (Fig. 1) are important chemical intermediates, but manufacturing pure isomers is difficult due to their similarity in physical properties [1–6]. Paraxylene is particularly important as its derivatives are precursors for polyester fibers, films, and solid-state packaging resins. As a result, global demand for *p*-xylene is projected to increase by an average of 6% annually, driven mainly by teraphthalic acid (TPA) and polyethylene terephthalate (PET) expansions in China, other Asian countries, and the Middle East [7]. Traditionally, xylene isomer purification has required energy intensive methods such as cryogenic crystallization or pressure swing adsorption to obtain sufficiently pure streams of the desired component [4]. Increase in demands for both xylene production and its energy efficient purification method has attracted attention to polymeric membranes for many industrial separations ranging from natural gas purification to pervaporation of organic liquids, including xylene isomers [8].

Membranes for pervaporation separation operate in a more complex manner as compared to gas separation membranes [9]. Membrane materials for organic liquids separation can be classified into two areas; organic polymeric and inorganic materials. Xylene separation has been studied with polyurethane [10,11], polyvinyl alcohol (PVA) [10,12], and polyimides [10,13,14], but none of them have produced substantial selectivies at reasonable permeabilities. For this reason, researchers began exploring the notion of blending bulk polymer with additives. Most of this work has focused on organic materials such as cyclodextrin (CD) [12]. Although CD blending shows a significant para/ortho selectivity of 2.96, experiments were performed at low temperature (25 °C). Polyvinyl alcohol (PVA) has been the most commonly investigated matrix, and since PVA has a low glass transition temperature (~77 °C), the membrane is not useful under a realistic industrial temperature above 150 °C. Further, with CD being comprised of several adjoined sugar rings, it is unclear as to the attainable thermal stability of the additive itself, and is unlikely to withstand more aggressive feed streams at higher temperature while maintaining membrane integrity. For these reasons, and the concern of thermal stability, these materials have questionable industrial utility.

With these concerns in mind, this work investigates the transport properties of xylene isomers in both casting and post casting annealed Torlon® 4000T membranes, which are robust and can be used up to 200 °C for extended period. The preferred membrane preparation technique was developed to ensure consistent xylene

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* Corresponding authors. Tel.: +1 404 385 2845; fax: +1 404 385 2683.
E-mail address: wkoros@chbe.gatech.edu (R. Chafin).

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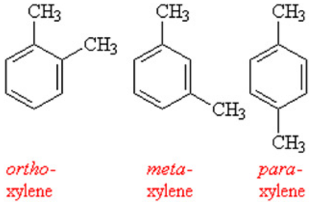

Fig. 1. Chemical structure of xylene isomers.

transport properties. Pervaporation results of xylene isomers are reported for both casting and post casting annealed Torlon® 4000T membranes.

2. Experimental

2.1. Materials

This research focuses on an established polyamide-imide, Torlon® from Solvay Advanced Polymers© in Alpharetta, Georgia. The chemical structure is shown in Fig. 2, as provided by Robertson et al. [15] and Table 1 shows the basic properties of Torlon® 4000T as published by Solvay Advanced Polymers ® [16]. Torlon® is designed to be chemically resistant, thermally stable, and mechanically durable. Also, it is believed that a "densely packed" polymer structure (one with a lower free volume) is likely to be useful for this particular organic liquid separation since the small relative size difference among xylene isomers demands a highly discriminating polymer like Torlon®. Torlon® has a rigid chemical backbone that will allow efficient packing, and is resistant to organic solvents due to the amide group that provides hydrogen bonding between neighboring segments. Torlon® 4000T was supplied in powdered form, partially wet (~3% water), and reported to be "almost completely" imidized. For the remainder of this research, all references to Torlon® refer to the 4000T variant.

2.2. Membrane preparation

The powder form of Torlon® 4000T was formed into thin dense films for pervaporation testing. All films used in the research were cast via the draw casting method, which requires highly viscous polymer solutions ("dope") that can easily form film morphologies with a drawknife. For this procedure, Torlon® powder was dried at 110 °C under vacuum to remove any residual water remaining in the "as-received" powder. The dried powder was then dissolved in a solvent to yield a final solution concentration of 20–25 wt.% total solids. This solution yields approximately a 1 mil film with a casting knife of ~12 mil clearance. The main solvent used for this work was N-methyl pyrrolidinone (NMP), and unless otherwise specified, will be referred to as the solvent herein. All pervaporation measurements were taken on films prepared in NMP. Dimethylacetamide (DMAc), and Dimethylformamide (DMF) were also used in rare occasions and all solvents were supplied from Sigma–Aldrich (Milwaukee, WI) in anhydrous form.

Table 1
Torlon® 4000T Powder Properties [16].

Possible Solvents	NMP, DMAc, DMF, DMSO
Particle Size Range	0–150 μm
Percent Solids	99%
Solution Viscosity, 25% Torlon® 4000T in NMP, 40 °C	7000 cp
Glass Transition Temperature, T_g	280 °C

Once the dope had been prepared and was free of agglomerations and vapor bubbles, composite films were prepared. Casting was performed inside a fume hood to accommodate the evaporation of solvents. A tempered glass substrate was thoroughly cleaned with soap and water, rinsed with de-ionized water, and finally rinsed with acetone. Once dry, the plate was leveled and heated on a hotplate to ~140 °C inside the fume hood. The casting knife (Paul N. Gardner & Co., Pampano Beach, Fl) was placed at the far end of the glass plate, to enable the drawing motion toward the person. The dope was poured slowly into an oblong "puddle" directly in front of the casting knife. The knife was then drawn in a smooth, even motion across the length of the plate and removed without hesitation. The remaining film was immediately covered with an inverted square glass "baking" dish that allows visual inspection of the film, and kept the atmosphere above the film saturated with solvent, thus reducing the rate of evaporation. A vitrified film was formed in ~1 h using a 20 wt.% viscous solution in NMP.

Once the film was formed, it must be completely free of solvent to provide reliable experimental results (See later discussion.). The film was easily removed from the glass substrate using a sharp razor blade and peeling up a corner. The film was "released" from the surface with little effort. The film was then suspended on a wire hanger, attached at top and bottom to maintain the film geometry as a flat plane. The suspended film was placed in a modified vacuum oven capable of controlled temperature ramping to various temperatures, and holding overnight, before cooling back to room temperature over 25 h. The resulting film was flat in geometry, and ready for further characterization.

2.3. Membrane testing methods

All Torlon® membranes were tested for isomer purification performance by pervaporation experiments. The permeability and selectivity are obtained from this measurement. Due to the flammable nature of the xylene feed mixture, a special apparatus was designed to safely and efficiently perform the desired experiments. The apparatus and procedure are described in the following sections. For all pervaporation experiments, the feed mixture was prepared before hand and verified to have the proper composition. All xylene pervaporation experiments were carried out with a feed composition of 30% p-xylene (99% Sigma–Aldrich), 30% m-xylene (99% Sigma–Aldrich), 30% o-xylene (97% Sigma–Aldrich), and 10% ethyl benzene (99% Sigma–Aldrich). This is a rough estimation of the composition for an actual industrial feed composition entering a p-xylene recovery unit. All compositions were made by weighing

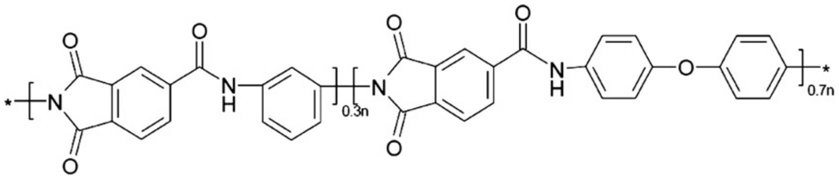

Fig. 2. Structure of Torlon® 4000T polyamide-imide proposed by [15].

each individual component to the tenth of a gram, and the total batch sizes were 400 g of solution.

2.3.1. Pervaporation apparatus

The performance of all membranes was determined based on permeability and selectivity from pervaporation experiments. The permeability and selectivity of gas pairs (para/ortho and para/meta) were determined using the standard isochoric (constant-volume, variable pressure) technique [17–19]. Due to the flammable nature of the xylene feed mixture, a special apparatus was designed to safely and efficiently perform the desired experiments.

A process flow diagram (PFD) of the experimental apparatus is shown in Fig. 3. The system is contained within a large microprocessor controlled vacuum oven (VWR model number 1430 M), and can be heated from room temperature to over 210 °C. The atmosphere surrounding the apparatus can be evacuated to ensure the removal of a flammable atmosphere, thus greatly reducing any chance of ignition in the case of a xylene leak at elevated temperatures. All fittings for the apparatus are stainless steel Swagelok® (Solon, OH) welds, tube fittings, or Swagelok® VCR® fittings.

The temperature of the system is measured via a thermocouple, and verified via an internal mercury thermometer to ensure accuracy. The temperature is maintained within 0.5 °C of the set-point, thus adequately maintaining the upstream vapor pressure or membrane feed pressure. The downstream transducer is a 10 torr Baratron® 615A bake-able pressure transducer supplied by MKS instruments (Andover, MA). The transducer signal is passed through a Baratron® (MKS) 270D signal conditioner before being recorded with a Keithly KCPI-3107 data acquisition board installed on a computer running Labview® software (National Instruments, Austin, TX) for data acquisition.

The pervaporation cell was designed to be contained inside the vacuum oven, and to operate reliably at high temperatures. The cell is constructed of stainless steel components with the exception of a PTFE magnetic stir bar. The cell consists of three components: the downstream face, the body, and the agitation lid. The downstream is flat with the exception of o-ring grooves for Viton® o-rings (supplied by McMaster Carr) for sealing. A piece of porous grade D sintered metal (Metron Technology; Austin, TX) is inserted in the downstream face, which is connected to the permeate reservoir. The body of the pervaporation cell provides a space where approximately 450 ml of feed solution can be agitated while in direct contact with the membrane. The agitation lid covers the body, and contains a magnetic stirring apparatus that is controlled by a magnet spinning bar above the cell. This keeps the solution well mixed, and prevents concentration polarization close to the

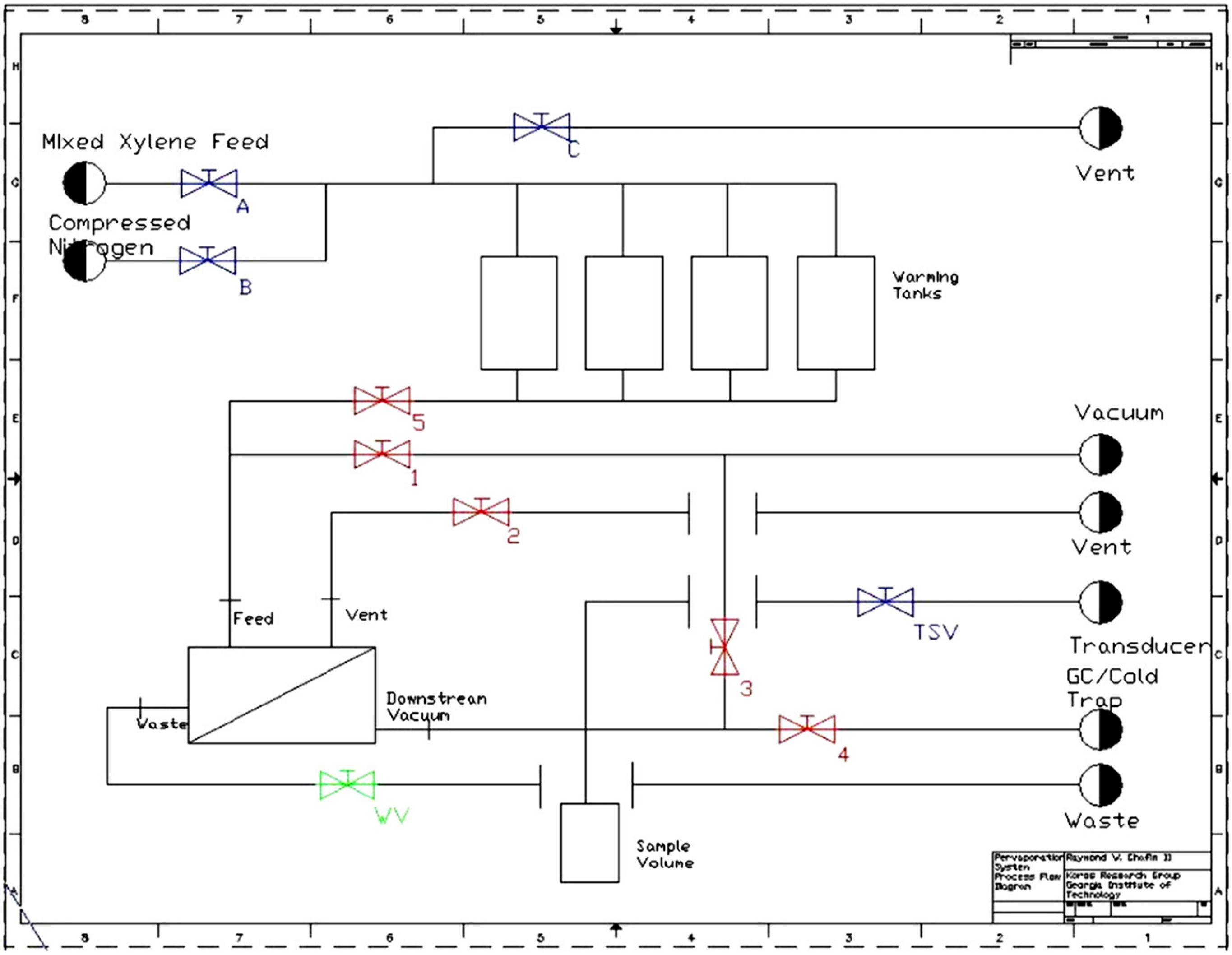

Fig. 3. Process flow diagram of pervaporation system. Valves A, B, and C are used to load and transfer feed mixture to pervaporation cell. Valves 1–5 are used to control pervaporation experiments for permeation and selectivity. The waste valve (WV) is used to remove the feed mixture from the apparatus via an external cold trap.

membrane surface. The cell contains inlets to allow the feed to be added, and contains outlets for venting, liquid removal, and permeate removal. A general drawing is shown in Fig. 4.

The entire apparatus is designed for safe operation while at temperatures in excess of 200 °C. This is accomplished by the removal of all control valves to the exterior of the oven. All valve handles are on top of the oven, while the valve stems extend within to control the process in the high temperature environment. Agitation also passes through the oven wall, with a large powerful stirring magnet residing approximately 0.25″ above the cell, and is controlled via a variable speed motor mounted on top the oven. The feed solution is weighed and measured in a graduated 1000 ml addition funnel, and is connected to the system on top of the oven. The liquid is then fed to four 150 ml holding tanks inside the oven via gravity. Once inside, the liquid can be moved to the body of the pervaporation cell with 20psi nitrogen pressure. At the conclusion of the experiment, the liquid can be removed via a "waste" vent connected to a 1000 ml vacuum dewar that leaves the pervaporation body essentially empty. This entire process can be completed without exposing the operator to excessive temperatures or chemicals.

2.3.2. Pervaporation procedure

This section outlines the basic procedure for testing membranes via pervaporation, and generally refers to Fig. 3. After the cell is inserted into the system, the main vacuum valve is opened to expose the downstream of the membrane to vacuum. The downstream pressure is monitored, and the rate of evacuation is indicative of seal quality, and judged by previous experience. Once the downstream is evacuated, the feed solution is gravity fed from a graduated addition funnel into four 150 ml holding tanks by opening the feed valve (A) and opening the holding tank ventilation valves (C) to relieve any pressure. Upon completion, the feed valve (A) and ventilation valve (C) are closed, and the compressed nitrogen valve is opened along with pervaporation cell valves (5) and (2) to allow the compressed nitrogen to move the liquid from the holding tanks to the pervaporation cell. This step can either be completed before or after the temperature set-point has been reached. Once the liquid is in contact with the membrane, the system is allowed to maintain temperature overnight, while the downstream is under active vacuum, to ensure steady state flux. To measure permeability, the vacuum valve (3) and the GC/cold trap valve (4) are closed to isolate the downstream. The pressure rise data are collected as discussed above, and then the vacuum valves (3 or 4) are re-opened. For selectivity measurements, the permeate is allowed to collect in a cold trap via valve (4). In this case the vacuum valve (3) is closed, and the vacuum is maintained through the cold trap, and condenses permeate in the liquid nitrogen trap. After collection, valve (4) is closed, the permeate is analyzed with an Agilent 6890 Gas Chromatograph for composition ratio. Upon completion of the experiment, the liquid is removed from the cell via a 1000 ml liquid nitrogen trap through the "waste valve" (WV). The feed solution is collected and analyzed via GC to ensure stable composition. The system is allowed to cool to room temperature before removal of the pervaporation cell and film.

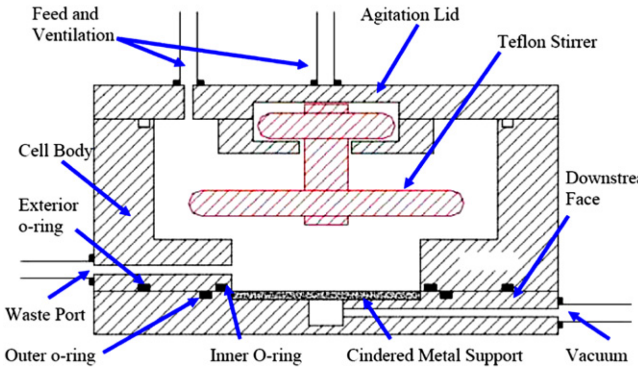

Fig. 4. A cross-section of the stainless steel pervaporation cell. The agitation lid holds a teflon stir bar controlled by a magnet spinning on top of the cell. The lid also contains a feed inlet, and ventilation opening. The cell body can contain ~450 ml of solution, and includes a waste port for draining of the feed mixture at experimental completion. The downstream face seals the membranes on the imbedded o-rings, and supports the membrane with cindered metal. Vacuum is established on the downstream face to maintain the chemical potential difference which is the driving force for separation.

2.4. Complementary characterization methods

2.4.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was used to determine solvent content, and degradation temperatures of membranes. TGA was performed in a Netzch STA 409 PC TGA (Burlington, MA). Samples can be heated in air or inert purge at rates of 1 °C–20 °C per minute.

2.4.2. Infrared spectroscopy (IR)

A Bruker Tensor 27 FTIR spectrometer outfitted with a Harrick MVP2 ATR mini-sampler was used to obtain infrared spectra (IR) of film and powder samples in order to compare levels of imidization. Both as-received powder samples and films prepared by the previous procedures were examined.

2.4.3. Measurement of film refractive index via waveguide coupling

A Metricon prism coupler was used to measure the refractive index of the thin, freestanding membrane films. This technique utilizes an optical prism, by pneumatically holding the prism base against the polymer film sample. A laser is then passed through the prism, reflected at its base, and then on to a photo-detector. At certain angles of incidence, the light can tunnel across the air-gap and into the film, causing a drop in detected intensity, or "node". From the node location, and node spacing, thin film refractive index and thickness can be determined. This work was expanded by Samuels et al. [20,21] to determine the refractive index in all three axes. These techniques were utilized to determine the average bulk refractive index of membrane films examined in this work. A more thorough overview of waveguide coupling is available from the Metricon website [22].

3. Results and discussion

3.1. Methods for Torlon® membrane optimization

Several authors have described methods to form solution processable films for gas separation [23]. Torlon® 4000T was processed in a similar manner to these conventional approaches. It was draw-cast into dense film membrane form, and vacuum dried at 200 °C over approximately 18hrs. The results shown in Table 2, indicate a significant variance in transport properties but suggest Torlon® is a more attractive candidate than previously published materials [10–14,24–26]. Resolving the film property variance and developing procedures for reliable, repeatable membrane formation was, therefore, identified as a high priority.

Solvay Advanced Polymers® published a "Powder Bulletin" [16], for each Torlon® variant that describes a series of processes that take place during proper formation of Torlon® polymer coatings. Solvay® publications recommend a high temperature cure of 250°–300 °C for polymer coatings. Solvay® indicates that three processes occur during this curing stage. *First*, final imidization should occur from 40° to 140 °C. *Second*, the majority of the casting

Table 2
Initial Torlon® results indicating poor transport property repeatability. Pervaporation was tested at 200 °C for all samples.

Film ID▾	Flux normalized by thickness	Selectivity	Selectivity	Para-Xylene Permeability
Units►	(cc(STP) × cm)/(cm^2 × sec)	Para/Unwanted[a]	Para/Ortho	Barrer
TOR-ANL-007	1.57E-07	2.80	2.45	0.68
TOR-ANL-008	1.31E-07	3.96	7.44	0.73
TOR-ANL-010	1.42E-07	1.81	2.23	0.54

[a] "Unwanted" means anything other than p-xylene.

solvent is removed from 140° to 232 °C. *Finally*, removal of the last traces of solvent and the molecular weight increase are suggested to occur from 232 °C and higher. Each of these three processes will be investigated in the following section, and some information will be used to form repeatable Torlon® membranes for xylene separation.

3.1.1. Thermally induced imidization

As-received powder samples and films prepared by the previously discussed procedure were scanned by IR. The resulting powder spectrum is shown in Fig. 5, along with identification of all the major peaks associated with the polyamide-imide backbone structure. In addition, Fig. 5 also shows a spectrum of a 200 °C temperature treated Torlon® membrane film (red line). Clearly, there is very little change in the overall IR spectra, with negligible change in the imide peaks associated with further imidization. As a result, it is fair to conclude that imidization is unlikely to have caused the poor repeatability (Refer to Table 2) in Torlon® membrane samples, and the polymer is essentially completely imidized upon receipt from Solvay®.

3.1.2. Molecular weight enhancement

Polyamide-imide average molecular weights can be estimated by inherent viscosity (η_{inh}) correlations using an Ubbelohde viscometer. Dilute polymer solutions are prepared in NMP and tested at 25 °C to determine if there is any change in molecular weight during high temperature treatments [27]. Table 3 shows the results of comparing an "as-received" Torlon® powder with films treated at different temperatures. The data in Table 3 suggests no significant trends in molecular weight for samples treated at or above 150 °C. There may be slight increases, but this increase is most likely not the cause for poor repeatability in transport properties.

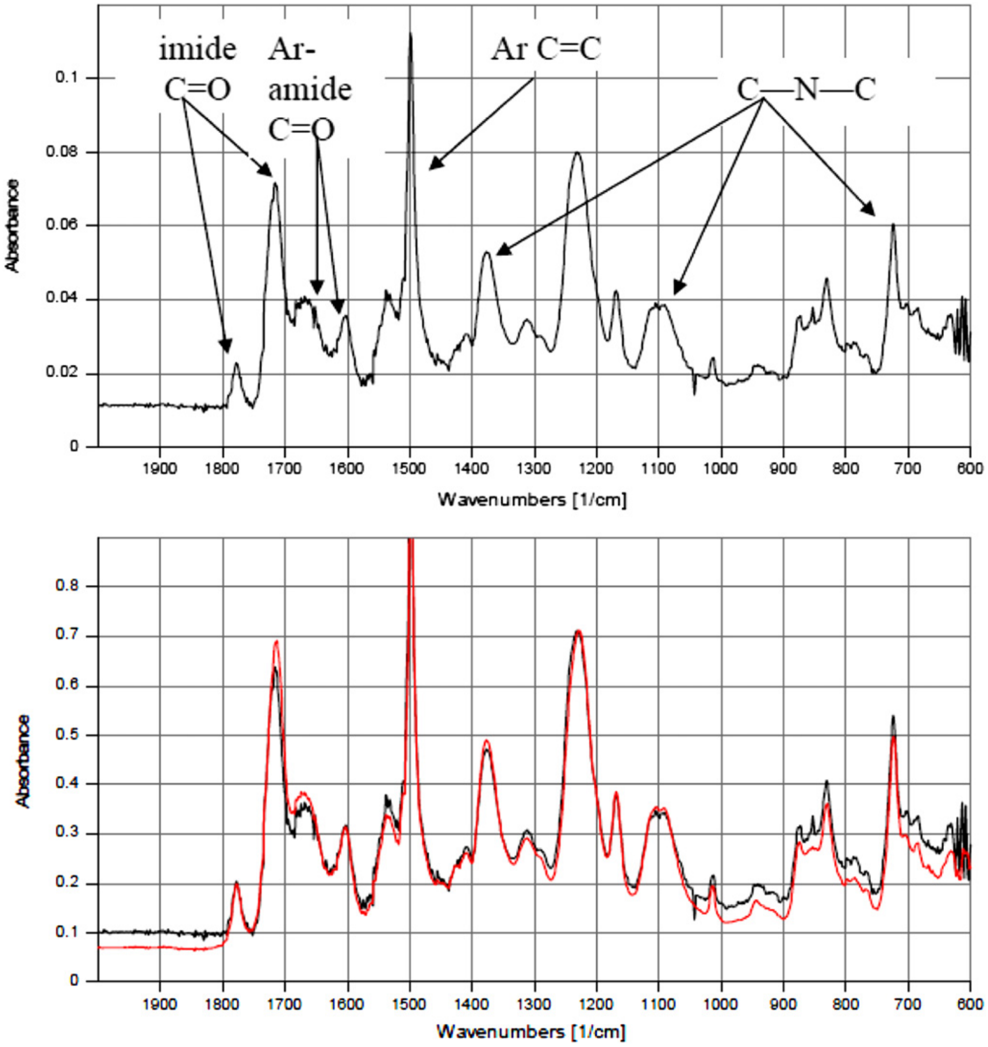

Fig. 5. Infrared Spectra of Torlon® 4000T powder as received from Solvay Advanced Polymers® (Top) and identification of all major peaks associated with chemical groups in the Torlon® chemical structure. Also shown is a comparison (bottom) of a 200 °C temperature treated Torlon® film with the as received powder, showing essentially no change in imidization peaks.

Table 3
Comparison of inherent viscosities of several Torlon® samples. Molecular weight data taken from published literature correlations [27].

Torlon® 4000T Samples	η_{inv} (dl/g)	~M_w (kg/mol)	
“As received” powder	0.53	20.1	23.6
Film cast from NMP, air dried overnight	0.44	17.6	19.9
Film with 8% xylene	0.50	19.3	22.4
Film, dried at 150 °C	0.52	19.8	23.2
Film, dried at 260 °C/24hrs/vacuum oven	0.59	21.8	26.1

3.1.3. *Solvent removal*

The last process investigated was solvent removal, which occurs at the higher temperature range of 232 °C to over 300 °C. Initial film preparation procedures require vacuum drying of polymer samples at 200 °C, without annealing the film above the glass transition temperature ($T_g = 280$ °C). In order to investigate the amount of solvent remaining in the films after membrane formation, thermogravimetric analysis (TGA) was completed on a series of film samples to determine residual solvent content. Fig. 6(a) shows the results of TGA on three separate polymer samples: Torlon® Powder, an NMP cast film, and a DMAC cast film. In these examples it can be seen that solvent desorbs from the sample over the temperature range of 100 °C to approximately 300 °C. First, it should be noted that the Torlon® powder contains a residual amount of NMP (~2 wt.%) in the “as-received” form, as evidenced by the mass loss around 270 °C. This residual amount of NMP in the powder is reduced with temperature treating to 250 °C, although it remains slightly apparent in the analysis. The NMP cast film contains a very high amount (nearly 20 wt.%) of residual solvent before temperature treatment overnight at 200 °C, after which nearly 6 wt.% of NMP still remains. This amount of solvent remaining in films to be used for membrane testing is unacceptable as it may induce an unexpected non-ideal effect. Another film using DMAC as the casting solvent was also tested, and was found to be an improvement over the NMP case, however, most commercial fiber spinning operations would prefer to operate with NMP as the casting solvent, and therefore a method to prepare essentially solvent free membranes is desirable. Fig. 6(b) shows the effect of different temperature treatment options as a method to reduce the overall remaining solvent content. It can be seen that once the polymer has been taken above the glass transition temperature of the structure, the polymer appears to more readily desorb the solvent molecules. By exposing dense films to 315 °C and vacuum overnight, essentially all of the residual NMP can be removed from the system. This should allow testing of the neat polymer’s properties for organic liquid separation without interference from the residual solvent.

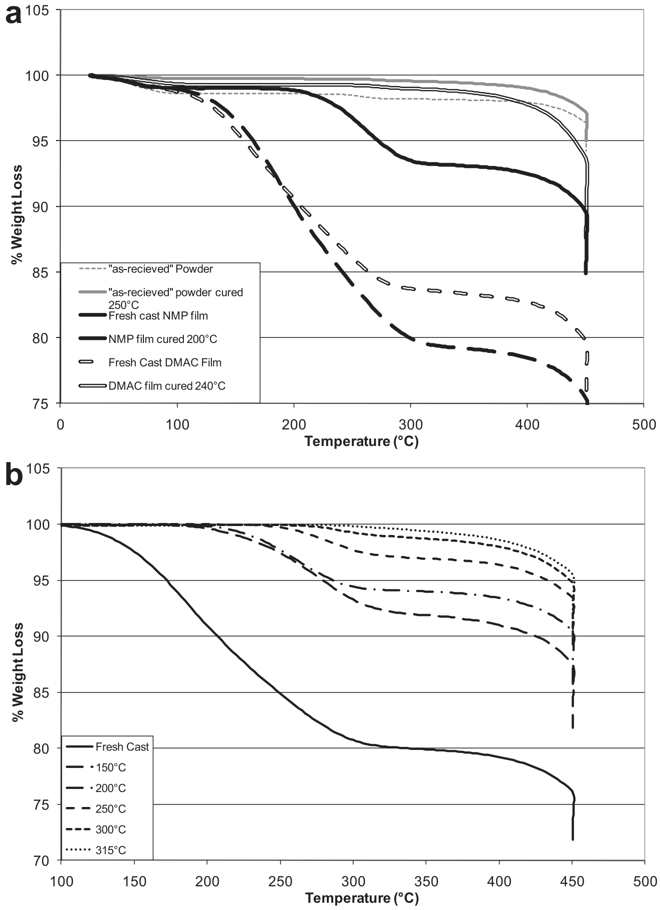

Fig. 6. (a) (top) TGA of three polymer samples: Torlon® powder, NMP cast film, DMAC cast film. Dashed lines show sample before temperature treatment, solid lines show samples after treatment. (b) (bottom) NMP cast films temperature treated up to 315 °C. The high temperature essentially removes all residual solvent.

3.1.4. *Final film methodology*

Based on the previous characterization, a new method was developed in order to provide solvent free, temperature treated films that provide repeatable transport properties. The procedure is as follows:

1. Torlon® powder is dried at 110 °C overnight, under vacuum to remove water.
2. Dehydrated Torlon® is mixed with dry NMP solvent, to yield an approximately 23% solution in 20 ml vials.
3. Solutions are rolled overnight to allow adequate mixing and dissolution of all polymer powder.
4. Polymer solutions are draw-cast on a heated tempered glass plate at ~115 °C, covered with an inverted baking dish, and allowed to vitrify for 1 h and 20 min.
5. Vitrified films are removed from the casting plate, and placed in a spring holder to maintain thin dense film shape.
6. Film and holder are treated in a vacuum oven at 315 °C for 24 h, and allowed to cool to room temperature over the following 25 h.
7. Cooled films are immediately tested for transport properties.

This procedure has yielded excellent and reproducible results. Films utilizing this procedure will be characterized in the next section.

3.2. *Characterization of Torlon® 4000T PAI for xylene purification*

3.2.1. *Pervaporation of Torlon® 4000T thermally treated films*

Membrane flux measurements were taken daily, while permeate was collected over different intervals, depending on the flux, and the collected liquid was analyzed by gas chromatograph for composition and selectivity. Due to the inability to determine permeate composition and flux data simultaneously, exact permeability data are not plotted. Instead, thickness normalized flux and selectivity in their actual intervals are reported. Thickness normalized flux is calculated by using a definition of permeability (equation (1)).

$$\text{Thickness Normalized Flux}_i = \frac{P_i \cdot \Delta p_i}{l} \tag{1}$$

where, P_i is permeability for component i, $\frac{\text{cc(STP)}\cdot\text{cm}}{\text{cm}^2\cdot\text{s}\cdot\text{cmHg}}$, Δp_i is a partial pressure drop across a particular membrane sample, cmHg, and l is the thickness of membrane, cm.

Separation factor, indicating a particular membrane's efficiency at separating one penetrant from another, in pervaporation is represented as:

$$\alpha_{A/B} = \frac{p''_A/p''_B}{p'_A/p'_B} = \frac{y_A/y_B}{x_A/x_B} \tag{2}$$

where, p''_A and p''_B represent the partial pressure of the components in the permeate stream, p'_A and p'_B represent the partial pressure of the components in the feed stream, y_A and y_B indicate the mole fraction of each component in the permeate stream, and x_A and x_B indicate the mole fraction of each component in the feed stream.

Equation (2) can be modified into equation (3) by considering following facts;

1. The ratio of the permeate partial pressures is also equal to the ratio of the individual species flux in the downstream receiver
2. Downstream pressure is negligible (i.e. vacuum permeate) with a constant membrane thickness
3. Partial pressure of permeate can be estimated by a modified Raoult's law at the feed temperature to account for non-ideal solution behavior in terms of P_i, γ_i, and p_i^* which corresponds to the permeability, activity coefficient and vapor pressure of component i, respectively.

$$\alpha_{A/B} = \frac{p''_A/p''_B}{x_A/x_B} = \left[\frac{(P)_A}{(P)_B}\right] \cdot \left[\frac{\gamma_A p_A^*}{\gamma_B p_B^*}\right] \tag{3}$$

since the final permeability and selectivity apply during stable periods of membrane performance, final membrane permeability will be reported.

The average results of three films are shown in Fig. 7. The first observation that is readily apparent from the data is the obvious decrease in membrane flux over time. This decrease appears to be an intrinsic property of the polymer under these testing conditions, and corresponds to an appropriate increase in the selectivity for the *para* isomer. It should be noted that this selectivity (3.1 p/o, and 2.1 p/m) is *the highest reported value to date at 200 °C for a polymeric material separating xylene isomers.* The permeability appears to reach a settled "equilibrium" at about 0.25 Barrer, which is questionably low for a commercially feasible membrane.

The "permeability collapse" apparent in Fig. 7 is an unusual phenomenon, not usually seen in typical gas separation applications. There is a large difference between gas applications versus pervaporation operating conditions in which an elevated feed activity and high operating temperature apply. It is possible that during the annealing step, NMP is removed from the system and leaves some free volume remaining in the material; i.e. a sorption site previously occupied by NMP is now presumably empty. It is also believed that the presence of the xylene isomers allows the polymer a certain amount of mobility, not possible without the xylene isomer, which eventually allows this excess free volume to relax and reach a more equilibrium state. The nature of the conditioning effect of the xylene isomers will be discussed over the next two sections.

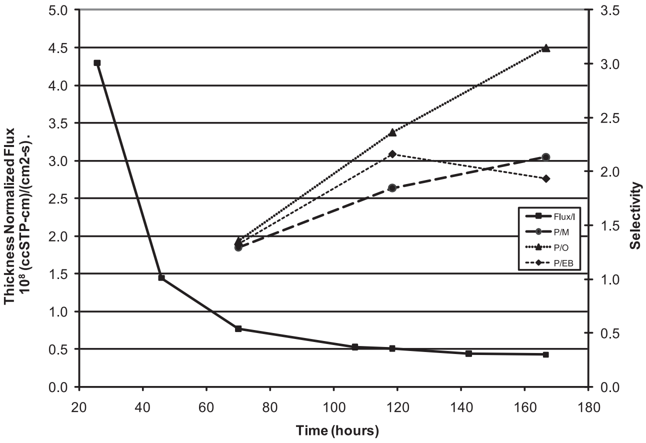

Fig. 7. Normalized flux and selectivity of thermally treated Torlon 4000T films. Normalized flux is represented by a solid red line, while selectivities for different components are represented by dashed lines.

3.2.2. *Thermal post-treatment of Torlon® 4000T*

The decrease in permeability could be due to either testing at elevated temperatures, exposure to high activity xylene, or a combination of both components. In order to decouple the effects of the high temperature atmosphere, a film was prepared in an identical manner as in Section 3.1.4. This film was then reheated in a vacuum oven to 200 °C and allowed to remain heated for 120 h, (the length of time needed for a "permeability collapse" to occur in Section 3.2.1). The film was subsequently cooled slowly, and then tested by pervaporation for xylene isomer permeation. Fig. 8 compares this film to the average film in Section 3.2.1, and an overall decrease in the location of the collapse, shifting the entire curve down, and ultimately causing a 40% change in the final membrane flux. The shape of the permeability decline is maintained, along with the overall difference. It appears the long-term temperature heating of the sample did slightly reduce the amount of available free volume in the polymer, and hence reduced the permeability. Duthie et al. [28] showed that thermal annealing causes a reduction in both the size and number of free volume elements in two typical polyimide membranes; BTDA-DAPI (poly(3,3′-4,4′-benzophenone tetracarboxylic-dianhydride diaminophenylindane) and 6FDA-TMPDA (poly 2,2′-bis(3,4′-dicasrboxyphenyl) hexafluoropropane dianhydride-2,3,5,6-tetramethyl-1,4-phenylenediamine). Although there appears to be an effect of the long-term thermal treatment, it is obvious that there is some additional effect that occurs due to the presence of xylene at high temperature.

3.2.3. *Relaxation theories*

The permeability decline phenomena observed in Figs. 7 and 8 are presumably related to aging effects reported in gas permeation literature [29,30]. The shorter time scale associated with the higher temperature conditioning study here is a differentiating

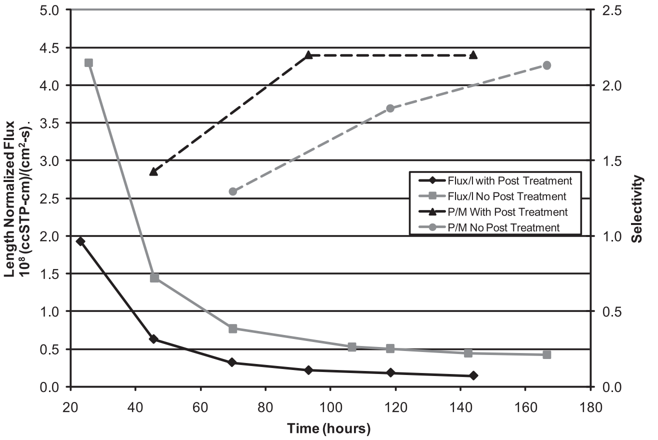

Fig. 8. A comparison of the average Torlon® film prepared by thermal annealing with a similar film that received a 5 day thermal treatment at 200 °C.

factor as compared to previous literature. Another differentiating factor may be the use of a more interacting penetrant vs. the simple penetrant gases. In any case, it is reasonable to presume that the permeability decrease may be caused by aging mechanisms similar to those reported in earlier studies. Therefore, lattice contraction [31,32] and diffusion of free volume [33], possibly accelerated in this case due to the operating conditions, appear to provide a reasonable framework to interpret the present observation. Both of these aging mechanisms could result in a material with an overall reduced amount and type of free volume available to a particular penetrant for transport. In theory, as a polymer material relaxes, packets of free volume will be removed, and diffusion of free volume will ideally allow the general location and size of the free volume packets to change [34]. This could create a more discriminating material with fewer opportunities for transport due to more infrequent adequately large size diffusion gaps to enable diffusion steps. Moreover, this process would be expected to lead to more size discriminating transport due to a reduced relative number of “large” diffusion gaps [34]. This ultimately describes a more dense structure after exposure to xylene and high temperature. It appears that aging in the presence of the desired feed produces a more favorable amount and distribution of diffusion-enabling free volume packets after the structure settles in to a more-or-less “altered, but stable” glassy matrix structure.

In order to corroborate this hypothesis, two separate avenues were explored. First, given the swelling nature of the penetrant and the glass transition temperature of the polymer at 280 °C, depression of the T_g can yield a system with higher chain mobility, thus rendering the polymer more conducive to free volume relaxation. Chow [35] has developed a theoretical relation (Equation (4)) for the estimation of T_g depression caused by a diluent.

$$\ln\frac{T_g}{T_{g_o}} = \beta[(1-\theta)\ln(1-\theta)+\theta\ln\theta] \tag{4}$$

where,

$$\theta = \frac{M_P}{zM_d}\frac{\omega}{1-\omega} \tag{5}$$

and,

$$\beta = \frac{zR}{M_p\Delta C_P} \tag{6}$$

in the above equations, T_{go} is the glass transition temperature for the pure polymer, while T_g is the value when the weight fraction of the diluent is ω. M_d is the molecular weight of the diluent, M_p is the molecular weight of the polymer repeat unit, and ΔC_P is the change in specific heat of the polymer at its glass transition. The parameter z is the average coordination number in the matrix and R is the gas constant. All of the above parameters are known or can be measured directly, with the exception of the coordination number. For this, Chow has suggested using the coordination number of 1. While the case for choosing a coordination number of 1 is physically not easily justified, it can be used as a base case for calculation, consistent with Chow’s suggestion.

Thermogravimetric Analysis (TGA) of films after exposure to xylene provides an estimate of the sorption capacity of xylene isomers in Torlon® 4000T films, and consistently point to ~5 wt.% xylene that is contained in the polymer during exposure to saturated liquid xylene feeds. Although there are inaccuracies in this technique, it serves as a useful estimate, and more rigorous testing of xylene sorption at 200 °C demands many challenging safety concerns. Using this sorption value and equation (4), an approximate reduction in T_g from 280 °C to ~265 °C can be calculated, which suggests that xylene transport in Torlon® at 200 °C is indeed occurring in the glassy regime, with some enhanced mobility over the neat polymer condition at 200 °C. With Chow’s method, the reduction in T_g with 5 wt.% xylene in Torlon® can also be estimated by the Fox equation [36]. Camacho-Zuniga and Ruiz-Trevino [37] proposed a method to estimate T_g of polymers and diluents. Based on their method, the T_g of each type of xylene was estimated to be −118 °C, −165 °C, and −144 °C in the order of ortho, meta, and para, respectively. If a value of 280 °C is used for the T_g of Torlon® with an average T_g of −142 °C for xylene in Fox equation, the estimated value of T_g is 202 °C, which is reasonably consistent with the estimation by Chow’s method and indicates the presence of plasticization.

The second avenue to explore in order to understand the results in Fig. 8 is the idea that reduction in free volume in the plasticized sample leads to a more densified polymer matrix. Directly measuring density changes of Torlon® films is difficult, since sorbed amounts of xylene cannot be desorbed without disturbing the free volume distribution in the matrix, and the density. In light of this challenge, optical methods were utilized, which measure refractive indices of dense polymer films [20,21]. This measurement can be corrected for the amount of solvent sorbed, to provide inferences about polymer density based on the known proportional relationship between refractive index and density for a given material. This methods use a helium laser, and an optical waveguide to measure refractive index in all three dimensions and yield an average refractive index for the material. Thus, an average polymer density can be estimated [20,21]. Three types of films were tested for refractive index and the results are shown in Fig. 9. Annealed films were first prepared under the same conditions as the 315 °C treated samples in Section 3.1.4. The annealed films have very similar refractive indices of approximately 1.7040, and are assigned the literature density of Torlon® given at 1.41 g/cc. After one day of xylene testing, (equivalent to the first data point in Fig. 7) the film shows a significantly lower refractive index of 1.7015, which is associated with a lower density and/or swollen state. However, after 5 days of xylene testing, the film shows a higher refractive index than the originally annealed sample, suggesting a densified film. This observation strongly supports the idea that the membrane is originally swollen upon initial xylene exposure, and then relaxes to a more densified, and more discriminating state.

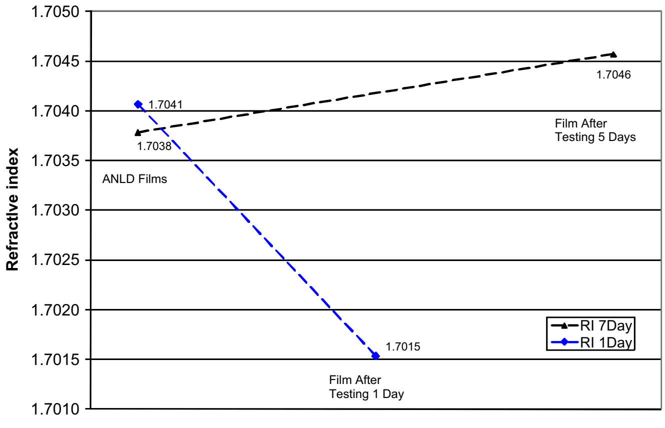

Fig. 9. Refractive Index (RI) measurements of separate films at different points during pervaporation testing. The blue line represents a film from the annealed state through 1 day of testing. The black line represents a film from the annealed state through 5 days of testing. The difference in the ending points shows a more dense film after exposure to high temperature and xylene. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 4
Free volume calculations of Torlon® membranes.

State	n	L	r [g/cc]	f
Annealed	1.7039	0.4876	1.4100	0.1086
1 Day	1.7015	0.4865	1.4069	0.1105
5 Day	1.7046	0.4879	1.4108	0.1080

To further probe the concept of densification, refractive index measurements can be further manipulated directly to free volume measurements within the polymer. Using the Lorentz equation,

$$L = \frac{n^2 - 1}{n^2 + 1} = \rho \cdot C \tag{7}$$

Refractive indices, *n*, can be used to obtain the Lorentz parameter, *L*, which is directly proportional to the polymer density via a constant, *C*. By assuming the annealed state has the literature density, the constant can be determined, and thus the density at different values of the refractive index can be determined. It would be preferable to have an accurate measurement of the density of Torlon® in the annealed state, but in the absence of such a measurement, this assumption does not introduce extreme errors and any later inferences made about *changes* in density are still valid. It is well known that fractional free volume, *f*, can be correlated to density as well as permeability, *P*, to fractional free volume, by the following two relationships:

$$f = 1 - \rho \cdot V_o \tag{8}$$

$$P = a \cdot \exp\left(\frac{-b}{f}\right) \tag{9}$$

where,

$$V_O = 1.3 V_w \tag{10}$$

V_w is the van der waals volume of the polymer chains calculated by group contribution methods by van Krevelen [38], and *a* and *b* are fitting parameters that have been shown to depend on the polymer family (*a*) and the penetrants relationship with the available free volume (*b*). Using these equations, Table 4 can be generalized. These results suggest that even very small changes in fractional free volume can have large effects on large molecule permeability, and also lead to significantly increased permeation discrimination between large molecules with similar sizes and shaped molecules like the xylene isomers and ethylbenzene. If the free volume values are used with the permeabilities from Figs. 7 and 8 values of *a* and *b* can be determined as ~275 and ~30, respectively. These values are shown in Table 5 in comparison with other molecule/polymer examples from literature and they compare well considering the size of the xylene molecule.

To further elaborate upon this possible conditioning scenario, Fig. 10 shows two illustrative free volume distributions that could arise from this type of relaxation process and help explain the observed results. The first free volume distribution (blue line) is a typical Gaussian distribution of free volume expected after annealing of a polymer film. In this illustration, molecules on the size order of xylene isomers have very little size discrimination due to the similar availability of free volume of the same size. However, after a hypothesized relaxation (red line) the free volume changes in such a way that it is no longer as accessible to molecules of similar size and shape of xylene isomers, and can in fact become discriminating between such isomers. For this particular illustration, there is very little difference in the area under the two curves, or two total free volumes available. It is difficult, if not impossible, to tell if this is exactly the scenario in the xylene/Torlon® system, however this suggestion is at least consistent with the previous explanation of mobility and fractional free volume. Positron annihilation has recently become an attractive method to probe such changes, and future work could possibly explore this avenue of characterization. We hope to be able to pursue this approach in the future [39]. Unfortunately, this technique requires specialized facilities that are not available to the authors at this time.

Table 5
Fit parameters for Equation (9), various polymers.

Penetrant	Polymer	a [Barrer]	b	Ref
CO_2	Polysulfone	1.08×10^{-4}	1.89	[14]
CH_4	Polysulfone	1.14×10^{-5}	2.04	[14]
N_2	Polysulfone	1.16×10^{-5}	2.01	[14]
Toluene	6FDA/DAM$_i$/DABA$_i$	81	13.82	[15]
Iso-Octane	6FDA/DAM$_i$/DABA$_i$	140	25.3	[15]
p-xylene	Torlon®	270	29.66	This Study

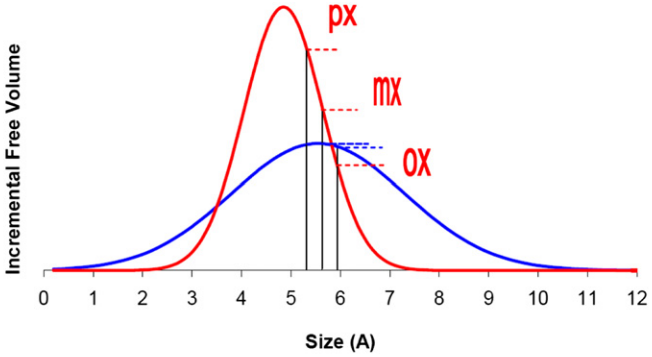

Fig. 10. An illustration of what a possible free volume relaxation may do. The blue represents a hypothetical annealed polymer sample with a Gaussian distribution around a mean free volume size. Upon relaxing, the size and standard deviation of the distribution could hypothetically change resulting in a more discriminating type of free volume as demonstrated by the red line. The area under the curve in each distribution, or the total free volume remains unchanged. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

4. Conclusions

Torlon® polyamide-imide has unique properties that are useful as a pervaporation membrane for para-xylene purification at high temperatures. As a result of this work, the following conclusions about Torlon® 4000T can be made.

- The resulting permeability and selectivity over the ortho and meta isomers for a Torlon® 4000T dense film are 0.25 Barrer, ~3.0, and ~2.0, respectively.
- During formation of Torlon® membranes, an annealing step to 300 °C was introduced that removes essentially all of the remaining NMP solvent from the dense film.
- Pervaporation of a representative industrial feed (30% para, 30% meta, 30% ortho, 10% ethyl benzene) at 200 °C has revealed a “permeability collapse” that appears to be an accelerated conditioning of the free volume distribution in the Torlon® membrane. This conditioning effect is not observed with heat alone, and could possibly be due to enhanced mobility of the Torlon® chains in the presence of the interacting aromatic penetrants.

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