

# Pervaporative Separation of Aromatic/Aliphatic Mixtures with Poly(Siloxane-co-Imide) and Poly(Ether-co-Imide) Membranes

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**S** Supporting Information

**ABSTRACT:** Aromatic random copolyimides were synthesized and tested as membrane materials for the separation of a mixture of aromatic and aliphatic hydrocarbons by pervaporation. The polymers were synthesized by a two-step polycondensation route with a total of 4 aromatic dianhydrides, 4 aromatic diamines, and 3 diamino-terminated aliphatic oligomers containing either ether or siloxane units. Pervaporation experiments were conducted at two temperatures with toluene/*n*-heptane and benzene/*n*-heptane mixtures as feed streams. All polymers were selective toward the aromatic hydrocarbon. Introduction of siloxane units in the polymer generally led to very high hydrocarbon permeability coefficients, but caused a reduction in selectivity relative to that of the aromatic homopolyimide. Incorporation of ether units, on the other hand, did not generally cause such large increases in permeability, nor large decreases in selectivity. The performance of these materials was compared with previous results reported in the literature for other polymers.

## 1. INTRODUCTION

Refinery streams can contain a mixture of aromatic and aliphatic hydrocarbons, with volumes that can reach 1600–8000 m<sup>3</sup>/day.<sup>1</sup> Many of these mixtures are difficult to separate because they contain close boiling compounds that generally have similar physical and chemical properties. Traditionally, such separations have been performed by extractive distillation, azeotropic distillation, and liquid–liquid extraction, leading to energy intensive and expensive processes.<sup>2,3</sup> Membrane technology, being more economical, energy efficient, and ecologically friendly, constitutes a promising alternative to these conventional separation technologies. Pervaporation, in particular, has been intensively investigated for the separation of aromatic/aliphatic mixtures.<sup>4–7</sup> However, a suitable polymeric membrane material to enable commercial application of this technology is yet to emerge.

Aromatic polyimides (APIs) have been investigated as membrane materials for aromatic/aliphatic separation by pervaporation.<sup>8–10</sup> A considerable amount of pervaporation data is available for polyimide membranes that have been tested for their ability to separate mixtures of benzene and cyclohexane,<sup>11–22</sup> but the same is not true for mixtures of aromatic and linear aliphatic hydrocarbons.<sup>23–26</sup> For the specific case of toluene/*n*-heptane and benzene/*n*-heptane mixtures, Ribeiro et al.<sup>27</sup> recently presented a structure/property survey of a series of aromatic polyimides and polybenzoxazoles, covering a total of 10 different monomers (6 diamines and 4 dianhydrides). Hydrocarbon permeability was shown to be highly dependent on the diamine moiety and spanned 4 orders of magnitude for the monomers tested. Overall, materials with enhanced transport properties compared to other previously tested APIs were reported. However, the highest combination of selectivity and permeability values for

the toluene/*n*-heptane system was associated with cross-linked aliphatic polyurethanes.

In spite of the importance of transport properties in the selection of a membrane material, other factors must also be taken into consideration for the target application. For example, the separation of hydrocarbon streams in refineries by pervaporation will require high operating temperatures,<sup>3</sup> so thermal stability of the membrane material must be considered. Compared to polyimides, polyurethanes have a lower thermal stability.<sup>9</sup> Hence, it would be interesting to develop improved materials that combine the high thermal stability of polyimides with the favorable transport properties of these aliphatic polyurethanes.

In this contribution, as a strategy to obtain such improved materials, diamino-terminated aliphatic oligomers containing either siloxane or ether units are copolymerized with an aromatic dianhydride and an aromatic diamine, producing random poly(siloxane-co-imide)s and poly(ether-co-imide)s. To the best of our knowledge, previous reports on the use of poly(siloxane-co-imide)s as pervaporation membranes have focused solely on the removal of organic compounds from water.<sup>8,9,28–32</sup> With regard to poly(ether-co-imide)s, Tanihara et al.<sup>12</sup> and Wang et al.<sup>26</sup> investigated their pervaporation properties for benzene/cyclohexane separation, but these authors worked with monomers different from those used to prepare the polymers reported in this study.

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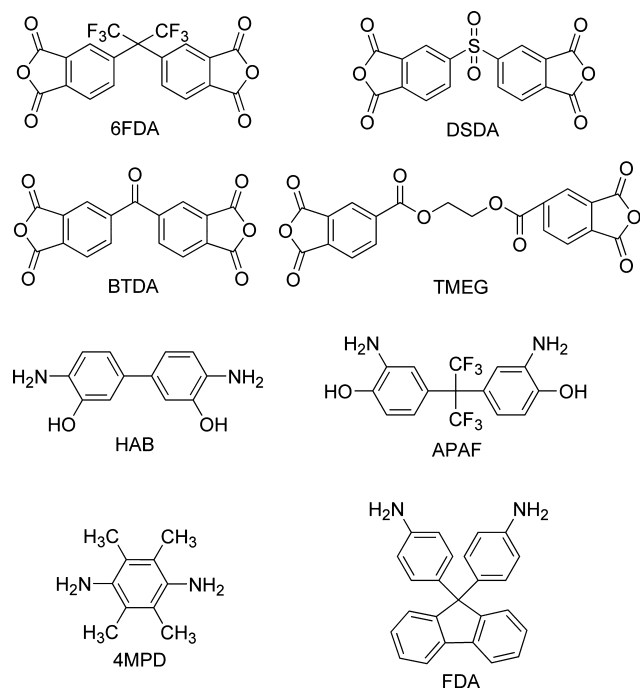
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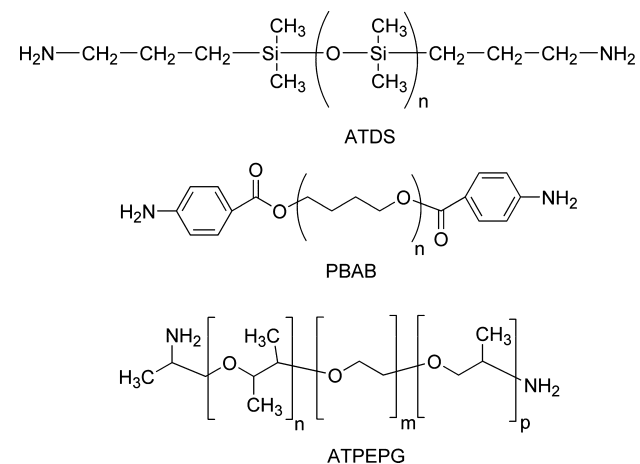
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## 2. EXPERIMENTAL SECTION

**2.1. Polymer Synthesis.** The chemical structures of the diamines and dianhydrides used in this work are shown in Figures 1 and 2. The following chemicals were purchased as



**Figure 1.** Aromatic dianhydrides and diamines used for polymer synthesis.



**Figure 2.** Amine-terminated oligomers used for polyimide synthesis.

monomer grade from Chriskev Company, Inc. (Lenexa, KS): 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB); 2,2'-bis-(3-amino-4-hydroxyphenyl)-hexafluoropropane (APAF); 2,3,5,6-tetramethyl-1,4-phenylenediamine (4MPD); 9,9'-bis-(4-aminophenyl) fluorene (FDA); 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA); 3,3',4,4'- diphenylsulfone tetracarboxylic dianhydride (DSDA), and ethylene glycol bis(trimellitic anhydride) (TMEG). Monomer grade 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) was purchased from Akros Organics (Pittsburgh, PA). TMEG was purified by drying at 170 °C for 6 h at low vacuum (~ 10 in. Hg), followed by drying overnight at 120 °C and high vacuum.

All other aromatic dianhydrides and diamines were purified as described previously.<sup>27</sup>

Aminopropyl terminated poly(dimethyl siloxane) (ATDS), with an average molecular weight of 1800 Da, was purchased from Gelest, Inc. (Morrisville, PA). This monomer was used as received. Its content of amino groups per unit mass was determined by titration with perchloric acid<sup>33</sup> using a mixture of glacial acetic acid and toluene as solvent. Two chemicals were used as diamino-terminated oligomers containing ether units, both purchased from Sigma-Aldrich (St. Louis, MO): poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol) bis(2-aminopropyl ether) (ATPEPG), with an average molecular weight of 2000 Da, and poly(1,4-butanediol)bis(4-aminobenzoate) (PBAB), with an average molecular weight of 470 Da. These two monomers were dried under vacuum at 25 °C overnight before use. Their content of amino groups per unit mass was determined by titration with perchloric acid using glacial acetic acid as solvent.<sup>33</sup>

All solvents were obtained from Sigma-Aldrich. 1,2-dichlorobenzene (ODB), tetrahydrofuran (THF), *N,N*-dimethylacetamide (DMAc), chloroform, benzene, toluene, and *n*-heptane were used as received, whereas 1-methyl-2-pyrrolidone (NMP) was distilled over calcium hydride prior to use.

Poly(ether-*co*-imide)s were synthesized by a two-step polycondensation method with thermal imidization in solution.<sup>34–36</sup> For example, to a 250-mL flask purged with nitrogen were added 6.0131 g of ATPEPG and 30 mL of NMP. The mixture was mechanically stirred to form a clear solution at room temperature. To this solution were added 5.8506 g of BTDA and 20 mL of NMP. After complete dissolution of the dianhydride, 2.5596 g of 4MPD and 30 mL of NMP were added to achieve 18% (w/v) solids content. The reaction between the diamines and dianhydride was performed at room temperature for 24 h to give a viscous poly(amic acid) solution. ODB (21 mL) and NMP (2 mL) were added to the flask to achieve 14% (w/v) solids content in an ODB/NMP (20/80 v/v) mixed solvent. The poly(amic acid) was thermally cyclized to the corresponding polyimide by heating the mixture to 180 °C for 24 h under reflux. Water produced by the cyclodehydration reaction formed an azeotrope with ODB and was removed using a Dean–Stark trap. Afterward, the polymer solution was cooled in air. The cooled polymer solution was precipitated in a blender using a methanol/water solution. The precipitated polyimide was filtered, washed several times with water, allowed to dry at room temperature for 24 h, and then finally dried under vacuum at 200 °C for at least 2 days.

The procedure detailed in the previous paragraph was slightly modified in the case of poly(siloxane-*co*-imide)s, since siloxane-containing monomers have low solubility in NMP and, in order to obtain a high molecular weight product, the copolymerization has to take place in a homogeneous solution.<sup>37</sup> Thus, following the procedure described by Arnold et al.,<sup>38</sup> a mixture of THF and NMP was used as solvent to prepare the poly(amic acid). The dianhydride of interest was first dissolved in this solvent mixture, followed by slow addition of ATDS to cap the siloxane oligomer through reaction of its amine end groups. The capped siloxanes possess greater solubility in the THF/NMP system. As a last step, the aromatic diamine, dissolved in NMP, was slowly added to the system.

**2.2. Polymer Characterization.** The polyimides were characterized by thermogravimetric analysis, infrared spectroscopy, nuclear magnetic resonance spectroscopy, and measurements of inherent viscosity and density. Thermogravimetric

analysis (TGA) scans were obtained in a Q500 thermogravimetric analyzer from TA Instruments, using a heating rate of 5 °C/min under nitrogen atmosphere.

Fourier-transform infrared spectroscopy (FTIR) studies were completed using the attenuated total reflectance (ATR) technique with a Nexus 470 Fourier-transform infrared spectrometer from Thermo Nicolet. A total of 128 scans were made for each spectrum, with the resolution of the spectrometer set to 2 cm<sup>-1</sup>.

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded on a Varian INOVA-500 spectrometer operating at 500 MHz. Deuterated chloroform was the default solvent for sample preparation, while deuterated dimethyl sulfoxide was used for polymers that did not dissolve in chloroform. Trimethylsilane (TMS) was added as a reference for all samples except those prepared using ATDS as monomer, in which case the solvent peak was used as reference.

The inherent viscosity of the polymer in NMP (0.5 g/dL solution) was measured at 25 °C using an Ostwald viscometer. Once the polymer was cast into a dense film, its density was measured at 23 °C using a density gradient column from Lloyd Instruments (model 772/AA) charged with aqueous Ca(NO<sub>3</sub>)<sub>2</sub> solution. Three to four film samples were loaded into the column and allowed to equilibrate overnight before measurement.

**2.3. Film Preparation.** Dense polyimide films were prepared from solution by controlled solvent evaporation. A solution containing approximately 3 wt % polymer in DMAc was passed through a 5-μm PTFE syringe filter and cast onto a clean Teflon disk previously leveled inside a vacuum oven. The solvent was slowly evaporated according to the following thermal treatment: 4 h at 80 °C, 100 °C overnight, and 200 °C under vacuum for 2 days. For some copolyimides, it was difficult to obtain films of homogeneous thickness when DMAc was used as solvent. In those cases, the problem was solved by using chloroform as solvent, which was allowed to evaporate at room temperature overnight. The films thus obtained were then dried under vacuum at 200 °C for 2 days.

The final film thickness was measured with a digital micrometer (Mitutoyo, model ID-C112E) readable to ±1 μm. For each film sample, thickness was measured at a minimum of 30 different points within the effective permeation area, and the average value was used.

**2.4. Pervaporation.** Pervaporation experiments were performed using the same apparatus and methodology described in detail previously.<sup>27</sup> A custom-made stainless steel permeation cell provided with a magnetic stirrer was used, with either a toluene/*n*-heptane or a benzene/*n*-heptane mixture as feed. The pressure on the downstream side was kept below 1 Torr with the aid of a vacuum pump. The permeation cell was immersed in a temperature-controlled oil circulation bath. Most tests were performed at 80 °C, but a few experiments at lower temperatures were also conducted. Permeate samples were collected in a crystallizer immersed in liquid nitrogen. Once steady-state was achieved, the permeate flux (*J*) was computed based on the mass of permeate (*m<sub>p</sub>*) collected within a given time interval Δ*t* according to eq 1:

$$J = \frac{m_p}{A\Delta t} \quad (1)$$

where *A* is the membrane area, whose value was 36.96 cm<sup>2</sup> in our permeation cell.

Feed and permeate samples were analyzed by gas chromatography, using a flame ionization detector, to determine the concentrations of each hydrocarbon. These concentrations were then used to calculate the separation factor of the membrane for components *i* and *j*, β<sub>*ij*</sub>, according to eq 2:

$$\beta_{i,j} = \frac{C_i^P/C_j^P}{C_i^F/C_j^F} \quad (2)$$

where *C* is the hydrocarbon concentration expressed in mass fraction. The superscripts *P* and *F* refer to permeate and feed samples, respectively.

Although widely used in the pervaporation literature to characterize membrane performance, the values of flux and separation factor are affected not only by the membrane material but also by the membrane thickness and operating conditions. As an alternative, membrane performance can be expressed in terms of permeability and selectivity, which are less sensitive to sample thickness and operating conditions than *J* and β. In this regard, the permeability of each hydrocarbon in the membrane was calculated according to the following relation:<sup>39,40</sup>

$$\mathcal{P}_i = \frac{J C_i^P L}{MW_i x_i^F \gamma_i^F P_i^{sat}} \quad (3)$$

where *L* is the membrane thickness, *MW<sub>i</sub>* and *P<sub>i</sub><sup>sat</sup>* are the molecular weight and the vapor pressure of component *i*, respectively, *x<sub>i</sub><sup>F</sup>* is the mole fraction of component *i* in the feed, and γ<sub>*i*</sub> is the activity coefficient of component *i* in the feed stream. The most common unit of gas permeability is Barrer (1 Barrer ≡ 1 × 10<sup>-10</sup> cm<sup>3</sup><sub>STP</sub> cm<sup>-1</sup> s<sup>-1</sup> cm Hg<sup>-1</sup>), and this unit will be used in this work. Activity coefficients and vapor pressures in eq 3 were calculated with the NRTL model and the Antoine equation, respectively, using, in both cases, parameters recommended by Gmehling et al.<sup>41</sup>

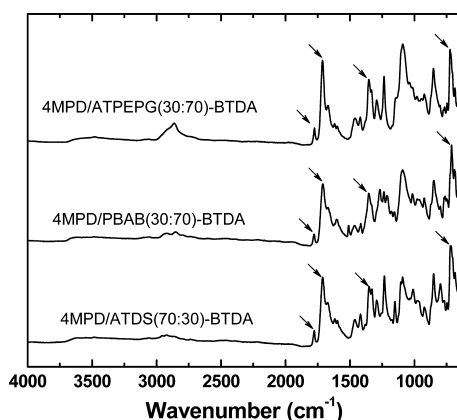
The selectivity of the membrane, α<sub>*ij*</sub>, is defined as follows:

$$\alpha_{ij} = \frac{\mathcal{P}_i}{\mathcal{P}_j} \quad (4)$$

**2.5. Pure-Liquid Sorption.** Sorption levels of pure benzene, toluene, and *n*-heptane were measured at 25 °C for selected polymers to provide some initial information about the solubility of these hydrocarbons in the materials. A known amount of a polymer film was placed in a sealed glass jar containing the hydrocarbon of interest. The jar was kept in a temperature-controlled circulation water bath. At different times, the film sample was quickly removed from the jar and weighed on an analytical balance after the excess liquid on its surfaces had been wiped off with filter paper. After weighing, the film sample was placed back into the jar and returned to the water bath. This procedure was repeated until the mass of the film remained constant as a function of time. Before each test, the film samples were degassed overnight at 50 °C in a vacuum oven, and the hydrocarbon-containing jars were kept in the water bath overnight.

### 3. RESULTS AND DISCUSSION

**3.1. Polymer Characterization.** The chemical structure of each polyimide synthesized in this work was confirmed by FTIR and <sup>1</sup>H NMR spectra. FTIR spectra, such as the ones shown in Figure 3, were used to verify the imide functionality in the polymers. In Figure 3, each polymer shows the four



**Figure 3.** FTIR spectra of representative polyimides synthesized in this work. The peaks highlighted with arrows are characteristic of phthalic imide rings.

characteristic peaks traditionally associated with the phthalic imide ring:<sup>35,42</sup> (i) symmetric C=O stretch around  $1780\text{ cm}^{-1}$ , (ii) asymmetric C=O stretch around  $1720\text{ cm}^{-1}$ , (iii) C–N–C stretch around  $1370\text{ cm}^{-1}$ , and (iv) C–N–C ring deformation around  $720\text{ cm}^{-1}$ .

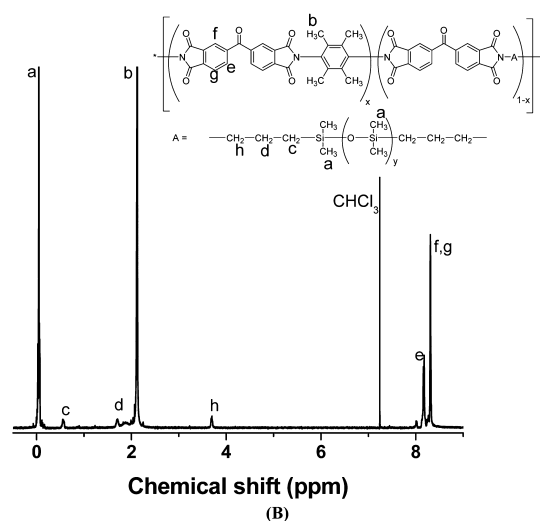
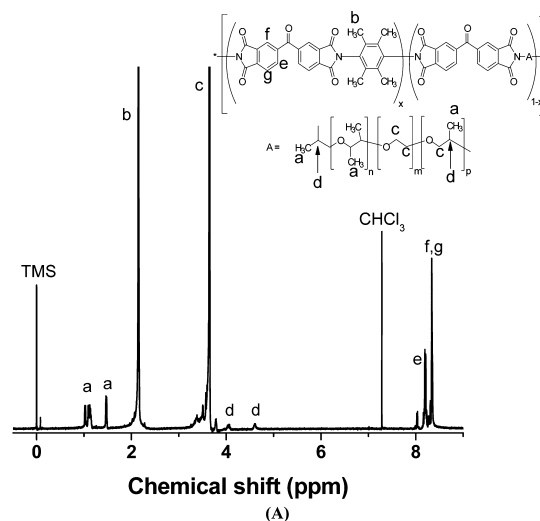
Figure 4 presents two examples of  $^1\text{H}$  NMR spectra for polyimides prepared in this work. From NMR, the incorporation of the two diamine moieties in the polymer structure is clearly confirmed, while the lack of additional peaks confirms the absence of byproducts or measurable amounts of residual solvent in the polymer.

All polyimides prepared in this work could be cast as self-supporting films, with values of inherent viscosity ranging from 0.17 to 0.59. A compilation of inherent viscosity values is recorded in Table 1. For each copolyimide, the numbers given in brackets correspond to the weight percent of each diamine used in the synthesis. Thus, for instance, in the preparation of the polymer HAB/ATDS(30:70)-6FDA, HAB accounted for 30% of the total mass of diamines used in the synthesis, while the other 70% was ATDS. For comparison, inherent viscosity values for the corresponding aromatic homopolyimides taken from our previous study<sup>27</sup> are also included in Table 1. Based on these data, the incorporation of either ATDS or ATPEPG into the polymer backbone leads to a reduction in inherent viscosity.

Table 1 also lists the density of some of the polymer films tested in pervaporation. Density values ranged from about 1.19 to  $1.35\text{ g/cm}^3$ .

**3.2. Transport Properties.** Pervaporation results for the separation of toluene/*n*-heptane mixtures with the copolyimides synthesized in this work are listed in Table 2. To better characterize the influence of the diamino-terminated aliphatic oligomers on the membrane performance, data for some aromatic homopolyimides from our previous work<sup>27</sup> are also included in Table 2. All flux values were normalized by the thickness of the dry polymer film. Average thickness values are reported in a table as Supporting Information.

The copolyimides in Table 2 are listed in the order in which they were tested. Initially, the siloxane-containing monomer was introduced in two materials whose hydrocarbon permeability was known to be very low, namely HAB-6FDA and APAF-6FDA. In both cases, a drastic increase in permeability (at least 3 orders of magnitude), and consequently in flux, was observed. Given the high permeability of poly-



**Figure 4.**  $^1\text{H}$  NMR spectra of two polyimides synthesized in this work.

**Table 1.** Inherent Viscosity ( $\eta$ ) and Density ( $\rho$ ) of Various Polyimides<sup>a</sup>

polymer	$\eta$ (dL/g)	$\rho$ (g/cm <sup>3</sup> )
APAF/ATDS(70:30)-BTDA	0.55	$1.3507 \pm 0.0002$
FDA/ATDS(50:50)-DSDA	0.39	$1.2357 \pm 0.0004$
FDA/ATDS(50:50)-TMEG	0.34	$1.2062 \pm 0.0006$
FDA/ATDS(50:50)-BTDA	0.69	$1.190 \pm 0.001$
HAB/ATDS(30:70)-6FDA	0.28	$1.259 \pm 0.001$
APAF/ATDS(30:70)-6FDA	0.17	$1.3507 \pm 0.0003$
4MPD/ATPEPG(30:70)-BTDA	0.50	$1.265 \pm 0.003$
4MPD/PBAB(30:70)-BTDA		$1.2919 \pm 0.0008$
APAF-6FDA	0.66	
HAB-6FDA	1.91	$1.4712 \pm 0.0006$
4MPD-BTDA	0.98	$1.2639 \pm 0.0005$
FDA-BTDA	0.90	$1.2891 \pm 0.0002$

<sup>a</sup>Values for copolyimides were measured in this work, while values for homopolyimides were reported by Ribeiro et al.<sup>27</sup>

(dimethylsiloxane)<sup>43</sup> and the previous results<sup>8,9</sup> reported in the literature for poly(siloxane-co-imide)s as membranes for removal of organic compounds from water by pervaporation, an increase in hydrocarbon permeability upon incorporation of siloxane units into the polymer was expected. Such enhancement in permeability was achieved with no significant change in

Table 2. Pervaporation Performance of Homo- and Copolyimides for the Separation of Toluene/*n*-Heptane Mixtures

material	toluene concn (wt %)		$J \times L$ (kg $\mu\text{m m}^{-2} \text{h}^{-1}$ )	$\beta$	permeability (Barrer)		$\alpha$
	feed	permeate			toluene	heptane	
$T = 80 \text{ }^\circ\text{C}$							
HAB/ATDS(30:70)-6FDA	39.6	46.3	$279 \pm 7$	1.3	$6.43 \times 10^4$	$3.54 \times 10^4$	1.8
HAB-6FDA <sup>27</sup>	40.6	48.5	0.037	1.4	8.9	4.6	1.9
APAF/ATDS(30:70)-6FDA	39.2	43.3	$833 \pm 10$	1.2	$1.81 \times 10^5$	$1.11 \times 10^5$	1.6
APAF-6FDA <sup>27</sup>	40.6	45.6	$0.485 \pm 0.086$	1.2	109	63	1.7
APAF/ATDS(70:30)-BTDA	41.2	41.8	$7.67 \pm 0.51$	1.0	$1.55 \times 10^3$	$1.08 \times 10^3$	1.4
4MPD/ATDS(70:30)-BTDA	40.6	81.9	$1.84 \pm 0.23$	6.6	$7.37 \times 10^2$	80	9.2
4MPD/ATDS(50:50)-BTDA	40.2	69.4	$24.97 \pm 0.42$	3.4	$8.53 \times 10^3$	$1.82 \times 10^3$	4.7
4MPD/ATPEPG(30:70)-BTDA	39.8	75.8	$5.08 \pm 0.37$	4.7	$1.90 \times 10^3$	$2.91 \times 10^2$	6.5
4MPD/PBAB(30:70)-BTDA	40.2	40.9	$151.5 \pm 3.5$	1.0	$3.05 \times 10^4$	$2.13 \times 10^4$	1.4
4MPD-BTDA <sup>27</sup>	38.9	77.0	$4.02 \pm 0.14$	5.6	$1.59 \times 10^3$	$2.08 \times 10^2$	7.6
FDA-BTDA	41.3	83.1	$1.341 \pm 0.013$	7.0	$5.36 \times 10^2$	55	9.7
FDA-DSDA <sup>27</sup>	40.9	84.9	$0.585 \pm 0.020$	8.1	$2.41 \times 10^2$	21	11.5
$T = 60 \text{ }^\circ\text{C}$							
FDA/ATPEPG(30:70)-BTDA	20.2	63.1	$3.52 \pm 0.29$	6.8	$4.08 \times 10^3$	$4.83 \times 10^2$	8.4
FDA/ATDS(50:50)-DSDA	19.5	34.9	$11.15 \pm 0.64$	2.2	$7.36 \times 10^3$	$2.67 \times 10^3$	2.8
FDA/ATDS(50:50)-BTDA	20.8	31.6	$51.5 \pm 1.0$	1.8	$2.92 \times 10^4$	$1.32 \times 10^4$	2.2
FDA/ATDS(50:50)-TMEG	20.4	24.4	$90.5 \pm 4.8$	1.3	$4.03 \times 10^4$	$2.54 \times 10^4$	1.6

selectivity toward the aromatic hydrocarbon for the materials containing either HAB or APAF. This result was definitely encouraging, even though the selectivity values measured for these materials were rather low.

In our previous structure/property investigation for aromatic/aliphatic separation using polyimides, the diamines FDA and 4MPD combined with the dianhydrides DSDA and BTDA gave the highest selectivity.<sup>27</sup> Therefore, siloxane-containing materials were prepared based on FDA-DSDA, FDA-BTDA, and 4MPD-BTDA (the polyimide 4MPD-DSDA is insoluble and was, hence, not considered in this study). In fact, some of the data in Table 2 provide further evidence of the beneficial effect of 4MPD on the selectivity toward aromatics. A comparison between the results obtained for APAF/ATDS(70:30)-BTDA and 4MPD/ATDS(70:30)-BTDA shows that, for a fixed ratio of aromatic to aliphatic diamine, the use of 4MPD instead of APAF led to a 6-fold increase in the permselectivity of the membrane.

Unfortunately, the incorporation of siloxane units in the homopolyimides with high selectivity toward aromatics did not follow the same overall trend observed for the HAB- and APAF-based materials. All copolyimides prepared with a 50/50 wt % mixture of ATDS and either 4MPD or FDA still showed a significant increase in hydrocarbon permeability, but at the expense of a drop in selectivity. Interestingly, the copolyimide synthesized with a 70/30 wt % mixture of ATDS and 4MPD showed the opposite trend. That is, selectivity increased and flux was lower compared to the homopolyimide 4MPD-BTDA. The rationale for this trend will be given together with the analysis of pure-liquid sorption data.

The effect of the dianhydride moiety on membrane performance for the poly(siloxane-*co*-imide)s is exemplified by the data for the last three polymers in Table 2. In this FDA/ATDS (50:50) series, selectivity decreases in the order TMEG < BTDA < DSDA, while flux increases in the reverse order. All these dianhydrides have polar groups that can enhance the affinity of the membrane toward aromatics, and, at the same time, increase the cohesion energy of the polymer, which can inhibit swelling.<sup>7</sup> A balance between these two effects contributes to the final results of flux and selectivity in the

pervaporation runs. The highest selectivity in the case of DSDA indicates that the sulfonyl groups provided the highest interaction among the polymer chains, and thus a more effective control of membrane swelling, which is confirmed by the pure-liquid sorption data presented in Section 3.4. This is in agreement with the results reported by Hao et al.<sup>13</sup> and Fang et al.<sup>44</sup> for sulfonyl-containing polyimides used as pervaporation membranes for aliphatic/aromatic separation. For FDA-based homopolyimides, DSDA also gave a higher selectivity and a lower permeability than BTDA. Unfortunately, steady-state permeation data with FDA-TMEG films could not be obtained, because the film ruptured after a few hours of successful operation with a toluene/*n*-heptane feed at 80 °C. This failure, however, is in agreement with a larger membrane swelling due to the presence of TMEG instead of BTDA or DSDA.

Focusing now on the poly(ether-*co*-imide)s, the data in Table 2 show that, for the 4MPD-BTDA based materials, the effects of ATPEPG and PBAB on the pervaporation performance of the membrane were significantly different. For the same ratio of aromatic to ether-containing diamines, ATPEPG led to an increase of about 20% in toluene permeability and a decrease of about 14% in selectivity; PBAB, on the other hand, increased the toluene and *n*-heptane permeability coefficients by 1 and 2 orders of magnitude, respectively, which resulted in a very significant gain in flux but an almost total loss of selectivity. As a result, PBAB was not considered further in this study in the preparation of poly(ether-*co*-imide)s.

In the case of the FDA-based poly(ether-*co*-imide)s, successful steady-state operation in pervaporation using a toluene/*n*-heptane (40/60 wt %) feed at 80 °C was not achieved due to membrane rupture caused by excessive swelling. Therefore, to obtain data regarding the pervaporation performance of these polymers, operating conditions were changed to reduce swelling. More specifically, the concentration of toluene in the feed was reduced to 20 wt %, and the feed temperature was fixed at 60 °C. These alternate operating conditions allowed us to obtain permeation data for FDA/ATPEPG(30:70)-BTDA. However, for FDA/ATPEPG(30:70)-DSDA, the affinity toward the aromatic hydrocarbon was so high that excessive swelling prevented successful steady-state

Table 3. Pervaporation Performance of Homo- and Copolyimides for the Separation of Benzene/*n*-Heptane Mixtures at 80 °C

material	toluene concn (wt %)		$J \times L$ (kg $\mu\text{m}^{-2}$ h $^{-1}$ )	$\beta$	permeability (Barrer)		$\alpha$
	feed	permeate			benzene	heptane	
4MPD/ATDS(70:30)-BTDA	41.0	83.5	4.28 $\pm$ 0.22	7.3	6.94 $\times 10^2$	1.80 $\times 10^2$	3.9
4MPD/ATDS(50:50)-BTDA	40.3	71.3	33.1 $\pm$ 1.2	3.7	4.65 $\times 10^3$	2.40 $\times 10^3$	1.9
4MPD/ATPEPG(30:70)-BTDA	39.7	77.9	10.68 $\pm$ 0.67	5.4	1.65 $\times 10^3$	5.88 $\times 10^2$	2.8
4MPD-BTDA <sup>27</sup>	39.1	79.5	9.18 $\pm$ 0.18	6.0	1.47 $\times 10^3$	4.66 $\times 10^2$	3.2
FDA-BTDA	40.5	84.5	2.07 $\pm$ 0.01	8.3	3.45 $\times 10^2$	79	4.4

operation even at 50 °C with a toluene/*n*-heptane (20/80 wt %) feed.

Although the data for the FDA- and 4MPD-based poly(ether-*co*-imide)s were obtained at different operating conditions, being therefore not fully comparable, the toluene selectivity was higher for the material prepared using FDA as the aromatic diamine. The same trend is observed in Table 2 for the BTDA-based homopolyimides prepared with these two aromatic diamines. The higher affinity of FDA-based poly(ether-*co*-imide)s toward aromatics is confirmed by the pure-liquid sorption results presented in Section 3.4.

Apart from the toluene/*n*-heptane system, a few runs were also performed using a benzene/*n*-heptane mixture as feed. To minimize the number of experiments with benzene, a carcinogenic compound, only materials with a permselectivity higher than 3 and a toluene permeability higher than 500 Barrer were considered. The results of these experiments are presented in Table 3. Since benzene uptake of a polyimide is normally higher than toluene uptake at the same operating conditions,<sup>15,27</sup> FDA-based poly(ether-*co*-imide)s were not considered for the experiments with benzene as the aromatic hydrocarbon.

All trends previously observed with the toluene/*n*-heptane system in terms of the effects of material composition on membrane performance were confirmed by results obtained with the benzene/*n*-heptane feed. For the same feed concentration and temperature, the total flux in experiments with benzene/*n*-heptane is always higher compared to the toluene/*n*-heptane system. This is mainly a consequence of the larger driving force for benzene pervaporation due to its higher vapor pressure compared to toluene.<sup>27</sup> Another consequence of this difference in vapor pressure is the fact that, for the toluene/*n*-heptane system, the separation factor is always lower than the membrane selectivity, whereas the opposite trend is verified when the benzene/*n*-heptane mixture is used as feed.

To understand this difference, one needs to express the relation between these two variables. Although all separation factors presented in Tables 2 and 3 were computed based on mass fractions, these values would be the same had they been calculated based on mole fractions, since the separation factor is a ratio of two ratios and hence does not depend on the unit of concentration used in its calculation.<sup>45,46</sup> The molar flux of component *i* during pervaporation,  $j_p$  is given by<sup>39,40</sup>

$$j_i = \frac{P_i}{L} x_i^F \gamma_i^F P_i^{\text{sat}} \quad (5)$$

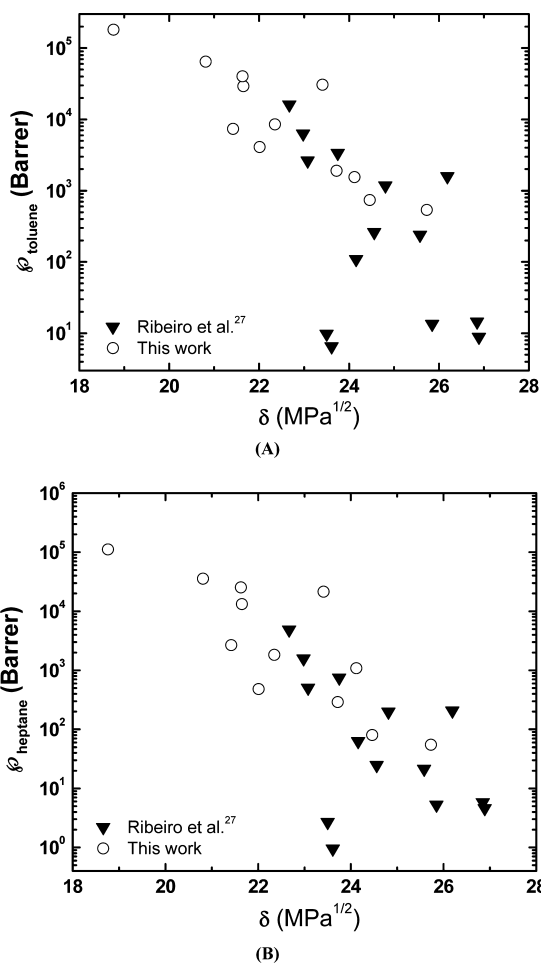
Using eq 5 to express the mole fraction of each component in the permeate for a binary system, together with the definition of selectivity (eq 4), the separation factor can be written as

$$\beta_{i,j} = \frac{P_i x_i^F \gamma_i^F P_i^{\text{sat}}}{P_j x_j^F \gamma_j^F P_j^{\text{sat}}} \times \frac{x_j^F}{x_i^F} = \alpha_{i,j} \frac{\gamma_i^F P_i^{\text{sat}}}{\gamma_j^F P_j^{\text{sat}}} \quad (6)$$

which explicitly shows the influence of the ratio of vapor pressures on separation factor. The ratio of activity coefficients in eq 6 is almost the same for benzene (40 wt %)/*n*-heptane and toluene (40 wt %)/*n*-heptane mixtures.<sup>41</sup> However, the vapor pressure of these three hydrocarbons increases in the order benzene > *n*-heptane > toluene. As a result, from eq 6,  $\beta > \alpha$  in the benzene/*n*-heptane system, while the opposite occurs when a toluene/*n*-heptane mixture is used as feed. This discussion highlights the impact of factors other than the material properties of the polymer being studied on separation factor. To isolate the influence of the membrane material on the separation properties, performance must be assessed in terms of permeability and selectivity.

Gas permeability in polyimides and other glassy polymers usually correlates well with fractional free volume, FFV, which is a measure of chain packing efficiency.<sup>47</sup> However, Ribeiro et al.<sup>27</sup> demonstrated that toluene permeability in polyimide pervaporation membranes is not well correlated with the FFV of the dry polymer. The lack of correlation was ascribed to the fact that the large membrane swelling during aromatic/aliphatic pervaporation, which influences permeability, was not taken into account in the estimation of FFV. The degree of swelling during pervaporation increases with the affinity of the polymer toward the permeants. One way of inferring the affinity between two substances is to compare their solubility parameters ( $\delta$ ): the smaller the difference, the higher the affinity.<sup>48</sup> Taking these aspects into account, the possibility of correlating permeability in pervaporation with the solubility parameter of the membrane material was tested. Figure 5 presents the permeability data for both toluene and *n*-heptane as a function of the solubility parameter of the polyimides, the latter estimated based on the group contribution method proposed by Fedors.<sup>49</sup> For comparison, the same permeability data are also plotted as a function of the FFV of the dry polymer in Figure 6. The FFV values were estimated using the experimental density of the polyimide films and the van der Waals volumes tabulated in the literature for the different groups in the repeating unit of the polymer.<sup>48,50</sup> Figures 5 and 6 include not only data from this study but also those from our previous work.<sup>27</sup> All FFV values are reported in a table as Supporting Information.

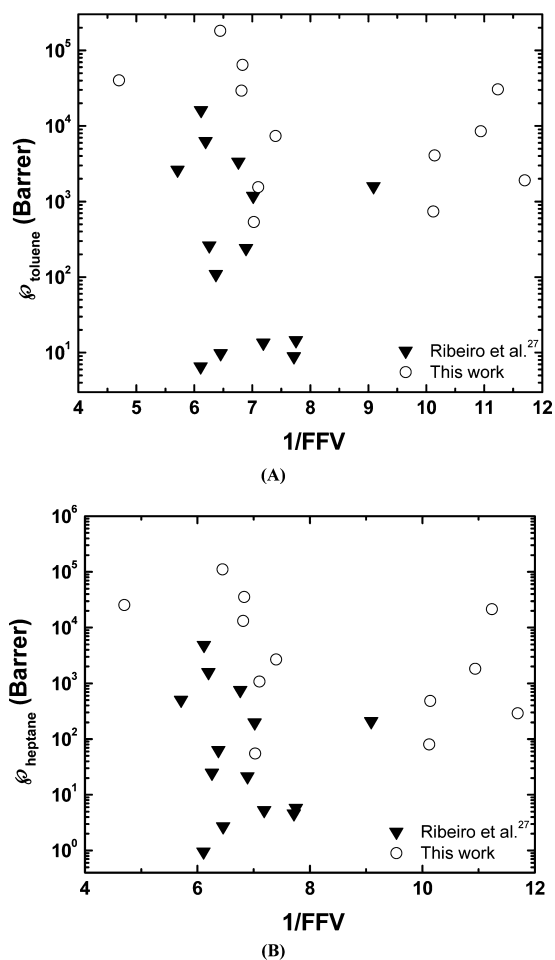
From Figure 5, the permeability of both hydrocarbons during pervaporation increases rapidly as polyimide solubility parameter decreases. Considering that the  $\delta$  values<sup>48</sup> for toluene and *n*-heptane are 18.2 and 15.3 MPa<sup>1/2</sup>, respectively, the trend shown in Figure 5 is in agreement with the reasoning that a higher affinity between the aromatic hydrocarbon and the polyimide leads to more membrane swelling, which, in turn, increases permeability. In contrast, variables such as the fractional free volume of the dry polyimide, which are not directly related to the affinity between the polymer and the permeant, do not provide a clear correlation with hydrocarbon permeability, as evidenced in Figure 6.



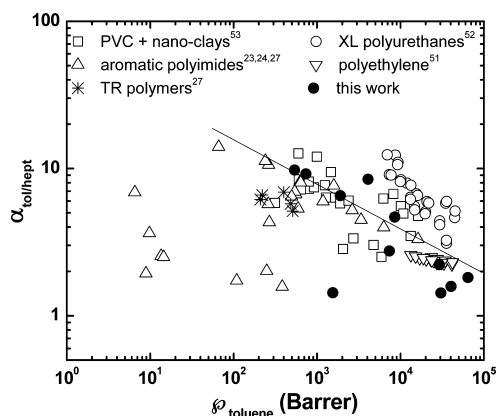
**Figure 5.** Permeability coefficients of toluene (a) and *n*-heptane (b) in polyimide membranes during pervaporation as a function of the solubility parameter ( $\delta$ ) of the polymer.

**3.3. Comparison with Other Materials.** Although the development of membrane materials for aromatic/aliphatic separation by pervaporation has been the subject of considerable research, most authors focus solely on the benzene/cyclohexane system.<sup>4,5,7</sup> For the particular case of toluene/*n*-heptane mixtures, previously investigated materials include polyethylene,<sup>51</sup> aromatic polyimides,<sup>23,24,27</sup> cross-linked aliphatic polyurethanes,<sup>52</sup> poly(vinyl chloride) containing inorganic fillers,<sup>53</sup> thermally rearranged (TR) polymers,<sup>27</sup> photomodified poly(acrylonitrile)s,<sup>54,55</sup> and polyelectrolytes.<sup>56</sup> A comparison among the transport properties of most of these materials and the polyimides synthesized in this work is shown in Figure 7. All permeability coefficients and selectivity values in Figure 7 were calculated with eqs 3 and 4 using either our own experimental data or flux and separation factor data collected from tables and/or graphs from previous publications. Unfortunately, all data for photomodified poly(acrylonitrile)s and polyelectrolytes were obtained with composite membranes whose thickness of the selective layer is not reported, which precluded us from including in Figure 7 the data related to these polymers.

The transport properties of aromatic polyimides for the target separation vary over a wide range, but there seems to be a limit for the performance of these materials, with many data for aromatic polyimides lying along a single diagonal line in Figure 7, indicating the possibility of a maximum trade-off



**Figure 6.** Permeability coefficients of toluene (a) and *n*-heptane (b) in polyimide membranes during pervaporation as a function of the fractional free volume (FFV) of the dry polymer.



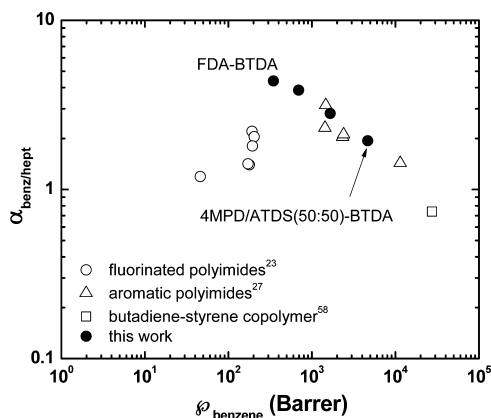
**Figure 7.** Comparison among the copolyimides prepared in this work and other membrane materials considered for the separation of toluene/*n*-heptane mixtures by pervaporation. The continuous line indicates a possible maximum trade-off between permeability and selectivity for aromatic polyimides based on the available data.

between permeability and selectivity for this class of polymers. This line was drawn in Figure 7 to aid the discussion. Interestingly, most data for the poly(vinyl chloride) membranes containing inorganic fillers fall either below or along this diagonal line, whereas all data for polyethylene and TR polymers fall below this diagonal line. Four of the materials

prepared in this work lie on this permeability-selectivity trade-off line, namely the aromatic polyimide FDA-BTDA, the poly(ether-*co*-imide) 4MPD/ATPEPG(30:70)-BTDA, and finally the poly(siloxane-*co*-imide)s 4MPD/ATDS(70:30)-BTDA and 4MPD/ATDS(50:50)-BTDA. Clearly, there is an intrinsic advantage in the use of BTDA as the dianhydride when preparing polyimides to be used as pervaporation membranes for aromatic/aliphatic separation.

A significant improvement in terms of transport properties for polyimides was achieved with the poly(ether-*co*-imide) FDA-ATPEPG(30:70)-BTDA, which lies above the trade-off line for aromatic polyimides in Figure 7. The performance of this copolymer is comparable to that of the best organic–inorganic composite membranes prepared by Aouinti et al.<sup>53</sup> (labeled “PVC + nano-clays” in this figure) and it is not very far from the performance of cross-linked aliphatic polyurethanes (labeled “XL polyurethanes” in the figure), the materials with the highest combination of selectivity and permeability values reported so far for the toluene/*n*-heptane system.

Considering now the benzene/*n*-heptane system, a comparison between the materials prepared in this work and other polymers studied in the literature<sup>23,27,57</sup> is given in Figure 8.

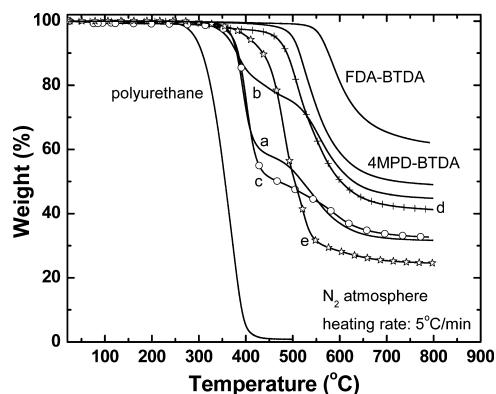


**Figure 8.** Comparison between the copolyimides prepared in this work and other membrane materials considered for the separation of benzene/*n*-heptane mixtures by pervaporation.

The poly(siloxane-*co*-imide)s and the aromatic polyimides tested in our previous work<sup>27</sup> follow a trade-off between permeability and selectivity, and, at the same time, perform better than the fluorine-containing polyimides prepared by Ye et al.<sup>23</sup> or the butadiene–styrene copolymer tested by Larchet et al.<sup>57</sup>

**3.4. Thermal Stability.** Although the transport properties are definitely important in the selection of a membrane material, they are not the only aspect to be taken into account. The separation of hydrocarbon streams in refineries by pervaporation will require high operating temperatures.<sup>3</sup> As a result, the thermal stability of the membrane material should also be considered, in which case polyimides show an advantage compared to aliphatic polyurethanes.<sup>9</sup>

Typical TGA results for the materials prepared in this work are shown in Figure 9. For comparison, data for two aromatic polyimides and an aliphatic polyurethane are also included. The polyurethane was prepared from 1,6-diisocyanatohexane (HDI) and poly(ethylene glycol) 600 (PEG600), following the procedure described by Grabczyk.<sup>58</sup> These two monomers were used by Roizard et al.<sup>52</sup> to prepare the cross-linked



**Figure 9.** Thermogravimetric analysis (TGA) of aromatic polyimides (4MPD-BTDA, FDA-BTDA), poly(ether-*co*-imide)s (a–c), poly(siloxane-*co*-imide)s (d, e), and an aliphatic polyurethane (HDI-PEG600): (a) 4MPD/ATPEPG(30:70)-BTDA, (b) 4MPD/PBAB(30:70)-BTDA, (c) FDA/ATPEPG(30:70)-BTDA, (d) 4MPD/ATDS(50:50)-BTDA, (e) APAF/ATDS(30:70)-6FDA.

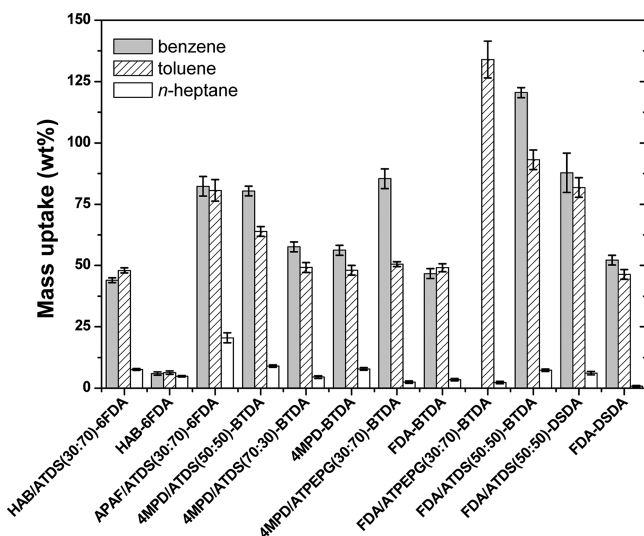
polyurethanes exhibiting the highest combination of selectivity and permeability values in Figure 7. Among the different materials compared in Figure 8, the aromatic homopolyimides show the highest thermal stability, with no sharp mass loss before 500 °C for 4MPD-BTDA, while, in the case of FDA-BTDA, the sharp decrease in mass only happens between 550 and 600 °C. Poly(siloxane-*co*-imide)s come second in decreasing order of thermal stability, with a sharp mass loss between 400 and 470 °C for the materials shown in Figure 8. A comparison between curves (d) and (e) indicates that the copolymer with a higher amount of ATDS used in its synthesis starts to degrade at a lower temperature. With regard to poly(ether-*co*-imide)s, all three materials included in Figure 8 exhibit a sharp mass loss between 350 and 400 °C, which indicates that a further loss in thermal stability is observed when siloxane units are replaced with ether units in the polymer chain. In spite of their lower thermal stability compared to the other polyimides in Figure 8, all poly(ether-*co*-imide)s still surpass the thermal stability of the aliphatic polyurethane. Under the conditions of these TGA runs, the polyurethane sample mass loss began around 270 °C, with a sharp mass loss between 300 and 350 °C and complete degradation by 400 °C.

**3.5. Pure-Liquid Sorption.** Equilibrium uptake of pure hydrocarbons for most of the polymers prepared in this study are shown in Figure 10. Given that transport in pervaporation membranes follows the solution-diffusion mechanism,<sup>39,40</sup> these results are useful in understanding the changes in hydrocarbon permeability with the chemical structure of the polymer.

All polymers have a higher affinity toward the aromatic hydrocarbons, which contributes to the selectivity of these materials toward aromatics in pervaporation.<sup>27</sup> The high levels of sorption of aromatics in these materials translate into large membrane swelling during pervaporation, which implies a concentration-dependent diffusion coefficient for the hydrocarbons in the membrane. In other words, in this system, both components of the permeability coefficient are directly affected by the solubility of the aromatic hydrocarbon in the polymer, which supports the correlation between permeability and solubility parameter values seen in Figure 5.

An increase in the equilibrium uptake of both aromatic and aliphatic hydrocarbons compared to the corresponding homopolyimide is observed for all poly(siloxane-*co*-imide)s in





**Figure 10.** Equilibrium uptake of pure hydrocarbons in different polymers at 25 °C. Values for HAB-6FDA, 4MPD-BTDA, and FDA-DSDA were taken from the literature.<sup>27</sup> Benzene uptake for FDA/ATPEPG(30:70)-BTDA could not be measured because the film partially dissolved in this hydrocarbon.

which ATDS accounted for 50 or 70 wt % of the total mass of diamines. This finding is in agreement with the increase in permeability and loss of selectivity seen for these materials in the pervaporation experiments. An interesting exception was the copolymer 4MPD/ATDS(70:30)-BTDA, which showed a reduction in the *n*-heptane uptake compared to 4MPD-BTDA but no change in the uptake of either benzene or toluene. This reduction only in the uptake of the aliphatic hydrocarbon is in agreement with the higher selectivity of the poly(siloxane-*co*-imide) compared with the homopolyimide measured in the pervaporation runs with both toluene/*n*-heptane and benzene/*n*-heptane as feeds.

With regard to the ATPEPG-based poly(ether-*co*-imide)s, regardless of the aromatic diamine, a decrease in the *n*-heptane uptake was observed compared to the homopolyimide. The uptake of aromatics also increased for both poly(ether-*co*-imide)s, but the effect was much more pronounced when FDA was used as the aromatic diamine. In fact, the FDA/ATPEPG(30:70)-BTDA polyimide actually became soluble in benzene. In agreement with its superior performance in the pervaporation runs with the toluene/*n*-heptane mixture, this same polyimide shows the largest difference between the uptake values for toluene and *n*-heptane in Figure 10.

#### 4. CONCLUSIONS

Soluble, high molecular-weight poly(siloxane-*co*-imide)s and poly(ether-*co*-imide)s were synthesized and tested for separation of toluene/*n*-heptane and benzene/*n*-heptane mixtures by pervaporation. All materials were selective toward the aromatic hydrocarbon. Introduction of siloxane units in the polymer generally led to very high hydrocarbon permeability coefficients, but caused a reduction in selectivity compared to the aromatic homopolyimide. Incorporation of ether units, on the other hand, did not generally cause such large increases in permeability, nor large decreases in selectivity. A correlation was found between the solubility parameter of the polymer and its hydrocarbon permeability in pervaporation. The best poly(siloxane-*co*-imide) membranes followed the trade-off

between permeability and selectivity shown for aromatic polyimides, whereas the limit of the same trade-off could be surpassed with one of the poly(ether-*co*-imide) membranes.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Tables with average film thickness and fractional free volume values. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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##### Notes

The authors declare no competing financial interest.

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