

Sulfur-Containing Copolyimides for the Membrane-Based Separation of Aromatic/Aliphatic Mixtures

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ABSTRACT: Recently, sulfur-containing copolyimides have attracted increasing attention as membrane materials for the separation of gaseous, vaporous, or liquid mixtures because of their superior separation properties. Therefore, a novel sulfur-containing copolyimide based on 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, 4,4'-diaminodiphenylsulfide, and 3,5-diaminobenzoic acid was synthesized, characterized, and extensively investigated in toluene/*n*-decane pervaporation experiments. To characterize the separation properties of the copolyimide, the flux and selectivity were determined with separation mixtures between 60 and 80 wt % toluene. The separation temperature was varied between 70 and 110°C. Thereby, we observed that when the temperature was increased from 70 to 90°C, the flux and selectivity did not change significantly. In contrast, a temperature change from 90 to 110°C caused an extensive increase in the flux. The most significant change was found for an 80 wt % toluene mixture, where an increase from 1.9 to 7 kg·μm·m⁻²·h⁻¹ was observed. Simultaneously, the selectivity which is a measure of the quality of the separation (α) decreased from $\alpha = 11.8$ to $\alpha = 9.3$. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: activation energy; membranes; polyimides

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INTRODUCTION

One of the major problems in the chemical industry is the separation and purification of mixtures. Particularly, the separation of aromatics/aliphatics, for example, the removal of toxic aromatic components such as benzene or toluene from fuel, is receiving more and more attention because of the continuous reduction of the maximum permissible concentrations.

Membranes can be used in different processes for the separation of gaseous and liquid mixtures. This means that membranes can substitute or amend energy-intensive and, thus, costly methods such as distillation, rectification, extraction, or crystallization and can lead to energy savings of up to 60%.¹ This is possible because membrane-based processes can be performed far below the boiling points of the components to be separated. Membranes can also be used in those cases, where conventional processes reach their limits, for example, when azeotropic mixtures have to be separated or when temperature-sensitive substances have to be purified. Additional advantages compared to conventional processes are the light weight and small footprint of the membrane units and the possibility of modular assembling. In cases where no replacement for conventional separa-

tion equipment is possible, it is feasible to combine membrane units with distillation, extraction, or absorption facilities in a so-called hybrid process.

In Figure 1, a membrane-based separation process, so-called pervaporation, is shown. In pervaporation, a liquid mixture (feed) flows over a polymeric membrane, and the feed components dissolve in the polymer and diffuse through it according to the concentration gradient that is applied between the feed and permeate side. Separation is achieved because of the differences in the solubility and diffusivity of the single components of the feed mixture in the membrane matrix.² The stream on the backside of the membrane is called the *permeate*. The mixture that is depleted in the preferentially permeating component is called the *retentate*. The driving forces for mass transport through the membrane are the partial pressure and concentration gradient of the different components between the feed and permeate sides of the membrane. In case of the pervaporation process, a phase transition occurs between the feed and permeate side; this means that the permeate is vaporous and has to be condensed in a cooling trap.

Generally, when products have to be purified or toxic or undesired components need to be removed, multicomponent mixtures occur.

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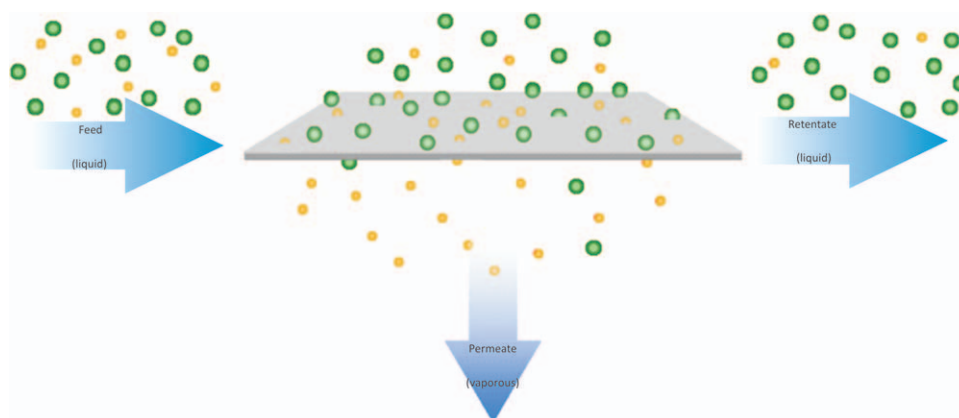


Figure 1. Membrane-based separation of a liquid mixture.³ [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

However, for the well-directed development of new membrane materials, it is necessary to understand the influence of the polymer structure on the transport properties of the different components to be separated. Therefore, binary mixtures are mostly used because, in most cases, if multicomponent mixtures are used, the feed components influence each other so that obtaining the desired correlation is rather difficult, and a large number of different separation experiments is necessary to evaluate high-potential membrane materials. Also, the complexity of the feed and permeate analysis are comparably high.

On the basis of its outstanding high thermal and chemical resistance, polyimides are of particular interest for industrially relevant separation applications. Therefore, companies such as Ube, DuPont, and Evonik are manufacturing miscellaneous polyimides as membranes or offer complete modules or facilities for different industrial applications, such as biogas, natural gas, or wastewater treatment.^{3–5} Polyimides rank among high-performance polymers because of their outstanding properties. For example, they are not flammable, they show high chemical resistance and thermal stability, have a great radiation resistance, and exhibit good semiconductor properties.^{6–9} One example is Kapton, which is offered by DuPont. It shows a high long-term heat resistance, which leads to a broad application potential for aerospace applications.^{10,11}

The separation of aromatic/aliphatic mixtures, especially the removal of toxic compounds from gasoline, has been investigated over the last couple of years with different polyimides and copolyimides. One commercially available polyimide is Matrimid. It is reported that Matrimid shows for the separation of toluene/*i*-octane high fluxes but a low selectivity.¹² Because the membrane thickness (δ_m) was not reported, the flux could not be compared to the other data shown in Table I. To get a rough estimation, the film thickness was extracted from the scanning electron microscopy pictures and was assumed to be approximately 2.5 μm . In that case, the normalized flux (J_n) was much lower than 10 $\text{kg}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, which represents an average but not an outstandingly high flux. In comparison to that, a 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA)–2,4,6-trimethyl-1,3-phenylene diamine (3MPD) based polymer showed much better separation properties for an equal mixture

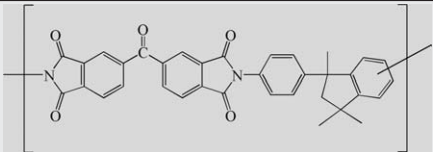
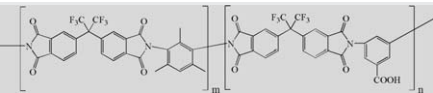
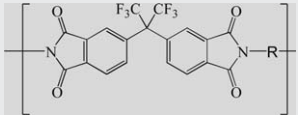
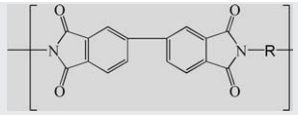
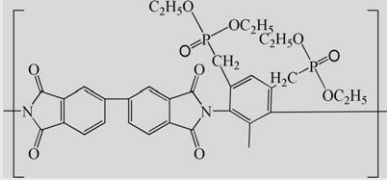
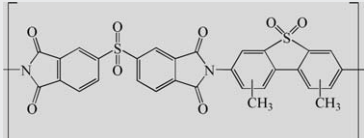
at a higher temperature. Table I gives an overview of different polyimide materials for aromatic/aliphatic separation.

Besides the different temperature ranges that were investigated for membrane-based aromatic/aliphatic separation, it should be mentioned that different feed mixtures have also been used. Many correlations between the polymer structure and separation properties have been worked out in the past with benzene/cyclohexane mixtures. Although these are components relevant to industrial separation processes, mixtures with benzene are now used rarely because of its high toxicity. Because it has been shown that toluene is an appropriate component for the evaluation of aromatic selective membrane materials,¹³ it is possible to compare mixtures containing either benzene or toluene.

For a broader discussion basis, in Table I data for benzene/cyclohexane mixtures with 6FDA and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) based polyimides are also listed. With aromatic contents between 50 and 60 wt % and feed temperatures of 50–70°C, the flux of the 6FDA-based polymers was in the range 0.5–12 $\text{kg}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, whereas selectivities between 4 and 6 were found.^{13,14} BPDA-based polyimides showed slightly higher fluxes in the range 5–14 $\text{kg}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ with somewhat better selectivities (α 's) of 5–10.¹⁵ However, a disadvantage of BPDA-based polyimides is that in many cases, the solubility of the polymeric material is generally low so that processing the poly(amic acid) with thermal imidization is necessary.

Outstandingly high selectivities in benzene/cyclohexane separation have been reported when phosphorylated or sulfur-containing polyimides were used. They showed selectivities up to $\alpha = 90$, but mostly, very small fluxes were observed.^{16,17} Furthermore, it has to be mentioned that for these types of polymers, a very limited number of publications is available so far dealing with the separation of liquid mixtures.^{17–19} One interesting example for sulfur-containing polyimides is 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA)–dimethyl-3,7-diaminodiphenylthiophene-5,5-oxide (DDBT; see Table I), which contains sulfur in the dianhydride and in the diamine monomer. Unfortunately, for pervaporation measurements with different membrane samples of the same copolyimide, strongly varying fluxes between 0.9 and 2.4 $\text{kg}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and selectivities in

Table I. Comparison of the Selectivity and Permeability of the Polyimide Membrane Materials in Pervaporation

Structure	Feed mixture	T_{Feed} (°C)	J (kg $\mu\text{m}^{-2} \text{h}^{-1}$)	α
	tol/ <i>i</i> -oct (50/50 wt %)	60°C	2.3 ^a	3
Matrimid ¹³ 	tol/ <i>i</i> -oct (60/40 wt %)	100°C	1.1–35	10–70
6FDA–3MPD/6FDA–DABA ²⁴ 	bz/ch (50–60/40–50 wt %)	50–70	0.5–12	4–6
6FDA-based polyimides ^{14,15} 	bz/ch (50–60/40–50 wt %)	50–70	5–14	5–10
BPDA-based polyimides ¹⁶ 	bz/ch (80/20 wt %)	70	0.02–16	11–90
P-PI (1,9–8,3% P, different crosslinked) ¹⁷ 	bz (60 wt %)/ch (40 wt %)	60	0.4	43
DSDA–DDBT ¹⁸ (data for two different batches)		60	2.4	20

tol, toluene; *i*-oct, iso-octane; bz, benzene; ch, cyclohexane; BPDA, 3,3',4,4'-biphenyltetracarboxylic dianhydride; P-PI, phosphorylated polyimide; P, percentage phosphorylation.

^aHollow fiber, thickness not reported.

T_{Feed} , Feed temperature, where separation measurements have been performed.

J , Flux according to equation (1).

α , selectivity according to equation (2).

the range of $\alpha = 20$ –32 for a benzene/cyclohexane (60/40 wt %) mixture at 78°C were reported.

Because the sulfur-containing polymers showed very promising results, the goal of this study was to combine the general properties of 6FDA polyimides concerning their high permeability and selectivity with the high selectivity obtained with sulfur-

based polyimides. Thereby, we assumed that the high selectivity for the sulfur-containing polyimides was caused by better interaction with the aromatic components in the feed; this was due to the fact that sulfur-containing polyimides are electron-rich compounds. The stronger interaction between the aromatics and the membrane material led to a higher sorption and,

Table II. Physical Properties of the Different Feed Components²⁵

Component	Boiling point (°C)	Vapor pressure (hPa; 20°C)
Benzene	80	100
Toluene	111	29
Cyclohexane	81	104
<i>iso</i> -Octane	99	52
<i>n</i> -Decane	174	160

according to the solution diffusion mechanism, as shown in Figure 1, to a higher permeation rate. Similar phenomena were observed in olefin/paraffin gas separation²⁰ for the olefin transport through sulfur-containing copolyimides. Strongly improved separation factors for the $-\text{CF}_3$ group polyimides compared to those with $-\text{CH}_3$ groups was demonstrated in aromatic/aliphatic separation with toluene/heptane mixtures by Ye et al.²¹ and in gas separation by Stern et al.²² To our knowledge, only some data for sulfur-containing polyimide use in pervaporation processes are available.^{20,23,24} In the case of gas separation selectivities up to $\alpha = 27$ for the separation of propene/propane (55/45%), a 50°C separation temperature and a 2-bar feed pressure were reported.²⁰ These were exceptionally high selectivities. In contrast, 6FDA-based polyimides without heteroatoms, for instance, showed selectivities of only 10–16 with propene permeabilities of 0.13–0.89 Barrer in $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ (55/45%) at 35°C and a 3.8-bar feed pressure.^{17,20}

The results presented in Table I were predominantly obtained with benzene and cyclohexane as feed mixtures. This feed mixture is an interesting example for separation because of the similar boiling points and similar vapor pressures, as indicated by the physical properties listed in Table II, but as mentioned before, mixtures with toluene are preferred because of its lower toxicity. Toluene/*i*-octane mixtures have both a comparatively low vapor pressure and a difference in the boiling point of 12°C. However, because of the formation of azeotropic mixtures, separation via distillation is difficult, and opportunities of membrane-based separation have been investigated, as shown by the data in Table I. For the separation factors, it has to be pointed out that with increasing branching of the structure of the aliphatic component, the separation factor dramatically increased because of the strongly reduced diffusion through the membrane material.

In the literature, mixtures of benzene and cyclohexane have mostly been used. Further data on mixtures for toluene/*iso*-octane separation are available. In this study, toluene was chosen as the aromatic component, and *n*-decane was used as the aliphatic component. Compared to the branched *i*-octane, the *n*-decane represented a very realistic average chain length of aliphatic components present in the fraction, which was converted to fuels. Both components were high-boiling liquids; this made separation by distillation energy-intensive and, as such, expensive. This mixture is economically interesting because the mixture could be separated by pervaporation below the boiling point of the lower boiling component. However, a direct com-

parison between the benzene/cyclohexane, toluene/*i*-octane, and toluene/*n*-decane mixtures, which were used in this study, was not possible because aromatic and aliphatic components are different. It should be pointed out here that Table I gives a general overview of membrane materials that have been investigated for aromatic/aliphatic separation and the data cannot be used for a direct comparison for the materials because benzene/cyclohexane, toluene/*i*-octane, and toluene/*n*-decane mixtures were used, and the aromatic and aliphatic components were different with regard to boiling points, vapor pressure, and diffusion coefficients.

The aim of this study was to synthesize a new class of 6FDA-based copolyimides containing sulfur heteroatoms in the polymer backbone. The idea was to combine the very high separation properties of the sulfur-containing polyimides with the excellent solubility and high fluxes and superior selectivities of CF_3 -group-containing polyimides.

Also, we desired to obtain a membrane material with functional groups because it was shown recently that this is extremely helpful when improvements in the chemical and thermal stabilities of the membrane material are necessary, for example, when applications at high temperature or in aggressive feed mixtures such as kerosene are investigated.^{25–27} It was also shown that functional groups are very helpful for tuning the membrane properties, for example, by side-group modification with suitable functionalized carbon nanotubes.²⁵ For this reason, sulfur-containing copolyimides, including carboxyl group functionalities, which have not been investigated in pervaporation experiments so far, were synthesized and characterized. Because the influence of the concentration of functional groups was investigated in different previous projects, that was not the intent of this study.^{28–31} Generally, it was found that with increasing 3,5-diaminobenzoic acid (DABA) content, a decrease in the flux and an increase in the selectivity were observed.

BACKGROUND AND THEORY

In 1866, Graham developed the so-called solution diffusion model to explain the permeation of gaseous components through rubber.³² The model is based on three steps: the sorption on the membrane surface, the diffusion through the membrane, and the desorption on the backside of the membrane, which is also called the *permeate side*.³³ The diffusion determines the rate of the mass transport because, in contrast to sorption and desorption processes, it is comparatively slow. It is assumed that a thermodynamic equilibrium is reached at the feed and permeate sides of the membrane, which is also called *steady state*. To compare the separation potentials of different membranes, two parameters are commonly reported in pervaporation, J_m normalized on $1 \mu\text{m} \delta_m$ and the selectivity:

$$J_n = \frac{m^p \delta_m}{tA} \quad (1)$$

where m^p is the amount of permeate, t is the defined time period, and A is the membrane area:

$$\alpha = \frac{w_i^p/w_j^p}{w_i^f/w_j^f} \quad (2)$$

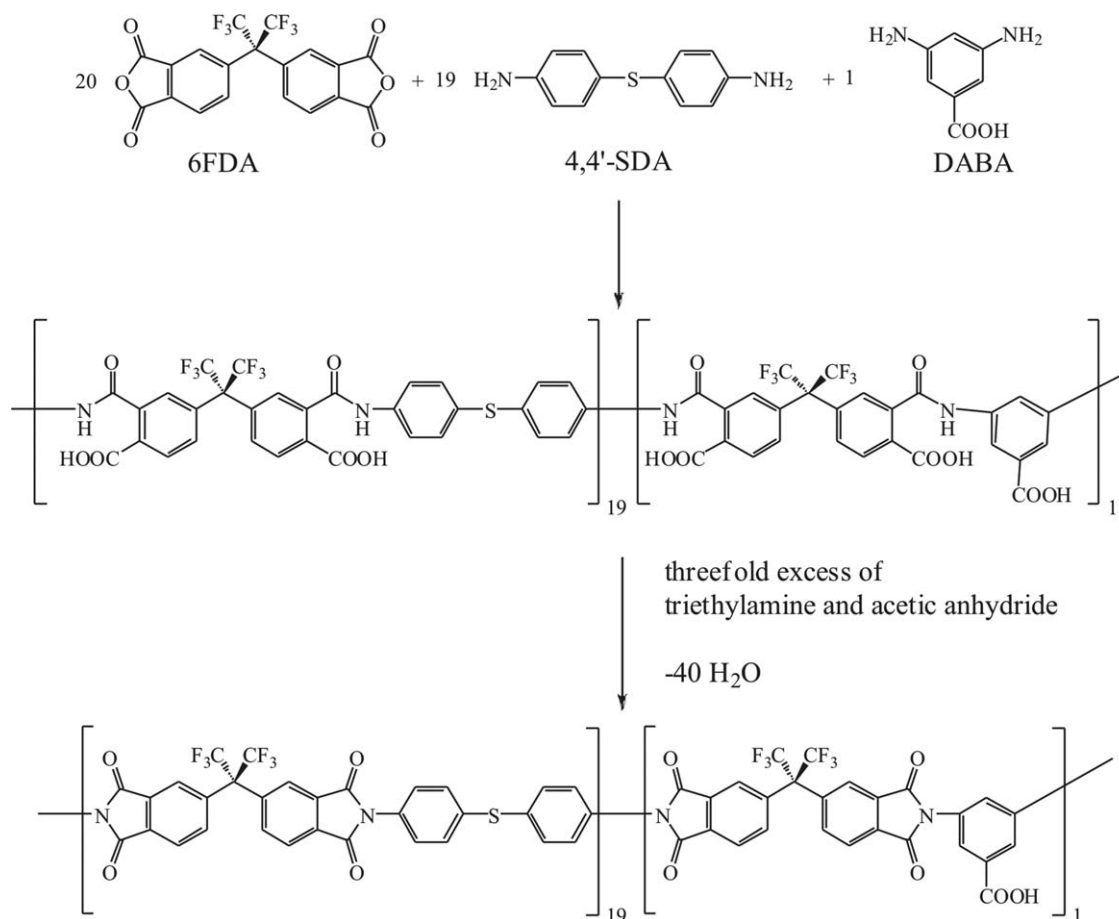


Figure 2. Scheme of the two-step polymerization reaction.

where $w_{i/j}^{P/F}$ is the weight fraction of the component i or j on the permeate or the feed side, respectively, and i is the preferentially permeating component.

EXPERIMENTAL

Materials

For the synthesis of the copolyimide, 6FDA, with a purity grade of 99%, and 4,4'-diaminodiphenylsulfide (4,4'-SDA), with a purity grade of 98%, were supplied by Alfa Aesar, Karlsruhe, Germany. DABA, with a purity grade greater than 99%, and *N,N*-dimethylacetamide (DMAc), with a purity grade greater than 99%, was supplied by Merck, Rockland, Massachusetts.

Polymer synthesis

All monomers were purified before the polymerization reaction was performed. For purification, 6FDA was sublimed at 0.1 mbar and a bath temperature of 215°C. The diamines DABA and 4,4'-SDA were sublimed at 0.1 mbar and a bath temperature of 195°C. DMAc was distilled over CaH₂ and was stored with a molecular sieve. The polycondensation reaction is schematically shown later in Figure 3. For the synthesis of the copolyimide in this study, chemical imidization of the polyamide acid in the second step of the polymerization reaction was performed.

In a moisture-free flask with a nitrogen inlet and magnetic stirrer, the diamine monomers were dissolved in DMAc, and 6FDA was added as a solid in one portion at room temperature. After a slightly exothermic reaction, the solution was stirred for 6–8 h at room temperature. Thereby, a strongly viscous poly(amic acid) was formed. The imidization was performed by the addition of a threefold excess of triethylamine and acetic anhydride to the reaction mixture and stirring for 30 min at 110–120°C. After it was cooled to room temperature, the viscous reaction solution was slowly poured into an ethanol/distilled water mixture. The precipitated copolyimide was homogenized in a blender, filtered, and washed several times with fresh ethanol. The obtained copolyimide was dried for 12 h at room temperature and afterward for 24 h at 85 mbar and 150°C.

The copolyimide investigated in this study is also shown in Figure 2. The physical properties, such as molecular weight, glass-transition temperature, and ¹H-NMR, are discussed in the following paragraphs.

Polymer characterization

The glass-transition temperature was measured with a 822^g Mettler–Toledo gadget and averaged 300°C. The molecular weight was measured at the Max Planck Institute for Polymer Research in Mainz and was detected with 101,000 g/mol (polystyrene standard, Germany). ¹H-NMR was measured with a Bruker

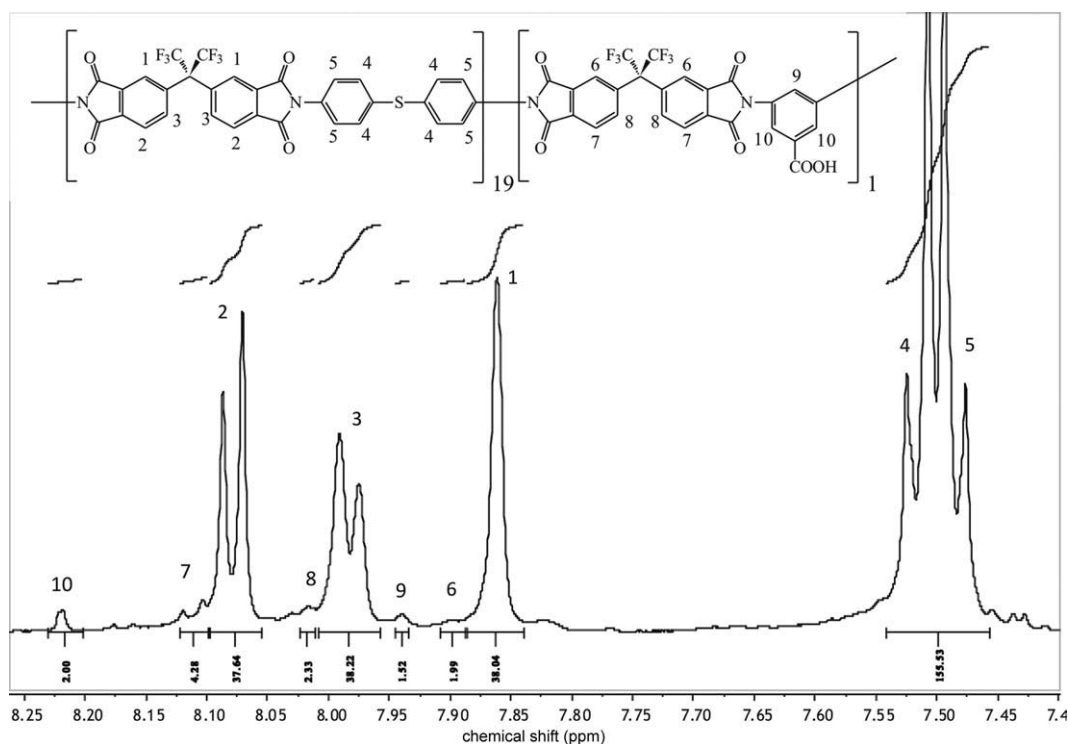


Figure 3. $^1\text{H-NMR}$ spectrum of the 6FDA-4,4'-SDA/6FDA-DABA 19 : 1 copolyimide chemical shift [ppm].

Advance 500 in tetrahydrofuran- d_8 at the University of Duesseldorf, Germany. The spectrum is shown in Figure 3.

By means of $^1\text{H-NMR}$ spectroscopy, it was possible to analyze the composition of the copolymers. In this study, a copolymer with the composition 19 : 1 6FDA-4,4'-SDA/6FDA-DABA was synthesized. Comparison of the integrals on the sulfur-containing diamine (4,5) with the protons on the DABA (9,10) showed a ratio of 167 : 2.8. This was very close to the theoretical ratio in a 19 : 1 6FDA-4,4'-SDA/6FDA-DABA copolyimide, which was calculated to 152 : 3.

Membrane preparation

To prepare a membrane approximately 30 μm thick and 10 cm in diameter, 300 mg of the membrane polymer 19 : 1 6FDA-4,4'-SDA/6FDA-DABA was dissolved in 10 mL of tetrahydrofuran. The solution was then filtered and effused in a plain metal platter. At room temperature, the solvent was evaporated within 14 h. After that, the membrane was flushed with distilled water to remove it from the metal platter. To get rid of solvent residues, the membrane was dried for 48 h in a vacuum drying cabinet at 85 mbar and 150°C.

Pervaporation measurements

The pervaporation apparatus used for the measurements was described previously.³⁴ All measurements were carried out in the following way. First, the membrane was cut to an appropriate size and placed into the pervaporation cell. A toluene/*n*-decane mixture was used as the feed. The membrane was exposed to the feed in a cell overnight. We started the measurements by reducing the pressure on the permeate side to 15–20 mbar and heating up the feed to the desired cell temperature. We determined the flux by weighing the condensed permeate in the

cooling trap during a certain time period. The permeate and feed composition were analyzed with gas chromatography to calculate the selectivity according to eq. (2).

RESULTS AND DISCUSSION

Pervaporation experiments

The influence of the feed temperature and composition on the chain mobility, which determined the flux and selectivity strongly, were analyzed by variations in the temperature and the feed composition during the pervaporation measurements. To optimize industrial membrane applications, it is important to know at which temperature a specific feed mixture can be separated. Different feed compositions with 60, 70, and 80 wt % toluene were investigated. For each mixture, pervaporation experiments were performed at 70, 90, and 110°C feed temperatures. In this work, both the flux and selectivity were established with an arithmetic average of three measurements. Thereby, average deviations of 7.3% for the flux and 3.4% for the selectivity were found. This was in good agreement with detailed error calculations for pervaporation experiments, which were previously carried out by Katarzynski and Staudt.²⁷ The membranes tested in this work had an area of 78.54 cm^2 with a thicknesses of 25–30 μm . The permeate pressure in all of the measurements was kept between 15 and 20 mbar. Every time the feed concentration was changed, the membrane was exposed to the mixture overnight, as described before.

Concentration-dependent separation properties

Concentration-dependent measurements were carried out to prove the membrane stability toward high aromatic concentrations. Therefore, three different feed mixtures with 60, 70, and 80 wt % toluene were used. In Figure 5 (right side, shown

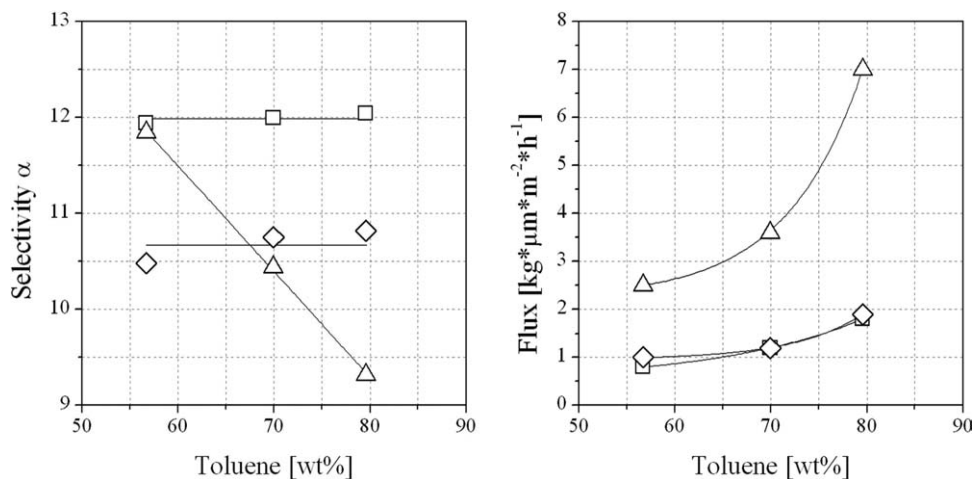


Figure 4. Concentration-dependent separation of the toluene/*n*-decane mixtures with a 6FDA–4,4′-SDA/6FDA–DABA 19 : 1 membrane at (□) 70, (◇) 90, and (△) 110°C feed temperature and 15–20 mbar of permeate pressure.

later), the total fluxes for the different feed concentrations at 70, 90, and 110°C are presented. Generally, an increase in the aromatics concentration in the feed led to a higher sorption of all components in the membrane material. As a result, larger fluxes were found. By increasing the feed concentration from 60 to 70 wt % at a 110°C feed temperature, it was found that the total flux increased by 130%. This effect was much more pronounced in the concentration range between 70 and 80 wt %, where the flux increased by 194%. As shown in Figure 4 (left side), with increasing toluene concentration at 70 and 90°C, nearly constant selectivities of 12 and 10.75, respectively, were observed.

The enrichment at 110°C was only slightly lower, for example, 97% toluene in the permeate for a 80/20 wt % feed mixture compared to 98% at 90°C. The selectivity showed a dramatic loss of 30% when the concentration of toluene was increased. From these data, we assumed that strong swelling effects occurred at elevated temperatures, and the membrane probably would not keep its separation performance over a long time period at such a high operation temperature.

Figure 5 shows the partial fluxes of *n*-decane and toluene at 70°C (left side) and 90°C (right side) as dependent on the aromatic concentration in the feed mixture. This demonstrates that the flux of the *n*-decane stayed nearly constant in contrast to the toluene flux, which increased by 130 and 150% respectively. Hence, the toluene decreased the total flux by more than 95%. As discussed later in Figure 8, at 110°C, the *n*-decane flux was no longer constant but strongly increased with increasing toluene concentration in the feed. We assumed that this was the main cause for the loss in selectivity.

Temperature-dependent pervaporation measurements

Because at higher feed temperatures, higher fluxes were obtained (this was desirable but in many cases was combined with a loss in selectivity), temperature-dependent experiments at 70, 90, and 110°C were carried out (Figure 6). As expected, with increasing temperature, higher fluxes were observed. In the case of 80 wt % toluene in the feed mixture and a 110°C feed temperature, the observed flux was more than three times higher than the one at 70°C. This showed that a higher feed temperature led to a higher flux because of the higher chain mobility and the higher diffusion

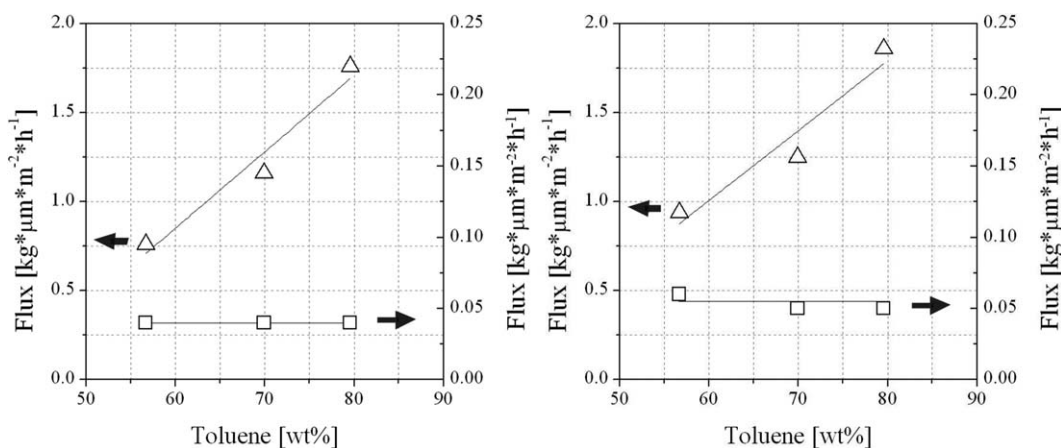


Figure 5. Concentration-dependent partial fluxes of (△) toluene and (□) *n*-decane at 70°C (left) and 90°C (right) with a 6FDA–4,4′-SDA/6FDA–DABA 19 : 1 membrane and 15–20 mbar of permeate pressure.

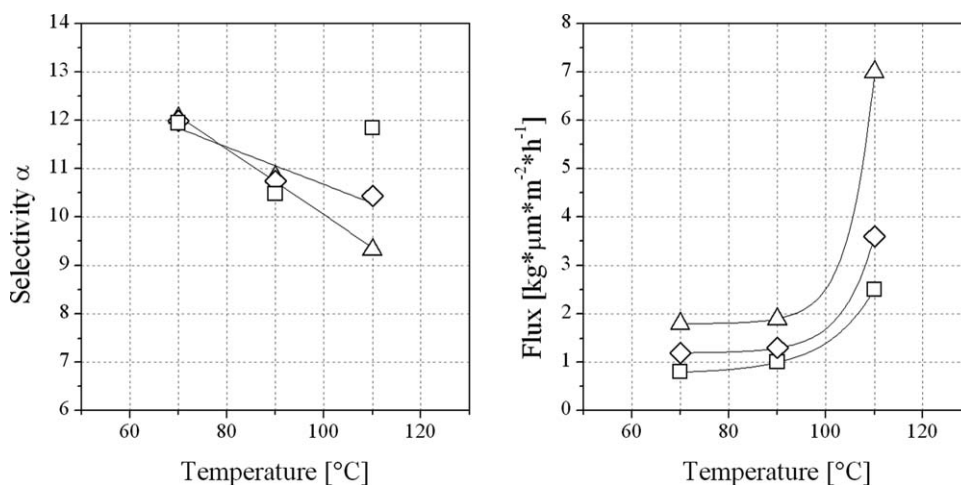


Figure 6. Separation of the toluene/*n*-decane mixtures with a 6FDA–4,4′-SDA/6FDA–DABA 19 : 1 membrane at (□) 60 wt % toluene, (◇) 70 wt % toluene, and (△) 80 wt % toluene and 15–20 mbar of permeate pressure.

rate. Furthermore, it was remarkable that the flux increased much more strongly when the temperature was changed from 90 to 110°C than when the temperature was changed from 70 to 90°C. We assumed that the chain flexibility at 90°C was not significantly higher than at 70°C. The fluxes at these temperatures with 0.8 up to 1.9 kg· $\mu\text{m}^{-2}\cdot\text{h}^{-1}$ were small in contrast to the fluxes at 110°C, which were between 2.5 and 7 kg· $\mu\text{m}^{-2}\cdot\text{h}^{-1}$. The increase in temperature not only led to an increase of the permeability but also to a decrease of the selectivity, as it is obvious from the data in Figure 6 (left side). The selectivity reached with an 80 wt % toluene feed mixture decreased about 25% when the feed temperature was changed from 70 to 110°C. Probably, the chain flexibility increased strongly so that even the component with the larger kinetic diameter, the *n*-decane, could permeate more easily through the membrane than at 70°C. Although several experiments were performed, it should be noted on that point that the selectivity for the different feed concentrations at 70 and 90°C were in the same range, whereas at 110°C, the data were scattered.

Figure 7 shows the partial fluxes of *n*-decane and toluene at 60 and 80 wt % toluene in the feed mixture at different feed temperatures. With a temperature change from 70 to 90°C, the toluene fluxes increased between 5% (Figure 7) and 20%, whereby a lower increase was found for the 60 wt % toluene feed (left side) compared to the 80 wt % toluene feed mixture (right side, Figure 7). Between 90 and 110°C, the toluene flux increased drastically, about 240 and 260%, for the lower and higher feed concentrations. In contrast to the temperature change from 70 to 90°C, where the *n*-decane flux stayed constant, in this case, the *n*-decane flux increased about 400% (right side, Figure 7). This showed clearly that the selectivity decrease with an increase in temperature, which was caused by the increasing decane partial flux. The temperature-dependent measurements showed that with temperature changes from 70 to 90°C, the flux increased moderately, and the selectivity stayed constant. A drastically increase of the flux occurred when the temperature was changed from 90 to 110°C. However, in this case, the selectivity decreased.

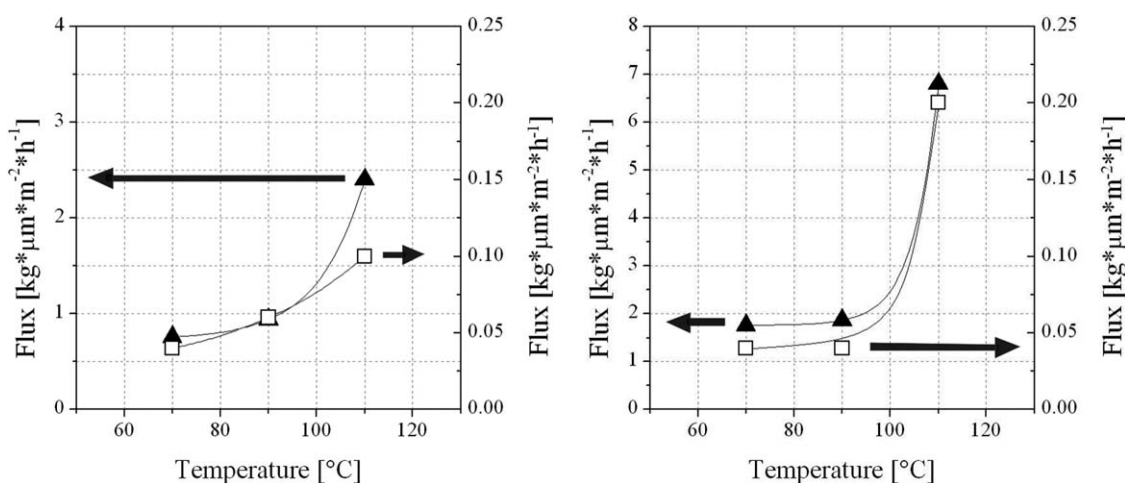


Figure 7. Temperature-dependent partial fluxes of (▲) toluene and (□) *n*-decane for the separation of toluene/*n*-decane mixtures containing 60 wt % (left) and 80 wt % toluene (right) with a 6FDA–4,4′-SDA/6FDA–DABA 19 : 1 membrane and 15–20 mbar of permeate pressure.

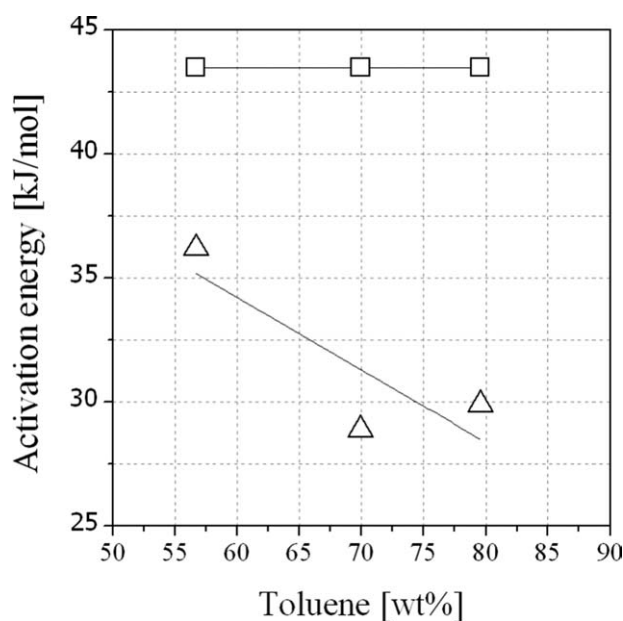


Figure 8. Concentration-dependent activation energies for (Δ) toluene and (\square) *n*-decane.

Figure 8 shows the activation energies for *n*-decane and toluene for the permeation through the synthesized membrane material at different feed concentrations. For the calculation of the activation energy, the logarithms of the partial fluxes were plotted against $1000/\text{temperature}$ in Kelvin. By means of the gradient, it was possible to calculate the activation energy. For that, J_n was transposed according to an Arrhenius equation:

$$J_n = J_0 e^{E_j/RT} \quad (3)$$

where J_0 is a pre-exponential factor, E_j is the activation energy of permeation (kJ/mol), R the ideal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), and T is the temperature (K). It is obvious that the activation energy for toluene was lower than the one for the *n*-decane and decreased with increasing toluene concentration, whereas the activation energy for the *n*-decane stayed constant independently of the toluene concentration in the feed mixture. Generally, with increasing temperature, a higher chain mobility was found. This seemed to influence the component with the smaller kinetic diameter, the toluene, significantly, whereas for the component with the larger kinetic diameter, the *n*-decane, no significant influence was observed. Hereby, the kinetic diameter is one of the most applied descriptions with regard to transport phenomena in membranes. It reflects the smallest effective dimension of a given molecule and is commonly used for the discussion of the permeation rate occurring in aromatic/aliphatics but also gas separations, such as carbon dioxide/methane or olefin/paraffins. However, if the molecules are not spherical, which is the case for most components, that is, toluene and *n*-decane, the smallest diagonal of a cylindrical shape where the molecule will fit in, depending on an energetically minimized arrangement of the bond angles, has to be used as a basis for discussion on kinetic diameters.

As shown in Figure 8, linear regression analysis for the toluene data showed a variance of $\pm 20\%$. Because the average devia-

tion of fluxes in membrane-based separation is already $\pm 10\text{--}15\%$, the deviation in temperature-dependent measurements and the calculation of activation energy on the bases of these data were within the range found in previous work.^{35,36} However, it was obvious from Figure 8 that the activation energy for the *n*-decane was significantly higher compared to toluene. This was in good agreement with previous works, where it was also found that the activation energy for the aliphatic components was also much lower compared to the aromatic component. A comparison of the activation energies with data from the literature for toluene ($\sim 38 \text{ kJ/mol}$)¹⁷ and *n*-decane ($>40 \text{ kJ/mol}$)³⁶ showed that they were in the same range.

CONCLUSIONS

In this study, a new membrane material, a sulfur-containing copolyimide, 19 : 1 6FDA-4,4'-SDA/DABA, was investigated with regard to its separation properties for different aromatic/aliphatic mixtures. As feed components, toluene and *n*-decane were used, and mixtures with toluene concentrations of 60, 70, and 80 wt % were investigated between 70 and 110°C. The constant selectivities at 70 and 90°C, even at high toluene concentrations, showed that the synthesized polymer was suitable membrane material for this separation problem. The loss in selectivity at temperatures of about 110°C led to the conclusion that the membrane process should not be operated at such high temperatures for a long time. After comparison of the data with Table I, we concluded that some results for the flux and the selectivity might have been better than those in this work. The data for polymers that were tested in a toluene/*iso*-octane mixture showed different results. Matrimid-based polymers, for example, showed much lower fluxes and selectivities than the 6-FDA based polymers. Those fluxes and selectivities were in the range of the results we found for our polymer. However, it should be kept in mind that a direct comparison was not possible because of the use of different feed mixtures.

All in all, the membranes tested in this work showed good selectivities. An increase of the permeability could be reached without a strong decrease of the selectivity.^{25,37}

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