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Entropic Selectivity Analysis of a Series of Polypyrrolones for Gas Separation Membranes

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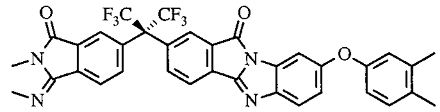
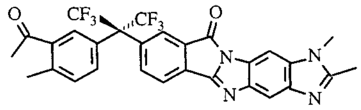
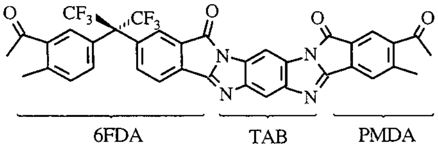
ABSTRACT: A series of 6FDA/PMDA−TAB polypyrrolone copolymers has been shown to exhibit performance lying on or above the so-called O_2/N_2 upper bound membrane separation tradeoff limit. Further analysis of diffusion in these high performance materials can potentially guide future structural enhancements, which may lead to improved separation properties. This work compares and analyzes diffusion in this attractive family of hyperrigid polymers using entropic and energetic selectivities. When the polymer structure and penetrant sizes are examined, possible polymer matrix configurations can be discussed with regard to the entropy of the molecules in the normal and activated states. This analysis extends to O_2/CH_4 and N_2/CH_4 entropic selectivities, which corroborate the trend observed with the O_2/N_2 gas pair, but the changes are more pronounced due to the larger difference in penetrant size.

Introduction

Previous work by Singh and Koros[1] demonstrated that the entropic selectivities of molecular sieving media such as zeolite and carbon molecular sieves (CMS) are substantially higher than for a polymer lying on the upper bound tradeoff line. The higher entropic selectivities of these molecular sieving materials are believed to arise from the materials' ability to limit the rotational degrees of freedom of N_2, the longer molecule, relative to O_2 in the diffusional activated state. On the basis of this analysis, a polymeric material possessing high entropic selectivity could potentially provide enhanced performance relative to other polymers reported to date. Currently, the highest previously reported polymeric entropic selectivity, equal to 1.2, is exhibited by 6FDA−TADPO, a polypyrrolone lying on the upper-bound tradeoff limit and shown in Table 1.[2]

Table 1. Polypyrrolones Used in Entropic Selectivity Analysis

polymer	structure
6FDA-TADPO	
6FDA-TAB	
6FDA/PMDA-TAB (50/50)	
6FDA/PMDA-TAB (25/75)	
6FDA/PMDA-TAB (10/90)	

The polypyrrolones studied in this work and shown in Table 1 possess a hyperrigid structure. These materials were tailored to mimic molecular sieving media structures to improve existing polymeric membrane performance. The polypyrrolones are shown to exhibit performance lying on or above the O_2/N_2 upper bound tradeoff line,[3] thus indicating superior performance to most polymers reported to date. Due to the rigidity of these materials, their performance appears to be classified between that of flexible polymers and carbon molecular sieves. Although previous gas permeation and sorption measurements in these materials have been reported,[3,4] a more detailed "picture" of diffusion in this interesting series of materials will be obtained here by examining the entropic and energetic selectivities.

Theory and Background

Gas permeation through polymers, permeable carbons, and zeolites occurs by the so-called sorption diffusion mechanism.[1] The gas permeability, P_A, calculated as the pressure and thickness normalized flux, is the product of the diffusion and sorption coefficients, D_A and S_A, respectively.

$$P_A = D_A S_A \tag{1}$$

The diffusion coefficient is kinetic in nature and is affected by penetrant size, chain packing, and polymer chain segment mobility.[5] The sorption coefficient is measured as the secant slope of the sorption isotherm at the upstream pressure when the membrane downstream pressure is negligible. Due to its thermodynamic nature, the sorption coefficient depends primarily on the penetrant condensability, polymer−penetrant interactions, and free volume in glassy polymer matrixes.

Membrane separation performance is characterized by the ideal selectivity of a membrane, $\alpha^*_{A/B}$, when the downstream pressure is negligible. This ideal selectivity is defined as the ratio of the permeabilities of the two gases and is the product of a diffusivity selectivity, D_A/D_B, and sorption selectivity, S_A/S_B, of the two gases in the membrane.

$$\alpha^*_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B}\right)\left(\frac{S_A}{S_B}\right) \tag{2}$$

Seven years ago, Robeson noted the O_2/N_2 "upper bound" tradeoff line between polymeric membrane gas selectivity and permeability.[6] More recent work has also considered gas transport properties of carbon molecular sieves (CMS), which often exhibit superior gas separa-

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Table 2. Energetic and Entropic Contributions to O_2/N_2 Diffusivity Selectivity in 6FDA−TAB, the 6FDA/PMDA−TAB Copolymers, Zeolite 4A, CMS, and 6FDA−TADPO

membrane	D_{O_2}/D_{N_2}	E_{d,O_2} (kcal/mol)	$\Delta E_{d,O_2,N_2}$ (kcal/mol)	energetic selectivity	entropic selectivity
6FDA−TAB	4.0	4.8	−0.7	3.0	1.4
6FDA/PMDA(50/50)−TAB	4.2	5.2	−0.4	1.8	2.3
6FDA/PMDA(25/75)−TAB	7.8	6.3	−2.2	33	0.24
6FDA/PMDA(10/90)−TAB	8.7	8.2	−2.7	78	0.11
Zeolite 4A[a]	104	4.5	−1.2	7.1	14.7
CMS[a]	25−45	5.5	−1.0	5.1	4.9−8.8
6FDA−TADPO[a]	5.1	5.3	−0.90	4.35	1.2

[a] Data from ref 12.

tion properties compared to traditional flexible polymers. For example, zeolite 4A and the CMS were shown to exhibit O_2/N_2 diffusivity selectivities 5−20 times greater than that for the upper-bound polymer.[1] Considering the differences in gas separation properties of these materials, Singh and Koros compared and analyzed the O_2/N_2 diffusivity selectivities of three gas separation materials: zeolite 4A, CMS, and 6FDA−TADPO, an upper bound polypyrrolone.[1] The enhanced O_2/N_2 diffusivity selectivities exhibited by molecular sieving media is believed to arise from the ability of these materials to hinder the rotational degrees of freedom of N_2 relative to O_2. Ultimately, these materials were shown to exhibit higher "entropic selectivities" than traditional polymeric materials. The theory associated with this analysis is described below.

The temperature dependence of the diffusion coefficient is described by an Arrhenius relationship[5]

$$D = D_o \exp\left[\frac{-E_d}{RT}\right] \tag{3}$$

where D_o is a preexponential factor and E_d is the activation energy for diffusion. From transition state theory, the preexponential factor is determined by[7]

$$D_o = e\lambda^2 \frac{kT}{h} \exp\left[\frac{S_d}{R}\right] \tag{4}$$

where λ is the average diffusive jump length, S_d the activation entropy of diffusion, k Boltzmann's constant, and h Planck's constant. When gases possess extremely similar kinetic diameters such as O_2 and N_2, λ is expected to be approximately equal. After substituting eq 4 into eq 3, the diffusivity selectivity can be described approximately as the product of enthalpic and entropic terms[1]

$$\frac{D_A}{D_A} = \underbrace{\exp\left[\frac{-\Delta E_{d,A,B}}{RT}\right]}_{\text{energetic selectivity}} \underbrace{\exp\left[\frac{\Delta S_{d,A,B}}{R}\right]}_{\text{entropic selectivity}} \tag{5}$$

where $\Delta E_{d,A,B}$ is the difference in the diffusion activation energy for penetrants A and B and $\Delta S_{d,A,B}$ the difference in the activation entropy of diffusion for penetrants A and B.

The diffusivity selectivity is, therefore, primarily equal to the product of the energetic and entropic selectivities as shown by eq 5. The energetic selectivity is a function of $\Delta E_{d,A,B}$ while the entropic selectivity is a function of $\Delta S_{d,A,B}$. For the O_2/N_2 separation, this difference in activation entropy, $\Delta S_{d,O_2,N_2}$, is defined by

$$\Delta S_{d,O_2,N_2} = (S^{\ddagger}_{d,O_2} - S_{d,O_2}) - (S^{\ddagger}_{d,N_2} - S_{d,N_2}) \tag{6}$$

where $S^{\ddagger}_{d,A}$ and $S_{d,A}$ are the entropies of the activated and normal states, respectively, of penetrant A. For a zeolite, the pore constriction and open cavity form the activated and normal regions, respectively, with negligible contribution from the matrix motion. A similar analogy can be drawn for the case of a "hyperrigid" polymeric matrix where penetrants make diffusive jumps in the activated regions, and penetrants exist in the sorbed state within the normal regions. For semirigid cases, where significant segmental motion contributes to the diffusion jump, the situation is more complicated, but some approximate conclusions still are possible.

Experimental Section

The polypyrrolone copolymers studied in this work are shown in Table 1. The copolymers incorporate various fractions of 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and pyromellitic dianhydride (PMDA) with 1,2,4,5-tetraaminobenzene (TAB). The polymer synthesis and film formation has been previously described.[3]

Pure gas permeation and sorption measurements in the range from 35 to 80 °C were completed as described previously.[3] The diffusion coefficient was determined by taking the ratio of the penetrant permeability and sorption coefficients, as shown in eq 1. Using the diffusion coefficients of the specified penetrants, the diffusivity selectivity in eq 5 was determined. The activation energy for diffusion, E_d, was determined from the activation energy for permeation and heat of sorption, which were calculated from the Arrhenius and van't Hoff expressions, respectively, fit to temperature dependent data. After $\Delta E_{d,A,B}$ was determined for the two penetrants under consideration, the energetic selectivity was calculated. The entropic selectivity is simply the ratio of the diffusivity selectivity and energetic selectivity. Even more simply, the entropic selectivity equals the ratio of the preexponential factors in eq 4 for the two penetrants.

Results and Discussion

O_2 and N_2 Analysis. The O_2/N_2 energetic and entropic selectivities of 6FDA−TAB and the 6FDA/PMDA−TAB copolymers are compared with that of zeolite 4A and CMS in Table 2. The uncertainties associated with the entropic selectivities are reported in the Appendix. As shown in Table 2, the O_2/N_2 diffusivity selectivity increases upon incorporation of PMDA in the 6FDA/PMDA−TAB copolymers. Similarly, the activation energy for O_2 diffusion also increases with greater PMDA fractions. More importantly, the 6FDA−TAB and 6FDA/PMDA (50/50)−TAB exhibit entropic selectivities greater than 1. In fact, these values are among the highest entropic selectivities reported for polymeric materials to date. An entropic selectivity of 1.2 was produced by 6FDA−TADPO, another polypyrrolone lying on the upper bound trade-off limit.[1] Although 6FDA−TADPO possesses a high fractional free volume like the hyper-rigid copolymers studied in this work, it *also* possesses a flexible ether linkage. It is likely that the elimination of this linkage in the 6FDA/PMDA−TAB copolymers contributes to the ability of 6FDA−TAB and 6FDA/PMDA (50/50)−TAB to exhibit even higher entropic selectivities.

Surprisingly, however, the 25/75 and 10/90 copolymers' entropic selectivities drop to values well below 1. For example, the 6FDA/PMDA (50/50)−TAB entropic selectivity decreases by 90% for 6FDA/PMDA (25/75)−TAB. A further reduction is observed upon limiting the copolymer composition to only 10% 6FDA. High energetic selectivities consequently compensate for the low entropic selectivities observed. These large energetic selectivities arise from the much larger difference in activation energies for diffusion between O_2 and N_2, $\Delta E_{d,O_2,N_2}$. As the $\Delta E_{d,O_2,N_2}$ term increases, the energetic selectivity increases. As a result, diffusion in the 25/75 and 10/90 copolymer matrixes is largely guided by energetic rather than entropic effects. The potential configurations of such rigid polymeric matrixes, which lead to these entropic selectivities, are described and analyzed later.

The zeolite 4A entropic selectivity of 14.7 signifies the "ideal" entropic performance created by the well-defined zeolite pore dimensions, which probably is unattainable by the inherently more disordered polymeric structure. Despite the high entropic selectivity exhibited by zeolites, the activation energy for diffusion is comparatively low relative to the values exhibited by the polypyrrolones studied here. Clearly, the highly selective diffusion in zeolites depends more on entropic than energetic effects. Although the polypyrrolones exhibited a wide array of entropic selectivities, at times even highly unfavorable, it is noteworthy that all of the materials possess gas transport properties lying on or above the upper bound tradeoff line. Hence, creation of high-performance materials does not apparently require high entropic selectivities even though attractive entropic selectivities, if present, would enhance performance.

Analysis of Penetrant Entropy in Various Gas Separation Materials. For comparison purposes, entropic selectivities can be placed in three categories: high, moderate, and low. High entropic selectivities are defined as values significantly greater than 1 while low values are less than 1. Similarly, moderate entropic selectivities are only slightly greater than 1. Mathematically, high entropic selectivities can only be achieved when eq 6 is a *positive* quantity and substituted into the entropic selectivity term in eq 5. In the same manner, moderate entropic selectivities are attained when eq 6 slightly exceeds zero. Finally, low entropic selectivities are observed when eq 6 is a *negative* value. An approximate molecular level analysis of the structures that may potentially lead to each of these entropic selectivity categories provides further understanding of diffusion in these unique polypyrrolone matrixes. Furthermore, it provides additional knowledge for tailoring high performance materials that are entropically selective.

Zeolite 4A structure provides a good model for describing the entropy changes of O_2 and N_2 from the normal to the activated state in high entropic selectivity materials.[1] The idealized schematic in Figure 1 shows the normal and activated regions as well as the entropy change of O_2 and N_2 from one region to the other in zeolite 4A. Although the figure is not drawn to scale, part c illustrates the relative changes in O_2 and N_2 entropy. Both O_2 and N_2 can rotate about their two axes in the zeolite cavity or in the normal state. Upon entering the pore constriction or activated region, O_2 can maintain its two rotational degrees of freedom because its length is less than the pore dimensions. On the other hand, the larger size of N_2 limits it from rotating about its two rotational axes while diffusing through the pore window. Oxygen experiences only a slight entropy decrease upon entering the pore window region due to the reduction of its translational degrees of freedom. As a result of the large reduction in rotational degrees of freedom, nitrogen experiences a larger entropy change, $S^{\ddagger}_{d,N_2} - S_{d,N_2}$. After the entropies of the two molecules in the two states are analyzed, eq 6 is a positive quantity, which yields an entropic selectivity much greater than 1.

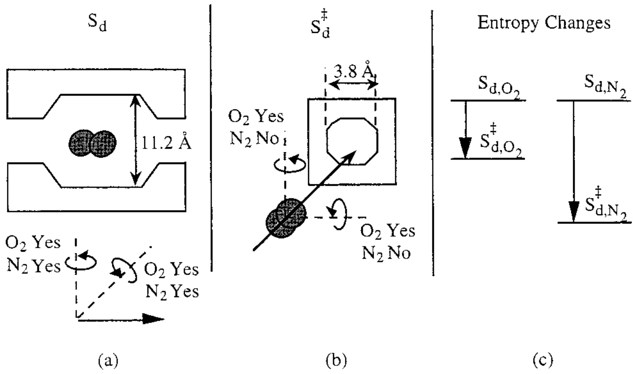

Figure 1. Idealized schematic of O_2 and N_2 in Zeolite 4A in the (a) normal state and (b) activated state with (c) a change in entropy for diffusion (portions reproduced from ref 1 with permission).

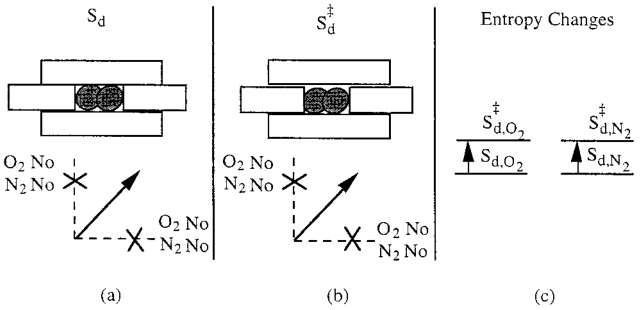

Figure 2. Idealized schematic of O_2 and N_2 in a tightly packed polymer matrix in the (a) normal state and (b) activated state with (c) a change in entropy for diffusion.

The molecular structure of a tightly packed, rigid polymer illustrates one potential configuration leading to material entropic selectivities equal to or approaching 1. Figure 2 shows the molecular rotational motions available in the normal and activated states as well as the relative O_2 and N_2 entropy changes in the two states. In the sorbed state, both O_2 and N_2 possess very little rotational mobility due to the very tightly packed nature of the material. Hence, their entropies in this normal state are essentially equal. Diffusion occurs in these types of matrixes when long-range segmental motions open a gap of sufficient size into which the penetrant can jump. Although the gap facilitates diffusion, it can only likely accommodate the penetrant itself without providing any additional space for molecular rotation. If a greater amount of space is present for the molecule to rotate in the activated state, it is minimal.

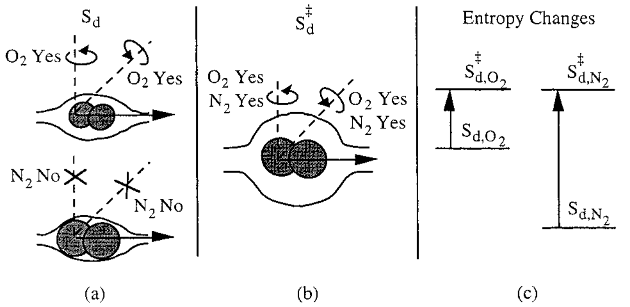

Figure 3. Idealized schematic of O_2 and N_2 in a flexible polymer matrix in the (a) normal state and (b) activated state with (c) a change in entropy for diffusion (modified from ref 2).

Assuming this situation, the penetrant entropies would increase only slightly in the activated state but likely to the same degree. As a result, the entropy change from the normal to the activated state would be similar for both O_2 and N_2. This configuration would result in eq 6 equaling nearly zero and lead to entropic selectivities of approximately 1. In this case, energetic effects on selectivity would be expected to be large.

A second polymer configuration, which is somewhat the reverse of Figure 2, also leads to materials with entropic selectivities approximately equal to one. Instead of both O_2 and N_2 having limited entropy in the normal and activated states due to tight packing, both molecules could have high, and nearly equal, entropy in both states in a significantly open polymer matrix. Such a matrix would consist of “slits” that are greater than 3.8 Å and would comprise the normal and activated regions. Hence, both O_2 and N_2 would be able to rotate about their two axes of rotation. Poly(1-trimethylsilyl-1-propyne) (PTMSP) is likely to represent one such polymer in this class. Its rigid, highly packing-resistant structure exhibits an O_2 permeability of approximately 10 000 Barrers and an O_2/N_2 permselectivity of 1.4.[8] Obviously, this material is extremely more productive than almost all permeable glasses but also nearly nonselective for conventional gas pairs. Due to the large interchain spacing of this material, diffusive differentiation between O_2 and N_2 is minimal. The primary reason impeding an entropic selectivity analysis of this material is the well-noted changes in permeability with time.[9]

Flexible, yet packable, polymers such as polycarbonate have been shown to possess entropic selectivities less than 1 (entropic selectivity = 0.12) and an explanation for this behavior has been proposed.[2] These entropic selectivities can potentially be explained by analyzing the sorbed and activated states within this flexible polymer matrix as shown in Figure 3. In the sorbed or normal state, the N_2 may be more “trapped” due to its larger size compared to O_2. As a result, the O_2 molecule has slightly more entropy in this sorbed state. In order for either of the respective molecules to make a diffusive jump, the flexible polymer chain must create a large gap through which that molecule can jump. Due to the flexible nature of these polymers, the gap may be large enough to allow each molecule to rotate in its respective activated state. In this situation, N_2 would experience a somewhat larger change in entropy when transitioning from the normal to the activated states than O_2. Consequently, the larger positive difference of the entropy of N_2 in the activated and normal states compared to O_2 results in a negative value for eq 6, which yields an entropic selectivity less than 1.

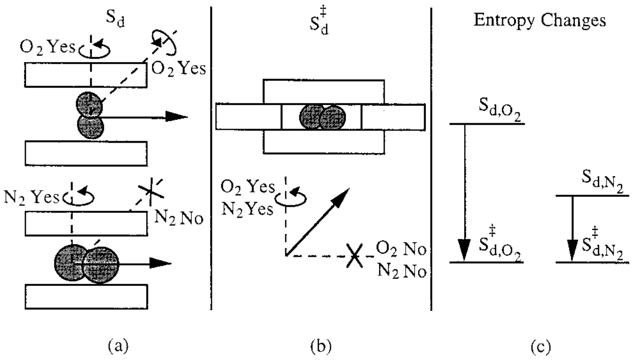

Figure 4. Idealized schematic of O_2 and N_2 in a hyperrigid polymer matrix in the (a) normal state and (b) activated state with (c) a change in entropy for diffusion.

A second situation leading to low entropic selectivities may exist in packable, hyperrigid polymers, such as the polypyrrolones studies in this work. Since these materials are hyperrigid, only very small chain motions occur when the molecule transitions to the activated state. This picture differs greatly from that described previously for flexible polymers that exhibit large molecular motions. The materials in this category possess confined restrictions which separate molecules based on size interconnected by regions of packing disruption created by bulky groups on the polymer chain or microvoids resulting from the nonequilibrium polymeric state. Figure 4 illustrates a possible description of O_2 and N_2 in their sorbed and activated states in these hyperrigid polymers. In the sorbed state, the interchain spacing is such that O_2 possesses greater rotational mobility compared to N_2 due to its smaller size. Since there is very little chain mobility, the chains form constrictions analogous to carbon molecular sieve pores. At these pore constrictions, the reduced polymer interchain spacing subsequently reduces the O_2 and N_2 entropy. Oxygen looses more entropy in transitioning from the sorbed to the activated state than N_2, which results in eq 6 being negative. A negative difference in the entropy for diffusion then produces a low entropic selectivity.

These four descriptions suggest various penetrant behaviors depending on the structure of the gas separation material. Minute changes in the polymer structure or interchain spacing can tremendously affect the relative change in entropy of both O_2 and N_2 between the sorbed and activated states. Other hypotheses may exist, but these appear to be the most likely at this time and to provide a reasonable framework for discussion of the polypyrrolones.

The descriptions above are consistent with the entropic selectivities observed in 6FDA−TAB and the 6FDA/PMDA−TAB copolymers. Since 6FDA−TAB and 6FDA/PMDA (50/50)−TAB possess the highest 6FDA fractions, their interchain spacings are the largest of those in the polypyrrolone family. On this basis, it is likely that the O_2 and N_2 entropy changes from the normal to activated states are analogous to that of zeolite. Since the interchain spacing is rather large, both O_2 and N_2 are able to rotate freely in the sorbed state. As the molecules approach constrictions in the polymer matrix, N_2 experiences a greater change in entropy due to its larger size that results in an entropic selectivity greater than 1. As the interchain spacing decreases with PMDA incorporation, the entropy of N_2 in the normal state is reduced, because rotation about its two axes are hindered. In addition, the size of the “pore” region

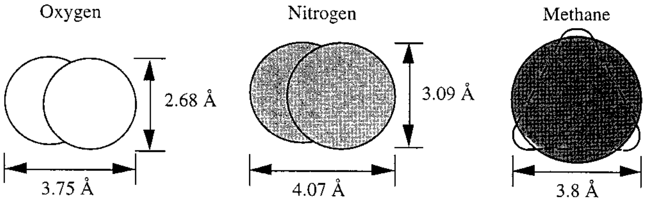

Figure 5. O_2 and N_2 molecular dimensions determined by Kihara potential and kinetic diameter of CH_4.

Table 3. O_2/CH_4, N_2/CH_4, and O_2/N_2 Entropic Selectivities of 6FDA−TAB and the 6FDA/PMDA−TAB Copolymers

	entropic selectivity		
polymer	O_2/CH_4	N_2/CH_4	O_2/N_2
6FDA−TAB	0.88	0.65	1.4
6FDA/PMDA(50/50)−TAB	7.9	3.5	2.3
6FDA/PMDA(25/75)−TAB	0.0060	0.025	0.24
6FDA/PMDA(10/90)−TAB	0.00075	0.0067	0.11

becomes even smaller, which reduces the ability of both molecules to rotate in this region. The material now behaves similarly to the hyperrigid polymer case described above. Oxygen experiences a larger *negative* change in entropy when going from the activated to normal state. As a result, entropic selectivities actually less than 1 are observed.

O_2/CH_4 and N_2/CH_4 Analysis. Gas molecules of various sizes have proven to provide one of the best probes of the complex separation environment in membrane materials. All analyses use pure gas measurement data. The previous entropic selectivity analysis focused solely on the O_2/N_2 gas pair. The addition of CH_4 to this analysis enables entropic effects to be analyzed for gas pairs with larger dimensional differences than O_2/N_2. The spherocylindrical shapes of O_2 and N_2 are compared to a spherical approximation of CH_4 in Figure 5, which is drawn to scale. The Kihara potential accurately describes the O_2 and N_2 length and width.[1]

The CH_4 molecular dimension is simply described by the kinetic diameter, 3.8 Å, in Figure 5, which is a good approximation for spherical molecules.[10] More specifically, the CH_4 molecule can also be modeled as a tetrahedron. Using the Kihara potential, the length of a CH_4 tetrahedron side is calculated to be 3.68 Å.[11,12] As CH_4 rotates about its three axes, this length describes the largest molecular dimension that would potentially limit the rotational degrees of freedom of CH_4 in size selective regions. For comparison purposes, consideration of CH_4 as a spherical molecule rather that tetrahedral simplifies the visual analysis. This approximation is believed to be reasonable for the approximate analysis considered here. The CH_4 diameter is comparable to the O_2 and N_2 lengths, whereas the CH_4 diameter is significantly greater than the widths of both O_2 and N_2.

The O_2/CH_4 and N_2/CH_4 entropic selectivities can be derived similarly to that described earlier for O_2/N_2 when still assuming a constant jump length, λ. This approximation is believed to be reasonable for the approximate first-order analysis considered here. Again, the diffusivity selectivity is the product of the energetic and entropic selectivities. The O_2/CH_4 and N_2/CH_4 entropic selectivities of 6FDA−TAB and the 6FDA/PMDA−TAB copolymers are compared with those for O_2/N_2 in Table 3. The uncertainties associated with these values are tabulated in the Appendix.

A similar, yet more pronounced, O_2/CH_4 and N_2/CH_4 entropic selectivity trend is observed with polymeric structural changes when compared to O_2/N_2. The entropic selectivities of the three gas pairs in 6FDA−TAB are near 1, when considering the uncertainties associated with each value. This indicates that for each gas molecule, the same magnitude of entropy change occurs as the molecule moves from the normal to the activated state. This similar entropic behavior is not surprising considering the “open” structure created by the 100% 6FDA incorporation.

A consistent increase in entropic selectivity is observed for all three gas pairs when progressing from 6FDA−TAB to 6FDA/PMDA (50/50)−TAB. The increase is the largest for O_2/CH_4, almost 9 times, which can likely be attributed to the fact that O_2 and CH_4 possess the largest molecular size difference of the three gas pairs analyzed. The N_2/CH_4 entropic selectivity experiences the second greatest entropic selectivity increase of over 5 times. Interestingly, the minimum size (3.09 vs 3.8 Å) difference between N_2 and CH_4 is the second greatest of the three gas pairs. Similar behavior is observed when transitioning to and from the 25/75 and 10/90 copolymers. The O_2/CH_4 entropic selectivity drops the most between the 50/50 and 10/90 copolymers compared to the other gas pairs. Similarly, N_2/CH_4 experiences the second greatest change.

Addition of the O_2/CH_4 and N_2/CH_4 entropic analysis confirms that significant polymeric chain packing changes occur between the 50/50 and 25/75 copolymer compositions. As a result, this chain packing heavily influences the relative change in O_2 and N_2 entropy as the molecules move from the normal to the activated state. Between these compositions, the O_2/CH_4, N_2/CH_4, and O_2/N_2 entropic selectivities drop by 1300, 140, and 10 times, respectively. In this composition range, the selective interchain spacing closely approaches the dimensions of these molecules. At and above copolymer compositions of 75% PMDA, O_2, N_2, and CH_4 diffusion is guided entirely by energetic effects rather than entropic ones.

Conclusions

The O_2/N_2 entropic selectivity increases from 1.4 to 2.3 in 6FDA−TAB and 6FDA/PMDA (50/50)−TAB, respectively. The entropic selectivity value for the (50/50) copolymer is essentially the highest polymeric entropic selectivity reported to date, indicating that this polymeric structure is approaching the molecular sieve type structure for which it was originally modeled. Surprisingly, the (25/75) and (10/90) copolymer O_2/N_2 entropic selectivities drop to values well below 1. In both of these materials, the enhanced gas separation properties are driven by the energetic contributions rather than the entropic. In hyperrigid materials like the (25/75) and (10/90) copolymers, it is speculated that O_2, due to its smaller size, possesses slightly more entropy in the sorbed state than N_2. When one is executing a diffusive jump, the entropies of both O_2 and N_2 are believed to be reduced due to the small constrictions created by the polymer chains. As a result, O_2 experiences a greater reduction in entropy relative to N_2, which yields a low entropic selectivity.

The analysis of entropic selectivities with CH_4, an essentially spherical gas molecule with a 3.8 Å diameter, as one of the gas components enables the gas separation environment to be further examined. A similar, yet more pronounced, data trend with copolymer composition is observed for the O_2/CH_4 and N_2/CH_4 entropic selectivities. The difference in the magnitude of entropic selectivity change is likely attributed to the molecular size difference of each gas pair.

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Appendix

An uncertainty analysis of the entropic selectivities is useful when comparing the polypyrrolone copolymers. Upon manipulation of eqs 3−5, it can be shown that the entropic selectivity is equal to the ratio of the diffusion preexponential factors.

$$\underbrace{\exp\left[\frac{\Delta S_{\mathrm{A,B}}}{R}\right]}_{\text{entropic selectivity}} = \mathrm{ES} = \frac{D_{\mathrm{o,A}}}{D_{\mathrm{o,B}}} \tag{A.1}$$

The entropic selectivity uncertainty equation was determined using a standard method[13] and is given by

$$\sigma_{\mathrm{ES,A/B}} = \mathrm{ES}\left[\left(\frac{\sigma_{D_\mathrm{o},\mathrm{A}}}{D_{0,\mathrm{A}}}\right)^2 + \left(\frac{\sigma_{D_\mathrm{o},\mathrm{B}}}{D_{0,\mathrm{B}}}\right)^2\right]^{1/2} \tag{A.2}$$

where $\sigma_{\mathrm{ES,A/B}}$ is the entropic selectivity uncertainty, $\sigma_{D_\mathrm{o},\mathrm{A}}$ the preexponential factor uncertainty of A, $\sigma_{D_\mathrm{o},\mathrm{B}}$ the preexponential factor uncertainty of B, and ES the entropic selectivity. The method used to determine $\sigma_{D_\mathrm{o},\mathrm{A}}$ has previously been described.[14] The uncertainties associated with the O_2/CH_4, N_2/CH_4, and O_2/N_2 entropic selectivities of 6FDA−TAB and the 6FDA/PMDA copolymers are shown in Table 4.

Table 4. Uncertainties for O_2/CH_4, N_2/CH_4, and O_2/N_2 Entropic Selectivities

polymer	$\sigma_{\mathrm{ES,O_2/CH_4}}$	$\sigma_{\mathrm{ES,N_2/CH_4}}$	$\sigma_{\mathrm{ES,O_2/N_2}}$
6FDA−TAB	0.38	0.26	0.4
6FDA/PMDA(50/50)−TAB	3.0	1.2	0.6
6FDA/PMDA(25/75)−TAB	3.1×10^{-3}	1.6×10^{-2}	0.1
6FDA/PMDA(10/90)−TAB	4.1×10^{-4}	2.4×10^{-3}	0.06

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