

Effects of the Nitrile Group Substitution on the Gas Separation Properties of Aromatic Polyamide Membranes

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Abstract: The effects of nitrile group substitution onto aromatic polyamide backbone on the gas permeability and permselectivity of the polymers are examined. The gas permeability of aromatic polyamides increase with increasing the content of nitrile group substitution, whereas the permselectivity decreases with increasing the nitrile group contents. The effects of chain linearity on the permeability and permselectivity are also examined. The non-linearity of the polymers increases the permeability. These behaviors are interpreted in terms of chain packing and crystallinity of the aromatic polyamides.

Keywords: Aromatic polyamide, Gas separation, Intermolecular chain packing, Chain linearity

Introduction

Polymeric membranes have been more widely used for gas filtration and separation processes as compared with other methods, such as physical/chemical adsorption and fractional distillation method[1]. The adsorption method is useful only for small scale, whereas the fractional distillation method is suitable for large scale but this process often has a purity problem.

Generally, the gas separation utilizes a difference in size-dependent diffusivity, although several workers have studied other factors such as chemical interactions between the gas and the membrane polymer[2-4]. Therefore, the size of free volume and its distribution become very important for gas separation.

Various polymers are used for the gas separation. Silicone polymer has been known as the most permeable one, and other polymers such as polytetrafluoroethylene and polyethylene also have good gas permeability. Polysulfonate[5], polycarbonate[6] and polyimides[7] have relatively good permeabilities but limited selectivity. On the other hand, several other polymers such as poly(acrylonitrile), poly(vinyl alcohol) and aromatic polyamides show very low permeability but excellent selectivity. In general, good permeability is accompanied with poor selectivity and vice versa, especially in case of size-dependent separation.

Aromatic polyamides, which show lyotropic liquid crystalline behavior, are expected to have very low gas permeability because of good chain packing due to strong hydrogen bonding between neighboring chains and the rigid chain structure. Nevertheless, it could be potentially used as a separation membrane because of its ultra-high selectivity. Therefore, we may expect that the permeability of aromatic

polyamides can be improved without significant loss of its selectivity when bulky substituent groups are introduced onto the chain backbone so that the chain spacings become broadened[8,9].

In this study, the nitrile groups are introduced as a substituent onto the aromatic polyamide backbone and the effects of the substituent on gas permeability and selectivity of the aromatic polyamide membranes are analyzed in terms of intermolecular chain spacing.

Experimental

Membrane Preparation

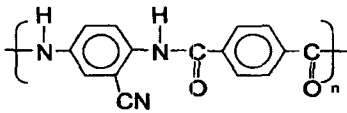
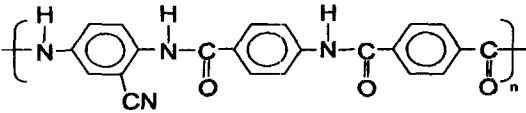
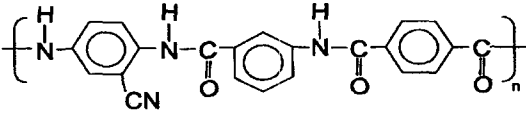
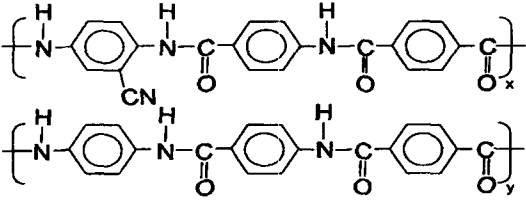
Chemical structures of aromatic polyamides used in this study are shown in Table 1. Details of synthesis of the polymers are described elsewhere[10]. The aromatic polyamides were first dissolved in LiCl/DMAc (0.05 g LiCl/ml DMAc) to prepare dilute solutions (concentration: 0.05 g/ml) and they were kept at 60°C for several hours. They were cast onto the glass plates, and the plates were immersed into 20°C water bath for solvent/non-solvent exchange for 2-3 days. They were then dried in the vacuum oven at 80°C for 24 hrs and 160°C for 2 days. Finally, the aromatic polyamide membranes were peeled off from the glass plate and dried at room temperature for 24 hours.

Permeability Measurement

Permeability (P) of the aromatic polyamide membrane was calculated using the relation $P = J \times (\Delta p/l)$, where J is the flux of gas, Δp is the difference between the downstream pressure and the upstream pressure, and l is the membrane thickness. Diffusivity (D) was calculated using the relation $D = l^2/6\tau$, where τ is the time lag observed at the initial stage of the permeability measurement. Solubility (S) was calculated using the relation $S = P/D$ [11].

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Table 1. Aromatic polyamides used for gas separation

Polymers	Abbreviations	Chemical Structures
Poly(6-cyano- <i>p</i> -phenyleneterephthalamide)	<i>p</i> -CPhT	
Poly(4,4'-diamino-6'-cyanobenzamide-terephthalamide)	<i>p</i> -DACBT	
Poly(3,4'-diamino-6'-cyanobenzamide-terephthalamide)	<i>m</i> -DACBT	
Poly(4,4'-diamino-6'-cyanobenzamide-terephthalamide-co-4,4'-diaminobenzamide-terephthalamide)	<i>x/y-p</i> -DACBT/DABT	

Permselectivities, diffusivity selectivities, and solubility selectivities of the aromatic polyamides, denoted as $PS_{A/B}$, $DS_{A/B}$, and $SS_{A/B}$, respectively, for gas A and gas B, were calculated using the relations $PS_{A/B} = P(A)/P(B)$, $DS_{A/B} = D(A)/D(B)$, and $SS_{A/B} = S(A)/S(B)$.

Characterization

Chain spacings of the aromatic polyamides were determined by X-ray diffraction (WAXD). The d-spacing

was calculated using the Bragg's law. To obtain informations about chain packing of the aromatic polyamides, densities were also measured in a density gradient column at 25°C [12].

Results and Discussion

Permeabilities, diffusivities, and solubilities of the aromatic polyamides are listed in Table 2. It shows that the

Table 2. Permeabilities, diffusivities, and solubilities of aromatic polyamides

Gases	Polymers					
	<i>m</i> -DACBT	<i>p</i> -CPhT	<i>p</i> -DACBT	75/25- <i>p</i> -DACBT/ DABT	60/40- <i>p</i> -DACBT/ DABT	50/50- <i>p</i> -DACBT/ DABT
P(He)	0.232	0.140	0.097	0.055	0.029	0.019
P(CO ₂)	0.004474	0.001543	0.000506	0.000249	0.000092	0.000050
P(O ₂)	0.000619	0.000228	0.000057	nd	nd	nd
D(He)	848.991	720.039	548.044	324.978	174.985	128.040
D(CO ₂)	27.100	21.213	10.097	5.120	2.224	1.435
D(O ₂)	12.104	9.508	3.540	nd	nd	nd
S(He)	0.002735	0.001946	0.001761	0.001705	0.001653	0.001510
S(CO ₂)	0.001651	0.000728	0.000501	0.000487	0.000415	0.000350
S(O ₂)	0.000511	0.000240	0.000160	-	-	-

*nd: not detected.

*Basic unit: P, Ba (Barrer); D, $\times 10^{-11}$ (cm²/s); S, dimensionless.

permeability of He gas ($P(\text{He})$) of *p*-DACBT is greater than that of 50/50-*p*-DACBT/DABT by several times. The permeability of O_2 gas ($P(\text{O}_2)$) of *p*-DACBT also shows higher value, since $P(\text{O}_2)$'s of 50/50-, 60/40-, and 75/25-*p*-DACBT/DABT are too low to be measured. The permeability of He gas increases with increasing the nitrile content in the polymers, indicating that the gas permeability of aromatic polyamides is strongly dependent on chain spacings between polymer chains. The increase in $P(\text{He})$ and $P(\text{O}_2)$ of *p*-DACBT is attributed mainly due to a large increase in diffusivity of He and O_2 gases ($D(\text{He})$ and $D(\text{O}_2)$), respectively, as shown in Table 2, indicating that He and O_2 molecules permeate via the size-dependent mechanism. However, permeabilities of CO_2 gas ($P(\text{CO}_2)$'s), which are higher than $P(\text{O}_2)$'s by 6~8 times, are affected dominantly by higher solubilities of CO_2 gas ($S(\text{CO}_2)$'s), which arises from the unique quadrupolar nature in CO_2 molecule. Therefore, the CO_2 gas permeates through not only size-dependent mechanisms but also chemical interactions with carbonyl groups of the aromatic polyamides.

The chain linearity may also affect the gas permeability of the aromatic polyamides. When the gas permeabilities of *m*-DACBT are compared with those of *p*-DACBT, it reveals that the gas permeability of *m*-DACBT is higher than that of *p*-DACBT for all gases examined. Furthermore, such an increase in gas permeability becomes more significant when

a larger gas molecule is used as a permeant.

Permselectivities, diffusivity selectivities and solubility selectivities of the aromatic polyamides are listed in Table 3. It shows that $PS_{\text{He}/\text{CO}_2}$ and $DS_{\text{He}/\text{CO}_2}$ decrease with increasing the content of nitrile groups in the aromatic polyamides. In other words, the introduction of nitrile groups on the main chain decreases the permselectivity although the permeability is increased with increasing the content of nitrile groups in the polymers. It also shows that the permselectivities of *m*-DACBT are smaller than those of *p*-DACBT, indicating that the non-linearity of the chain decreases the permselectivity.

Table 4 compares gas transport properties of *m*-DACBT with those of various other commodity polymers. It is noteworthy that the gas permeability of *m*-DACBT is very small compared with other polymers, but the permselectivity of *m*-DACBT is much higher than others. Considering that aromatic polyamides have an advantage for preparation of ultra-thin membranes over other commodity polymers because of their excellent mechanical strength, the aromatic polyamides could be potentially used as a separation membrane.

The WAXD experiment was performed to verify the hypothesis that the nitrile substituent onto aromatic polyamides leads to an increase in chain spacings which in turn improves the gas permeabilities, and the results are shown in Figures 1 and 2. The 2θ values at the maximum intensity decreases with increasing the content of nitrile

Table 3. Permselectivities, diffusivity selectivities, and solubility selectivities of aromatic polyamides

	Polymers					
	<i>m</i> -DACBT	<i>p</i> -CPhT	<i>p</i> -DACBT	75/25- <i>p</i> -DACBT/ DABT	60/40- <i>p</i> -DACBT/ DABT	50/50- <i>p</i> -DACBT/ DABT
$PS_{\text{He}/\text{CO}_2}$	51.8	93.3	189.7	220.9	248.0	287.9
$PS_{\text{CO}_2/\text{O}_2}$	7.3	6.6	8.9	nd	nd	nd
$DS_{\text{He}/\text{CO}_2}$	31.3	34.0	54.3	63.5	70.1	77.6
$DS_{\text{CO}_2/\text{O}_2}$	2.2	2.2	2.9	nd	nd	nd
$SS_{\text{He}/\text{CO}_2}$	1.7	2.7	3.5	3.5	3.5	3.7
$SS_{\text{CO}_2/\text{O}_2}$	3.2	3.0	3.1	nd	nd	nd

*nd: not detected.

Table 4. Comparison of gas permeabilities and selectivities of *m*-DACBT in this study with various other polymers

Polymers	$P(\text{He})/\text{Ba}$	$P(\text{CO}_2)/\text{Ba}$	$P(\text{O}_2)/\text{Ba}$	$P(\text{N}_2)/\text{Ba}$	$PS_{\text{He}/\text{CO}_2}$	$PS_{\text{O}_2/\text{N}_2}$	Ref.
Polyethylenesulfide	8.0	2.8	-	-	2.9	-	14
Polysulfonate	13.0	5.6	1.4	0.3	2.2	5.6	15
Polycarbonate	13.0	6.8	1.6	0.4	1.9	4.6	16
Polyisobutylene	11.2	8.7	2.1	0.6	1.3	3.6	17
Polyethylene	70.8	21.0	5.1	1.9	3.4	2.7	17
Polypropylene	-	11.8	3.1	0.6	-	4.9	17
Cellulose acetate(DS: 2.85)	19.6	6.6	1.5	0.2	3.0	6.4	18
Polyvinylbromide	-	-	2.0	0.4	-	4.9	19
Polyvinylpyrrolidone	-	-	0.5	0.1	-	5.7	19
<i>m</i> -DACBT (This study)	0.273	0.001964	0.000297	0.000054	51.8	11.4	-

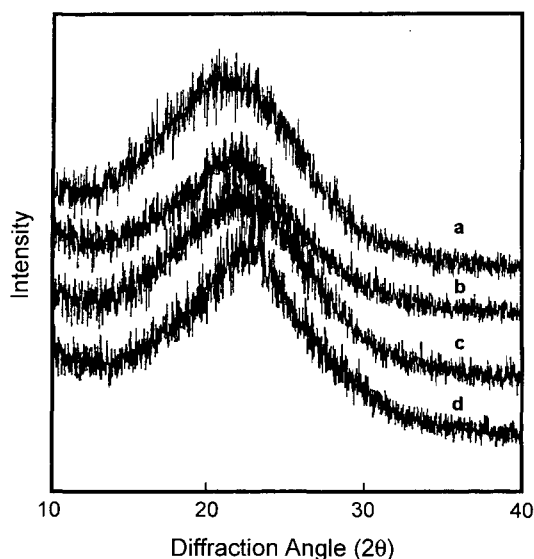


Figure 1. X-ray diffraction patterns of the aromatic polyamides: (a) *p*-DACBT, (b) 75/25-*p*-DACBT/DABT, (c) 60/40-*p*-DACBT/DABT, and (d) 50/50-*p*-DACBT/DABT.

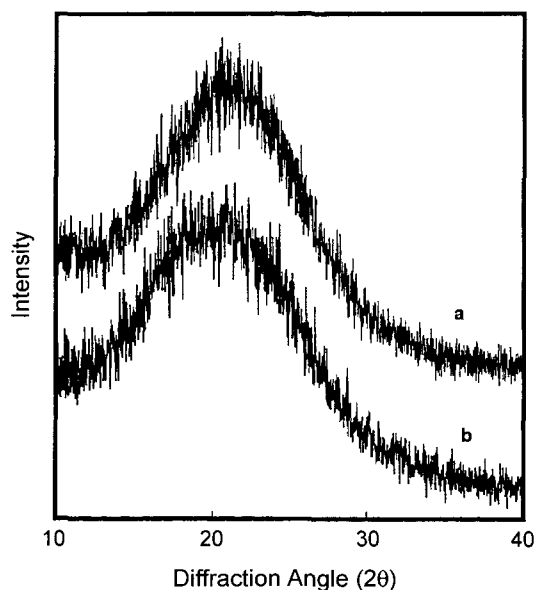


Figure 2. X-ray diffraction patterns of the aromatic polyamides: (a) *p*-DACBT and (b) *p*-CPhT.

groups in the polymers, indicating that the chain spacings (or d-spacings) increase with increasing the nitrile content. For example, the d-spacing of *p*-DACBT is 8.5 Å, which is larger than that of 50/50-*p*-DACBT/DABT (7.7 Å). However, the increment in d-spacings is not so large as expected. This relatively small increase of d-spacing may be responsible for the small increase in gas permeabilities.

Figure 3 shows that the d-spacing of *m*-DACBT is slightly smaller than that of *p*-DACBT, although the permeability of

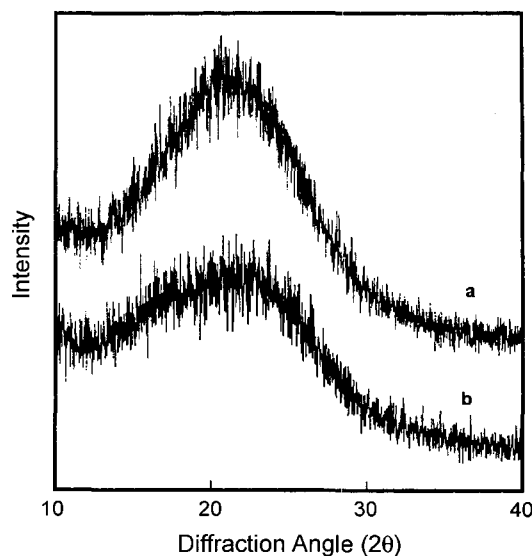


Figure 3. X-ray diffraction patterns of the aromatic polyamides: (a) *p*-DACBT and (b) *m*-DACBT.

Table 5. Densities and degrees of crystallinity of aromatic polyamides

	ρ_a	ρ_c	ρ	X_c (vol%)
<i>m</i> -DACBT	1.333	1.485	1.345	7.89
<i>p</i> -CPhT	1.338	1.490	1.357	12.50
<i>p</i> -DACBT	1.349	1.503	1.370	13.63
75/25- <i>p</i> -DACBT/DABT	1.356	1.509	1.374	11.76
60/40- <i>p</i> -DACBT/DABT	1.360	1.514	1.377	11.27
50/50- <i>p</i> -DACBT/DABT	1.362	1.517	1.382	12.90

* X_c : calculated using $\rho = \rho_a(1 - X_c) + \rho_c X_c$.

* ρ_a and ρ_c : calculated using the group contribution method of van Krevelen[13].

m-DACBT is larger than that of *p*-DACBT. This could be interpreted by considering the crystallinity. The diffraction pattern of *m*-DACBT is much broader than that of *p*-DACBT, which implies that the degree of crystallinity of *m*-DACBT was lower than that of *p*-DACBT. As a result, *m*-DACBT has higher gas permeability than *p*-DACBT, because gases permeate much more freely through amorphous regions than crystalline regions.

The degree of crystallinity can also be estimated from the density measurement, as listed in Table 5. The degree of crystallinity of *m*-DACBT is lower than that of *p*-DACBT, supporting the fact that the gas permeability of *m*-DACBT is higher than that of *p*-DACBT although the d-spacing of *m*-DACBT is rather smaller than that of *m*-DACBT.

Conclusions

Gas permeabilities of the aromatic polyamides are

improved when nitrile groups are introduced on the polymer chain. The gas permeability increases with increasing the content of nitrile groups in the aromatic polyamides. An increase in chain spacings, measured by X-ray diffraction, also supports the increase in gas permeability with increasing the nitrile group content. The chain linearity of aromatic polyamides also affects their gas permeability. The gas permeability of meta-substituted aromatic polyamides is higher than that of para-substituted ones. Permselectivity of the aromatic polyamide decrease with increasing the content of nitrile groups in the aromatic polyamides, as generally expected. Aromatic polyamides can be used as ultra-high gas purification despite of their lower gas permeability, because they have high permselectivity and good mechanical properties for preparation of ultra-thin film.

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