

Structure/Permeability Relationships of Polyamide-Imides

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SYNOPSIS

Structure/permeability correlations for a family of aromatic polyamide-imides are presented. The variations in chemical structure lead to significant changes in permeability. The crystallization of PAP results in a very low permeability. The introduction of bulky group tends to increase permeability without a corresponding decrease in permselectivity. This result contributes to the inhibition of chain packing and segmental mobility. Wide-angle X-ray diffraction measurements of average segmental spacing of the materials and fractional free volume calculations characterize the packing of the different polymers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The ability to control gas permeability and selectivity of polymer membranes demands a good understanding of relationships between the chemical structure of polymers and their gas permeability. A better understanding of these relationships is of great importance for the development of new processes for the separation of gases by selective permeation through polymer membranes.

Aromatic polyimides have high gas selectivity, excellent physical properties, and versatile chemistry, and this fact makes them prospective materials for preparing polymer membranes. Gas permeability of such membranes has been reported by many researchers.¹⁻⁹ It is also of interest to study the structure/permeability relationships of polyamide-imides. The present study extends the study of the effect of side groups of the diamine to permeability and selectivity of polyamide-imides. Moreover, the effect of soft central moiety in diamine is also investigated.

EXPERIMENTAL

Materials

The polymers used in this study, shown in Figure 1, were synthesized in our laboratory. The monomers used are shown in Figure 2. All the monomers were purchased and were purified prior to use. Polymerization was carried out by dissolving a small amount of the diamine in *N,N*-dimethylacetamide (DMAc). When the solution was cooled to 0°C, an equimolar quantity of trimellitic anhydride monoacid chloride was added to the rapidly stirred solution 4 times during half an hour, and stoichiometric amounts of triethylamine (Et₃N) were dripped into the mixture. The temperature of the solution was maintained between 0–5°C in the above procedure, and the solids were totalled 15% by weight of the mixture. The solution was then heated to 30°C and reacted for another 3 h. The precursor was deposited by pouring into 10 volume times of ethanol and filtered, and then was washed with ethanol 3 times. The precursor was dried at 100°C in vacuum and then dissolved in DMAc with a concentration of 10% solids by weight. The solution of the precursor was filtered and stored for film casting.

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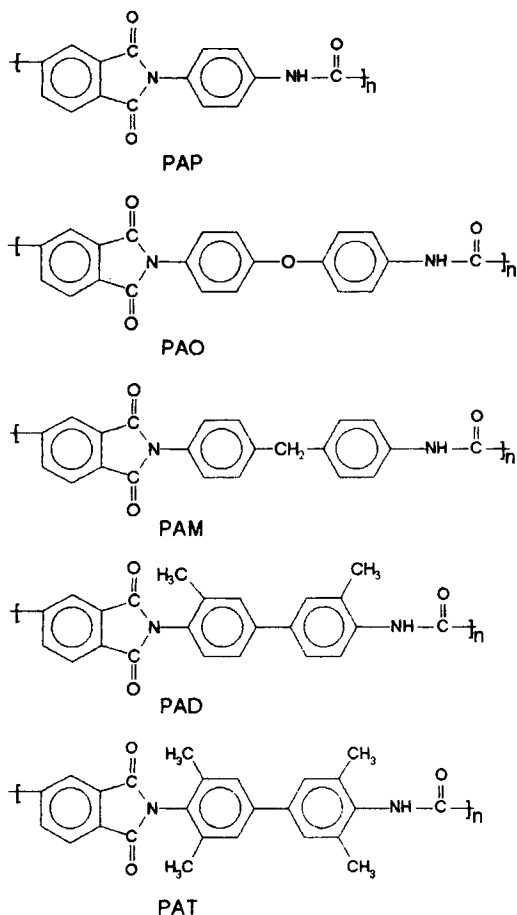


Figure 1 Polymers used in this study.

Film Preparation

Films were prepared by casting the precursor solutions on clean glass plates and heated at 60°C for 1

h to evaporate most of the solvent. Then the films were imidized for 1 h each at 100°C, 200°C, and 300°C in argon. The films were removed from the glass plates by soaking in water and were dried.

Permeability Measurements

The permeabilities of H₂, O₂, and N₂ were measured with a gas transmission rate measurement apparatus (K-315N-01, RSK Rikaseiki Kogyo Co., Ltd.) at 30°C and 1 atm. The purity of the gases used in the study was 99.5% or higher. The permeability of a membrane can be written in terms of a product of a diffusivity coefficient, *D*, and a solubility coefficient, *S*^{6,10}:

$$P = DS \quad (1)$$

The diffusivity coefficient can be measured by the time-lag method¹¹ using eq. (2):

$$D = l^2/6\theta \quad (2)$$

where θ is the time lag (s), *l* is the thickness of membrane. Then the solubility coefficient can be calculated from *P* and *D*.

The ideal separation factor, α^* , can be defined by the following equation¹²:

$$\alpha_{A/B}^* = P_A/P_B = (D_A/D_B)(S_A/S_B) \quad (3)$$

Density and Fractional Free Volume

Density of the polymers except the PAT shown in Table I was measured at 25°C in methylene chloride

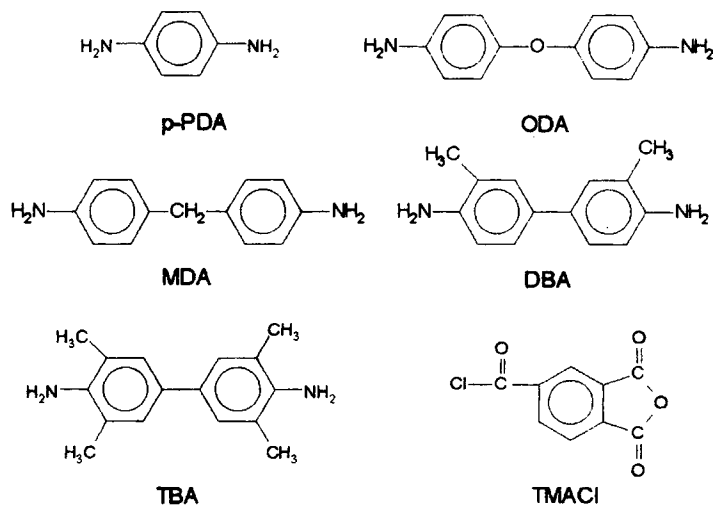


Figure 2 Monomers used in this study.

Table I Physical Properties

Polymer	Density (g/cm ³)	Fractional Free Volume	<i>d</i> -Spacing (Å)
PAP	1.460	0.05961	
PAO	1.413	0.08536	4.4
PAM	1.344	0.09043	5.0
PAD	1.306	0.09442	5.2
PAT	1.241	0.1097	6.0

and chloroform mixtures of various compositions, while the density of PAT was measured in a mixture of methylene chloride and petroleum. A PAAR DMA45 density meter (made in Austria) was used to determine the densities of the mixtures.

Once the density of the polymers is known, the fractional free volume can be estimated by the method of Lee,¹³ which uses the group contribution correlation of Van Krevelen¹⁴ for the calculation of Van der Waals volumes. The fractional free volumes are dependent on the occupied volume assigned to the constituent moieties comprising the polymer.

X-Ray Diffraction

Wide-angle X-ray diffraction was carried out on a Rigaku Dmax-3B diffractometer. The information obtained from diffraction patterns of amorphous polymers is informative; however, it is far less definitive and precise than that for crystalline structure.^{15,16} In amorphous polymer there is no long-range order, but there is a minimal kind of short-range order consisting of the most probable distances between neighboring chains. The center of the broad peak of a diffraction pattern is attributed to intersegmental spacing. The *d*-spacing can be calculated using Bragg's equation.¹⁷

RESULTS AND DISCUSSION

The gas permeability and permselectivity of the polyamide-imides at 30°C and 1 atm are compared in Table II. The values of *P* for three penetrant gases in the five polymers studied decrease in the order:

$$P(\text{H}_2) > P(\text{O}_2) > P(\text{N}_2)$$

This is also the order of increasing kinetic molecular diameter and, probably, of decreasing diffusivity of these penetrants.¹⁸

The diffusivity and solubility coefficient data are summarized in Tables III and IV, respectively. The diffusivity coefficient, which is a measure of the mobility of the penetrant between the upstream and downstream conditions in the membrane, is determined by packing and motion of the polymer segments and by the size of the penetrant molecule. The solubility coefficient is thermodynamic in nature and is determined by: (i) the inherent condensibility of the penetrant, (ii) polymer-penetrant interactions, and (iii) the amount of excess volume existing in the glassy polymer.^{12,19}

Referring to Tables II-IV, it is seen that the increases in permeability and permselectivity are due primarily to increase in diffusivity and diffusivity selectivity, respectively. Since there is no extremely attractive action between the three penetrants and the five polymers, diffusivities are apparently different, while solubilities are not. The diffusivity selectivity is determined by the ability of the polymers to discriminate between the penetrants on the basis of their sizes and shape, and is governed by intrasegmental motions and intersegmental packing. The solubility selectivity, like the solubility, is thermodynamic in nature.

The extra-low permeability of the PAP for each gas is due to the crystallization, which is reflected

Table II Permeabilities at 30°C and 1 atm

Polymer	Permeability (Barriers) ^a			Ideal Permselectivity	
	H ₂	O ₂	N ₂	H ₂ /N ₂	O ₂ /N ₂
PAP	0.0412	0.00205	0.000331	124	6.2
PAO	0.380	0.0173	0.00302	126	5.7
PAM	1.97	0.103	0.0194	102	5.3
PAD	3.12	0.171	0.0328	95	5.2
PAT	15.9	0.894	0.175	91	5.1

^a 1 barrier = 10⁻¹⁰ cm³ (STP) cm/cm² s cmHg.

Table III Diffusivities at 30°C and 1 atm

Polymer	Diffusivity ^a			Ideal Diffusivity Selectivity	
	H ₂	O ₂	N ₂	H ₂ /N ₂	O ₂ /N ₂
PAP	0.661	0.0154	0.00304	217	5.1
PAO	3.76	0.0820	0.0173	217	4.7
PAM	16.0	0.361	0.0980	163	3.7
PAD	26.4	0.695	0.179	147	3.9
PAT	108.	2.70	0.754	143	3.6

^a Unit: 10⁻⁹ cm²/s.

by the X-ray diffraction spectra shown in Figure 3. Since the crystalline domains are not accessible to penetrant molecules,^{20,21} the gas permeability of polymers decreases as the crystalline volume-fraction of a polymer increases. So, the PAP has a very low permeability for gases.

The permeability of PAO and PAM for the three gases is significantly higher than that of PAP. Factoring the diffusivity and solubility results showed that differences in both diffusivity and solubility affect the permeability. However, larger differences in diffusivity than in solubility are apparent. Therefore, the diffusivity is the principal factor that alters the permeability. Although introduction of soft moieties into polymer backbone may improve the diffusivity and permeability,⁹ the crystallizability is the primary factor determining the diffusivity and permeability in this study. When the flat, rigid, and easily packed *p*-PDA moiety was replaced with ODA or MDA, the chain packing and segmental mobility were changed and resulted in a sharp decrease in crystallization, which could be indicated by the X-ray diffraction spectra. Penetrant permeabilities for the PAM are greater than those for the PAO. As in the previous

section, the diffusivity differences between two polymers are the dominant factors responsible for the differences in the permeability of a given penetrant. The increase in the diffusivity of H₂ is only a factor of 4.2 in the PAM as compared to the PAO, whereas the diffusivity of other penetrants increases more. The larger mean interchain spacing (*d*-spacing) and fractional free volume in the PAM indicated that the chain packing of PAM is looser than that of PAO and causes an increase in the diffusivity of all penetrants, but benefits the larger penetrants more than H₂. So, PAM has the highest permeability of all penetrants and a relatively low permselectivity.

As can be seen from a comparison of PAD and PAM, the former is more permeable than the latter by 58% or more for the three gases studied. The permselectivity of H₂/N₂, and O₂/N₂ decreases by 7% and 2%, respectively. Referring to Tables III and IV, it is seen that the permeability and permselectivity are controlled by diffusivity. The disruption of chain packing may contribute to the increased diffusivity in the PAD, as indicated by the fractional free volume shown in Table I. The fractional free volume of the PAD is 0.09442; that of PAM is

Table IV Solubilities at 30°C and 1 atm

Polymer	Solubility ^a			Ideal Solubility Selectivity	
	H ₂	O ₂	N ₂	H ₂ /N ₂	O ₂ /N ₂
PAP	0.623	1.33	1.09	0.57	1.22
PAO	1.01	2.11	1.75	0.58	1.21
PAM	1.23	2.85	1.98	0.62	1.44
PAD	1.18	2.46	1.83	0.64	1.34
PAT	1.47	3.31	2.32	0.63	1.43

^a Unit: 10⁻³ cm³ (STP)/cm³ cmHg.

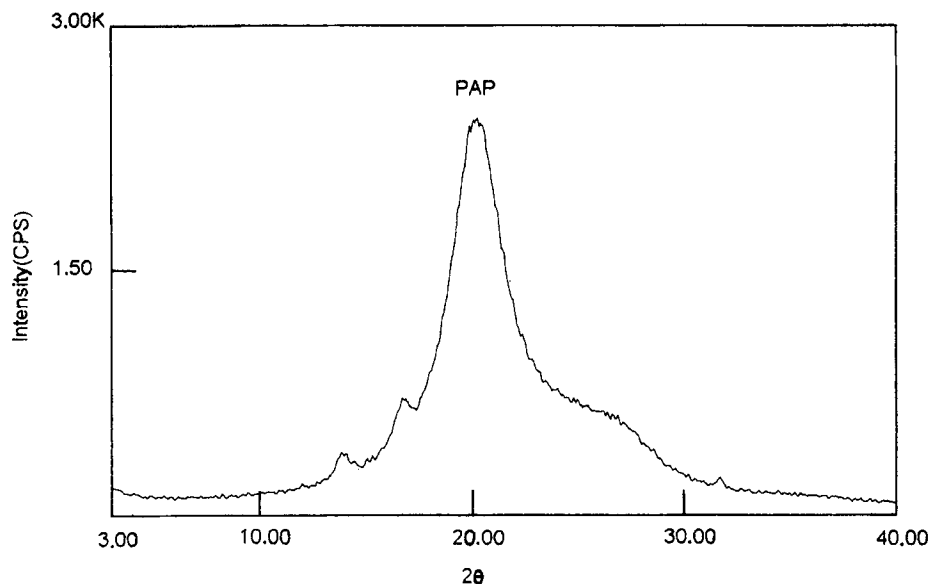


Figure 3 X-ray diffraction curve of the PAP.

0.09043. The increased inhibition to chain packing is also indicated by the increased d -spacing of the PAD ($d = 5.2 \text{ \AA}$) over that of PAM ($d = 5.0 \text{ \AA}$). In fact, introduction of the bulkier $-\text{CH}_3$ side group inhibits not only the chain packing, but also the segmental mobility. As a result, the permeability of gases in PAD is increased while maintaining the permselectivity.

Compared with PAD, the permeability of PAT for H_2 , O_2 , and N_2 increases by 4.1, 4.2, and 4.3 times, while the permselectivity of H_2/N_2 and O_2/N_2 only decreases by 4% and 2%, respectively. Since all the four *o*-positions of amine moiety in the PAT were substituted by $-\text{CH}_3$ group, there is no doubt that the inhibition of chain packing and segmental mobility is much more severe than that of PAD. The inhibition of chain packing by the bulky methyl substituents is evidenced by the higher d -spacing (6.0 \AA vs. 5.2 \AA) and higher fractional free volume (0.1097 vs. 0.09442) of PAT compared to PAD. Packing hindrance due to the bulky PAT structure is identified as the principal cause of the higher diffusivity. Similarly, the increased permeability may be due to an increase in the diffusivity of each penetrant. As reported by Kim et al.,^{7,22} significant increase in diffusivity and diffusivity selectivity can be obtained by simultaneously inhibiting intrasegmental motion and intersegmental chain packing. So, it is reasonable that the permeability of PAT is significantly increased while maintaining permselectivity.

CONCLUSIONS

The permeability of PAP is very low for its crystallizability. When the *p*-PDA moiety in the polyamide-imide backbone was replaced by flexible moiety or bulky moiety, the crystallization was sharply decreased and resulted in a significant increase in permeability. Compared with PAO, PAM showed higher permeability and lower permselectivity because the chain packing of the former was tighter. The permeability of PAT to the gases studied was at least 4 times larger than that of PAD, whereas the selectivity of the two polymers was about the same. A similar situation was found between PAD and PAM. The results for the effect of introduction of bulky group supported the hypothesis that simultaneous inhibition of chain packing and intramolecular motion may increase permeability while maintaining permselectivity.

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