Polymer Bulletin 49, 165-172 (2002)

Polymer Bulletin

Gas permeability coefficients of isomeric aromatic polyamides obtained from 4,4'-(9-fluorenylidene) diamine and aromatic diacid chlorides

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Received: 6 June 2002/Revised: 19 September 2002/Accepted: 23 September 2002

Summary

Three isomeric aromatic polyamides were synthesized using as a basis 4,4'-(9-fluorenylidene) diamine and different phtalic diacid chlorides. The influence of structural changes on polyamide properties when the phthalic moiety changed from *para* linked, poly(fluorenylidene terephthaloyl amide), BFA/TERE, to *meta* linked, poly(fluorenylidene isophthaloyl amide), BFA/ISO, phenyl substitution or *meta* linked phenyl substitution with a large pendant group, poly(fluorenylidene tertbutyl isophthaloyl amide), BFA/TERT, on these polyamides were assessed. Thermal properties measurements indicate that BFA/TERE has the highest thermal decomposition temperature above 450° and Tg, while BFA/ISO and BFA/TERT have thermal properties that are only slightly lower. Gas permeability coefficients of the three isomeric aromatic polyamides were measured at different temperatures. The results indicate that BFA/TERT has the largest permeability and diffusion coefficients while BFA/ISO shows the lowest. These results are attributed to a larger fractional free volume in the former compared to the later. Permeability coefficients for all gases tested show an Arrhenius type behavior with temperature for these aromatic polyamides.

Introduction

Aromatic polyamides are considered a class of high temperature resistant engineering polymers that are thermally stable with excellent physical and mechanical properties. A Polycondensation reaction in solution is the conventional method for the synthesis of aromatic polyamides. Some methods use aromatic diamines that react with aromatic diacylchlorides at low-temperature[1-4], and other methods use high-temperature where diamines react with aromatic diacylchlorides[5] or aromatic dicarboxilic acids such as Yamazaki's reaction[6,7]. Thermal properties of aromatic polyamides make them potential candidates for their use as membrane materials for gas separations at high temperatures. A problem that arises frequently with aromatic polyamides is their low-solubility in different solvents, which combined with their high glass transition or melting temperatures make them difficult to process for membrane formation. However, it has been reported that cardo-type polymers[9], manly those based on fluorene, present high glass transition temperatures and they are also soluble in common solvents. In general, introduction of bulky pendant groups enhances polymer solubility and it also increases their permeability due to an increase in fractional free volume; however, other properties are modified due to the effect of the new lateral groups introduced[8-11].

Understanding the effect that structural modifications have on aromatic polyamides final properties would be helpful to design polymers with properties tailored for specific uses, v.g. membranes for gas separation at high temperatures.

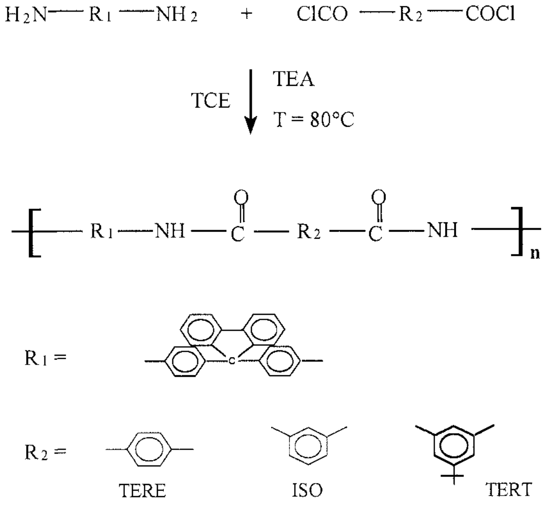
In this work, we present the synthesis, thermal and gas transport characterization of three aromatic cardo-type polyamides with isomeric aromatic groups. These polyamides were synthesized by a high-temperature polycondensation reaction using terephthaloyl dichloride, isophthaloyl dichloride and 5-tertbutylisophthaloyl dichloride reacting with an aromatic cardo-type diamine, 4-4'-(9-fluorenylidene)diamine. These aromatic polyamides were characterized by solution viscosity, thermal analysis, and density measurements. Finally, gas permeability coefficients were measured at four different temperatures and the influence of the different isomeric substitutions on gas transport and separation properties was assessed.

Experimental

Three different aromatic polyamides were synthesized from 4,4'-(9-fluorenylidene) diamine, BFA, and three different diacid chlorides; terephthaloyl chloride, TERE, isophthaloyl chloride, ISO, and 5-tertbutyl isophthaloyl dichloride, TERT. Prior to the synthesis 4,4'-(9-fluorenylidene)diamine was vacuum sublimated. Terephthaloyl chloride was recrystallized from petroleum ether. Isophthaloyl chloride was purified by vacuum distillation. 5-tertbutyl isophthaloyl dichloride was prepared from the reaction between 5-tertbutyl isophthalic acid and thyonil chloride using pyridine as a catalyst. The procedure for the later monomer preparation is described elsewhere[12]. Triethylamine, distilled under atmospheric pressure, was used as a catalyst for all aromatic polyamides synthesis. 1,1,2,2,-tetrachloroethane was the solvent for the solution polymerization and it was used as received. Methanol, technical grade, was used for polymer precipitation after the reaction. Dimethyl acetamide was purified by vacuum distillation. All reactants were purchased from Aldrich Chemical Co.

A typical polymerization reaction is as follows for the synthesis of poly(fluorenylidene terephthaloyl amide), BFA/TERE. A schematic representation of the reaction is given in Scheme 1. In a 100 ml three neck

flask, equipped with magnetic stirring and under nitrogen atmosphere, 1.51 g (4.35 mmol) of 4,4'-(9-fluorenylidene) diamine, BFA, in 8.7 mL of 1,1,2,2-tetrachloroethane, TCE, were stirred until complete dissolution of BFA. At this point, a solution containing 0.88 g (4.35 mmol) of terephthaloyl chloride, TERE, in 4.36 ml of TCE was added at room temperature. Next, 2.40 mL (4.35 mmol) of triethyl amine, TEA, was added dropwise and the solution was stirred for around 15 minutes. At this point, the solution was heated to 80°C and it was kept at this temperature for 4 hrs. After this time, the resultant solution was cooled down to 50°C and the polyamide was precipitated in 500 mL of methanol under vigorous stirring. The precipitated polymer was filtered and washed with methanol and hot water. Finally, the product was dried at 120°C in a vacuum oven for 24 hrs. The other polyamides poly(fluorenylidene isophthaloyl amide), BF/ISO, and poly(fluorenylidene tertbutyl isophthaloyl amide), BFA/TERT, were synthesized using the same method and conditions.
Films of the polyamides were cast by dissolving 0.5 g of each polyamide in 6 ml of dimethyl acetamide, DMAC. The solution was filtered and poured on a glass plate with an aluminum ring and the solution was evaporated slowly at 70°C. Once the film was strong enough, it was dried in a vacuum oven increasing the temperature gradually up to 220°C. The films were kept at this temperature for 48 hrs in order to eliminate completely the solvent. These films were used for thermal analysis and for gas permeation properties measurements. Thermal decomposition measurements for BFA/TERE, BFA/ISO and BFA/TERT were performed in a thermogravimetrical analyzer (TGA-7, Pekin Elmer, Co.) The tests were carried out on 5 mg samples, between 50 and 650°C, at a heating rate of 10°C/min under nitrogen atmosphere. Glass transition temperatures for the isomeric polyamides were determined using differential scanning calorimetry in a DSC-7, (Perkin-Elmer Inc) in 10 mg samples between 100°C and 400°C at a heating rate of 20°C/min under nitrogen atmosphere.



Scheme 1.- General reaction for BFA aromatic polyamide synthesis.

The density gradient column method was used to determine the density of the polyamides. The column was prepared at 21°C using calcium nitrate solutions between 1.18 and 1.30 g/cm^3. A second column was prepared with a density range between 1.15 and 1.24 g/cm^3. Gas permeability coefficient for 5 different gases, He, O_2, N_2, CH_4 and CO_2 were determined in a permeation cell of the constant volume type[13]. The measurements were made at 35, 45, 55 and 65°C for each pure gas. The permeability coefficients were determined under steady state conditions.

Results and Discussion

The properties of the three isomeric polyamides based on 4,4,-(9-fluorenylidene) diamine synthesized are summarized in Table 1. As can be seen BFA/TERE has a glass transition temperature that is 20°C higher than the one presented by BFA/ISO which also has higher T_g than BFA/TERT. This is attributed to a higher rigidity in the chain for the *para* substituted phenyl, TERE, in the phthalic moiety that imparts an increasing rigidity than the *meta* substituted phenyl ring, ISO, as reported elsewhere[12]. It is also seen that the substitution of the tertbutyl moiety, TERT, in the phenyl ring that is in the *meta* position for the phthaloyl moiety gives a further decreases on T_g. The last effect may be related directly with an increase in fractional free volume, as discussed later, in the BFA/TERT polyamide as compared to the BFA/ISO. It should be pointed out that the differences in T_g found are small between these isomeric polyamides, and that they present T_g values above 280°C, High T_g's are common feature in aromatic polyamides since the high number of aromatic rings confer higher rigidity to the polymer structure[14].

Table 1 Thermal properties, density and fractional free volume of isomeric BFA polyamides.

Polyamide	Tg (°C)	Td (°C)	Weight loss at 500 °C (%)	Density (g/cm^3)	FFV
BFA/TERE	319	468	13.7	1.239	0.141
BFA/ISO	301	467	23.3	1.245	0.134
BFA/TERT	284	488	12.9	1.170	0.149

The temperature for the onset of decomposition, T_d, for these aromatic polyamides is situated above 460°C. The results indicate that BFA/TERE and BFA/ISO have T_d's that are similar while BFA/TERT has a T_d which is 20°C higher. Given the similarity between the structure of the isomeric polyamides BFA/TERE and BFA/ISO, and since the difference is only in the *para* to *meta* connection of one of the phenyl rings, the result indicates that the onset of thermal decomposition does occur in a similar fashion. On the other hand, BFA/TERT that has the tertbutyl substitution in the *meta* connected aromatic ring, of the phthalic moiety, increases the onset of decomposition temperature. The weight loss at 500°C was recorded in order to compare the thermal stability of the isomeric polyamides after decomposition has started. The results indicate that BFA/TERT and BFA/TERE have similar stability with mass loss around 13 wt% at this temperature while BFA/ISO shows a larger decrease in mass, up to 23 wt%. This implies that the isomeric polyamide with the *meta* substitution has lower thermal stability once the decomposition has started. Density measurements show that the BFA aromatic polyamide containing the large tertbutyl group substitution in the phthalic moiety, BFA/TERT has the lower density while the *meta* connected aromatic polyamide BFA/ISO shows the larger density of these isomeric polyamides. There are reports in the literature that indicate that the *meta* connected structures in aromatic polymers tend to have large density than the *para* connected structure [15]. In here the results indicate that isomeric polyamide with the large tertbutyl substitution in the *meta* connected phthalic moiety, BFA/TERT, hinders the packing of the polyamide chains, decreasing the density as compared to the other isomeric polyamides. The effect is that it shows larger fractional free volume, FFV, defined as:

$$FFV = \frac{V_o - V}{V_o} \tag{1}$$

Where V_0 is the occupied volume that can be approximated using Bondi's group contribution method from the Van Der Walls volume, V_w, as $V_0=1.3V_w$ [16]. The FFV for the isomeric BFA polyamides is given in Table 1. It is found that BFA/TERT shows the larger FFV while BFA/ISO has the lowest FFV of the three isomeric polyamides synthesized.

Gas permeability coefficients, P, in amorphous polymers are accepted to be the result of the product of a diffusion coefficient, D, and solubility coefficient, S.

$$P = DS \tag{2}$$

From a single transient experiment, both permeability, P, and an apparent diffusion coefficient, D_a, can be obtained from the time lag θ measurement using

$$D_a = \frac{l^2}{6\Theta} \tag{3}$$

Permeability and apparent diffusion coefficients for five gases He, O_2, N_2, CH_4 and CO_2 through dense membranes for the three isomeric BFA polyamides at 35°C and 2 atm upstream pressure are given in Table 2. Of these isomeric aromatic polyamides BFA/TERT shows the highest permeability and apparent diffusion coefficients followed by BFA/TERE. BFA/ISO shows the lowest permeability for all gases. This result is similar to the one observed in other amorphous glassy polymers where permeability and diffusion coefficients increase as fractional free volume in the polymer increases[9-11]. It is also observed that the permeability coefficient follow the order $H_e>CO_2>O_2>CH_4>N_2$ from the gas that has the smallest kinetic diameter, He, to the ones with the larger kinetic diameter CH_4 and N_2.

Table 2. Permeability, apparent diffusion coefficients and ideal separation factors for BFA polyamides at 35°C and 2 atm upstream pressure

Polyamide	P (Barrer)			$D_a X10^8$ (cm^2/s)		P_{O2}/P_{N2}	P_{CO2}/P_{CH4}
	He	O_2	CO_2	O_2	CO_2		
BFA/TERE	24.7	3.0	15.3	4.5	1.4	5.8	27.9
BFA/ISO	15.8	1.2	5.3	1.4	0.4	6.1	41.3
BFA/TERT	53.4	8.0	37.7	9.8	4.2	5.7	24.4

$1\text{Barrer} = 1x10^{-10}\left[\frac{cm^3(STP)cm}{cm^2 scmHg}\right]$

The temperature dependence of gas permeability coefficients follows an Arrhenius type behavior of the form:

$$P = P_o \exp\left[-\frac{E_p}{RT}\right] \tag{4}$$

Where P_o is a pre-exponential factor, E_p is the activation energy for gas permeation, R is the gas constant and T is the temperature in °*K*. In order to determine E_p and P_o it is necessary to determine experimentally the permeability coefficients of a given gas in a membrane at different temperatures. Figure 1 shows Arrhenius plots for permeability coefficients as function of temperature in BFA/TERE, BFA/ISO and BFA/TERT between 35 and 65°C, for the five gases tested. It can be seen in that permeability coefficients increase as the temperature increases following closely an Arrhenius behavior. From a regression of these results, the activation energies for permeation, for each gas tested were obtained and they are listed in Table 3. The results indicate that BFA/TERT shows lower activation energy for permeation than BFA/ISO and BFA/TERE. In general higher activation energies translate into lower transport coefficients. It is also seen that as fractional free volume increases in the BFA/polyamide isomers, the activation energies decrease.

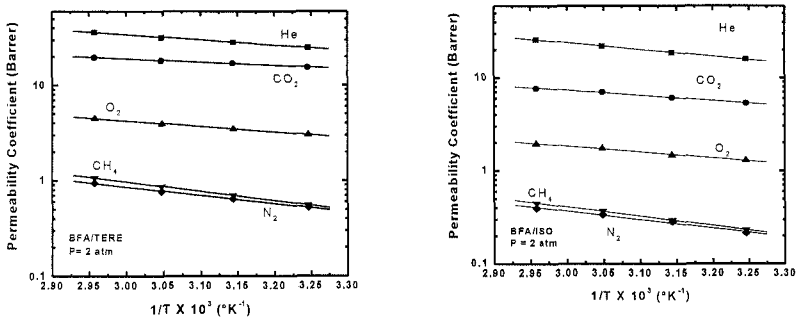
Table 3. Activation energies for permeation in BFA-polyamides

	BFA/TERE	BFA/ISO	BFA/TERT
Gas	E_P (KJ/mol)	E_P (KJ/mol)	E_P (KJ/mol)
He	10.7	13.9	9.0
CO_2	6.7	10.6	3.5
O_2	11.1	12.1	8.9
N_2	16.8	17.5	16.1
CH_4	18.8	19.1	17.9

A measure of the ability of a membrane to separate a gas pair A, B is given by the ratio of pure gas permeability coefficients:

$$\alpha_B^A = \frac{P_A}{P_B} \qquad (5)$$

The ideal separation factors of O_2/N_2 and CO_2/CH_4 pairs for the three isomeric BFA polyamides reported here are given in Table 2 at 35°C and 2 atmospheres upstream pressure. The results indicate that as gas permeability coefficient increases the ideal separation factor, α, decreases. This is a trade-off generally observed in other glassy polymers[10,17]. For example, BFA/TERT has the highest permeability coefficients but it presents the lowest ideal separation factors of the polyamides tested here.



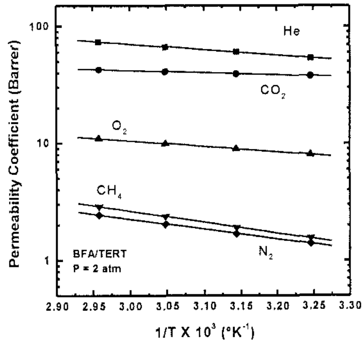


Figure 1. Gas permeability coefficients as a function of temperature between 35 and 65°C, polyamides BFA/TERE, BFA/ISO and BFA/TERT

Conclusions

Three isomeric aromatic polyamides, poly(fluorinylidene terephthaloyl amide), BFA/TERE, poly(fluorinylidene isophthaloyl amide), BFA/ISO and poly(fluorinylidene tertbutyl isophthaloyl amide), BFA/TERT, were synthesized by solution polymerization. Thermal properties measurements indicate that these aromatic polyamides are amorphous polymers with glass transition temperatures, T_g's above 260°C with the highest T_g shown by BFA/TERE. This result is attributed to higher rigidity in the chain as compared to BFA/ISO and BFA/TERT. The onset of decomposition temperatures, T_d's for the aromatic polyamides is also above 460°C, and they show high thermal stability with weight losses below 20 wt% at 500°C. These results situate them as engineering polymers with high temperature resistance. It was found that the isophthalic aromatic polyamide shows higher density than the terephthalic one and the tertbutylisophthalic polyamide shows the lowest density. The result is attributed to higher packing of the chains in BFA/ISO polyamide as compared to BFA/TERE and BFA/TERT. These results have influence in the gas permeation properties since it was found that BFA/TERT, that has the lowest density, presents the largest permeability and apparent diffusion coefficients while BFA/ISO, that has the highest density, shows the lowest ones. It was also found that ideal gas separation factors were high in BFA/ISO and those of BFA/TERT were low, a trade-off that is usually found in this type of polymers. Permeability coefficients follow an Arrhenius behavior as a function of temperature for all the polyamides in the temperature range tested here.

Acknowledgements. This research was performed under CONACyT's grant No. 31237-U. R. López-Nava and R. Palí-Casanova are grateful for CONACYT scholarships during this work.

References

[1] Negi Y S, Suzuki Y I, Kawamura I, Kakimoto M A, and Imai Y, 1996, *J. Polym. Sci. Polym. Chem.* **34** 1663.

[2] Varma I K, Kumar R, and Bhattacharyya A B, 1990, *J. App. Polym. Sci.*, **40** 531.

[3] Yamashita M, Kakimoto M A and Imai Y, 1993, *J. Polym. Sci. Polym. Chem.* **31** 1513.

[4] Carter K R, Furuta P T and Gong V, 1998, *Macromolecules*, **31**, 208.

[[5] Kakali F, Andrikopoulos V, Gravalos K and Kallitsis J K, 1998, *Polymer*, **39**, 1493.

[6] Higashi F, and Kawabata J, 1974, *J. Polym. Sci. Polym. Chem.* **12** 2149.

[7] Yamazaki N, Matsumoto M, and Higashi F, 1975, *J. Polym. Sci. Polym. Chem.* **13** 1373.

[8] Yang CP, Oishi Y, Kakimoto MA and Imai Y, 1989, *J. Polym. Sci.; Polym. Chem.*, **27** 3895

[9] Stern SA, *J. Membr. Sci.*, 1994, **94** 1

[10] Aguilar-Vega M and Paul DR, *J. Polym. Sci.; Polym. Phys. Ed.*, 1993, **31** 1599

[11] Pixton MR and Paul DR, *Polymer*, 1995, **36** 2745.

[12] Palí R, Loría-Bastarreachea MI, Vázquez-Torres H, Angulo JL and Aguilar-Vega M, *High Perform. Polym.*, 2002, in Press.

[13] Bixler HJ and Sweeting OJ, in *The Science and Technology of Polymer Films*, Ed. Sweeting OJ, 1971, Wiley-Interscience, N.Y., **1**

[14] Korshack VV., Vinogradova SV and Vygodskii YS, *J. Macromol. Sci. Rev., Macromol. Chem.* 1974, **C11** 45.

[15} Aitken C L, Koros WJ and Paul DR, *Macromolecules*, 1992, **25** 3424

[16] Van Krevelen DW and Hoftyzer PJ, *Properties of Polymers*, 1976, Elservier Amsterdam.

[17] McHattie JS, Koros WJ and Paul DR, *Polymer*, 1991, **32** 2618.